Report on Great Lakes Indian Fish and Wildlife Commission Water Sampling in the:

Presque Isle River Zone

By

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1. Introduction

Monitoring of water quality can indicate how existing industrial activities are affecting streams, rivers, and lakes. It can also indicate how new activities affect those water bodies if monitoring establishes a representative baseline before the new activities begin. Determining effects on water quality is important for understanding consequences for ecosystems, for fish populations, and for Ojibwe and others who consume fish that may be contaminated.

Great Lakes Indian Fish and Wildlife Commission (GLIFWC) staff have monitored water quality in the Lake Superior Ojibwe Treaty-ceded Territories for more than ten years. This monitoring program has primarily sought to establish baseline water quality in relatively intact ecosystems. In those study zones, potential or proposed industrial activities could impact water quality in the future. The program has also assessed water quality impacts from existing and historical industrial activity.

The Presque Isle River zone, in the 1842 Treaty-ceded Territory in Michigan (Fig. 1), is one of the zones for which GLIFWC has established baseline water quality. The zone is in the upper reaches of the Presque Isle River, which flows into the *Gichigami* (Lake Superior) at the state-designated Presque Isle River Scenic Site. Although some mineral exploration occurred in the zone, USGS (2016) records suggest that at most only one small iron mine operated in this zone.

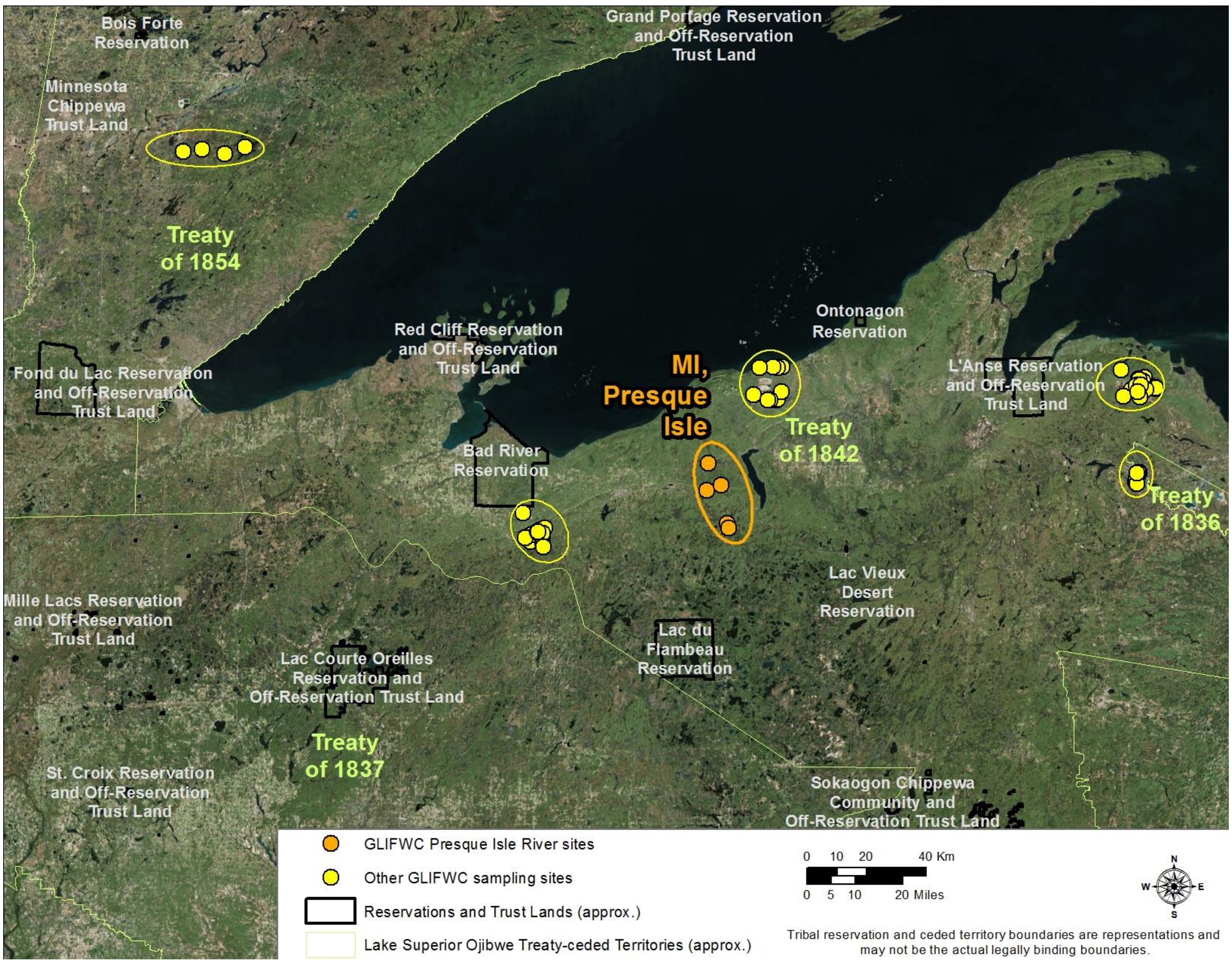

Figure 1. Map of the Presque Isle River zone water quality monitoring sites relative to other GLIFWC monitoring sites and Reservation and Territories boundaries.

The main branches of the Presque Isle River are federally-designated as a Wild and Scenic River (recreational or scenic; 16 USC Ch. 28; Fig. 2). This designation should protect those sections of the river from federally-supported dams or activities that would cause pollution of the waters of the river, and should limit mining claims on federal lands near those rivers (16 USC Ch. 28). Waste water lagoons for the town of Marenisco and for an upstream correctional facility may discharge into the River.

Assessments on attainment of designated uses are mostly lacking for the upper Presque Isle River system, but 2014 and 2016 assessments indicated that the main river branches and one tributary stream were supporting other indigenous aquatic life and wildlife uses (Fig. 2; MI DEQ 2017). The Little Presque Isle River, however, was not supporting that use or fish consumption use (Fig. 2; MI DEQ 2017). That impairment was for mercury in the water column, for which a TMDL was scheduled for 2022 (MI DEQ 2017).

The GLIFWC monitoring assessed water quality in the upper Presque Isle River zone beginning in 2011 to determine baseline conditions and assess similarities and differences between study sites. This report summarizes findings up through 2018.

2. Methods

Field methods

Field measurements

Field data collection used standard surface water monitoring protocols (USGS variously dated; USEPA 2012) and recorded measurements with multimeter field instruments (Coleman & Chiriboga 2011; Table 1). Staff calibrated specific conductance once per week and calibrated chloride, pH, and DO sensors daily. Field staff also measured total water depth at the sampling location.

Table 1. Field water quality measurements.

Field measurement	Instrument
Chloride	YSI Pro Plus, YSI ProDSS
Dissolved Oxygen	YSI Pro Plus, YSI ProDSS
pH	YSI 556, YSI Pro Plus, YSI ProDSS (also checked with pH paper)
Specific conductance	YSI 556, YSI Pro Plus, YSI ProDSS (and checked with Hanna Instruments 98311)
Water temperature	YSI 556, YSI Pro Plus, YSI ProDSS

Sample collection

Staff collected surface water samples for alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), chloride and sulfate, and metals and other trace elements (Coleman & Chiriboga 2011; Table 2). We used a hand dip/grab sampling technique as near as possible to the middle of the stream. We kept bottles capped when submerging into or removing from the water. We did not filter samples in the field, but preserved metal and trace element samples in nitric acid and kept all samples at < 6°C (Table 2). We collected a blank sample for 13 % of samples and collected field sequential replicates for 23 % of samples.

Laboratory analyses

The Water and Environmental Analysis Laboratory (WEAL), located on the University of Wisconsin-Stevens Point campus, analyzed our water quality samples according to standard laboratory methods (Table 2). The Northern Lakes Service laboratory in Crandon, Wisconsin, also analyzed seven replicate samples with the same methods as WEAL except for the use of ICP-MS (EPA 200.8) for selenium and arsenic, ion chromatography (EPA 300.0) for chloride and sulfate, and SM 4500P-E for phosphorus.

Table 2. Types of water quality samples and associated sampling, preservation, and analysis methods.

Analysis category	Analytes	Analysis type	Laboratory method	Field sampling bottle type	Field preservation
General characteristics & major anions	Alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Total hardness Chloride Sulfate	Titration (alkalinity, hardness), gravimetry (TDS and TSS), various	SM2320B (alkalinity), SM2540C (TDS), SM2540D (TSS), SM2340C (hardness) SM4500 Cl E or G (Cl^-) EPA 200.7 (sulfate)	High Density Polyethylene (HDPE) 500 ml	< 6 C
Metals & other trace elements	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Zn	Inductively-coupled plasma optical emission spectroscopy	EPA 200.7	High Density Polyethylene (HDPE) 250 ml	< 6 C, acidified with HNO_3

Statistical analyses

We calculated summary statistics for each characteristic. In summarizing results of laboratory analyses with measurements below the Limit of Detection (LOD), we used ½ of the LOD. We compared results to relevant state water quality criteria (Rule 57 final chronic values or drinking water values[1] unless otherwise indicated) and USEPA (the criterion continuous concentration for aquatic life, or secondary drinking water or other criterion where noted) and Canadian Council of Ministers of the Environment (CCME variously dated; for aquatic life, long-term) recommended criteria. In some cases, we compared with Canadian Federal Environmental Quality Guidelines (CFEQG, variously dated) or Canada Health (2019) values as well. For hardness-dependent criteria, we used hardness values measured in this study to determine relevant criteria values. We also assessed relationships between sites using Principal Components Analysis (PCA) and cluster analysis (using Ward's hierarchical accumulative method with squared Euclidian distances and z-score standardization). For those analyses, we log-transformed site median values of characteristics and only used characteristics with non-detects (measurements < LOD) representing < 10 % of data.

[1] Drinking water criteria, marked herein as "health," from Groundwater: residential and non-residential Part 201 Generic cleanup criteria and screening levels/Part 213 risk-based screening levels. https://www.michigan.gov/documents/deq/deq-rrd-Rules-Table1GroundwaterResidentialandNon_447070_7.pdf

Study sites and frequency

Monitoring included four surface water sites in rivers (Table 3, Fig. 2). Sampling began in 2011 and occurred at least twice per year through 2017, and once in 2018. We did not include in this report data from an additional sites at which staff only recorded field measurements or sampled less than twice (data available from GLIFWC 2019).

Table 3. Location, type, and sampling effort for sites in this report.

Site ID	Location	Latitude	Longitude	Type	Number of days of field measurements	Number of samples[1]
MI-01	Presque Isle & M28 [stream gage location]	46.546727	-89.777243	River	19	15
MI-02	Little Presque Isle 1.5 miles NW of Wolf Mtn.	46.462213	-89.786601	River	17	15
MI-03	Presque Isle & Copps Rd. north of Theilers	46.478664	-89.721304	River	18	15
MI-04	Presque Isle east off Old Michigan 64 near State Line Trail	46.361915	-89.6971	River	17	15

[1] Excluding QAQC samples (blanks and sequential replicates).

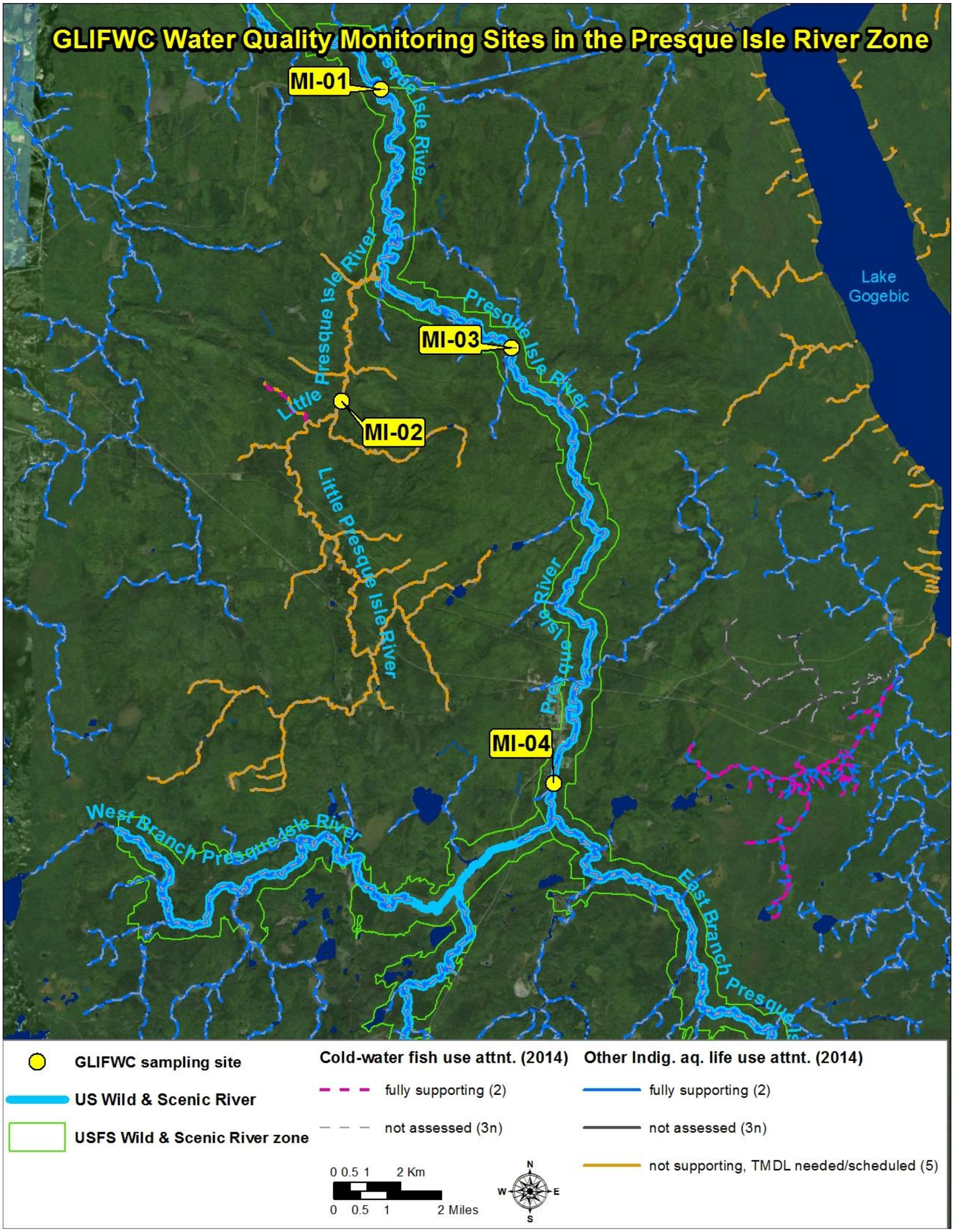

Figure 2. Map of GLIFWC sampling sites and Michigan Department of Environmental Quality select assessments of attainment of designated uses (cold-water fish and other indigenous aquatic life and wildlife) for water bodies in the Presque Isle River zone. The reach not supporting other indigenous aquatic life and wildlife use was also not supporting fish consumption use.

3. Results

(A) Summary statistics

Field measurements

Individual measurements and site means were all greater than 8 mg/l for dissolved oxygen (DO) and greater than 6.5 for pH (Table 4, Figs. 3-4). Chloride means were all less than 8 mg/l, but individual measurements reached 20 mg/l (Table 4, Figs. 3, 13). Specific conductance means and individual measurements did not exceed 230 µS/cm (Table 4, Figs. 4, 13). None of the recorded field measurements exceeded state, USEPA, or CCME criteria (Table 4).

Table 4. Field measurement means ± standard deviation (minimum – maximum, *n*) and criteria or recommended criteria. Bold font indicates greatest and smallest mean measurements. CCME = Canadian Council of Ministers of the Environment.

Criterion source/ site code	Dissolved oxygen (mg/l)	Chloride (mg/l)	pH	Specific conductance (µS/cm)
US EPA		230, 250[1]	6.5-9.0	
MI	4-7[2]	150 (50, 125, 250 health[3])	6.5-9.0	
CCME	5.5-9.5[4]	120, 250[5]	6.5-9.0	
MI-01	**9.7** ± 1.1 (8.7-11.3, 5)	5 ± 3 (0-13, 13)	7.5 ± 0.3 (7.0-8.1, 12)	122 ± 40 (47-188, 19)
MI-02	10.5 ± 1.6 (8.0-12.2, 5)	**7** ± 5 (0-18, 12)	**7.5** ± 0.3 (6.9-7.9, 11)	**140** ± 60 (40-222, 17)
MI-03	**11.0** ± 1.5 (8.8-11.9, 4)	5 ± 5 (0-20, 12)	**7.8** ± 0.5 (7.2-8.7, 12)	**118** ± 36 (50-187, 18)
MI-04	9.8 ± 0.9 (8.6-10.8, 5)	**3** ± 2 (0-6, 12)	7.7 ± 0.3 (7.4-8.2, 11)	119 ± 35 (53-180, 17)
Entire zone	10.2 ± 1.3 (8.0-12.2, 19)	5 ± 4 (0-20, 49)	7.6 ± 0.4 (6.9-8.7, 46)	125 ± 44 (40-222, 71)

[1] USEPA secondary drinking water criterion

[2] Criterion is a minimum that depends on season and designation as coldwater fisheries/trout stream

3 Criteria in parentheses apply to drinking water, public water supply, and health-based limits, respectively

[4] Criterion depends on water temperature class

[5] Canada Health drinking water aesthetic criterion

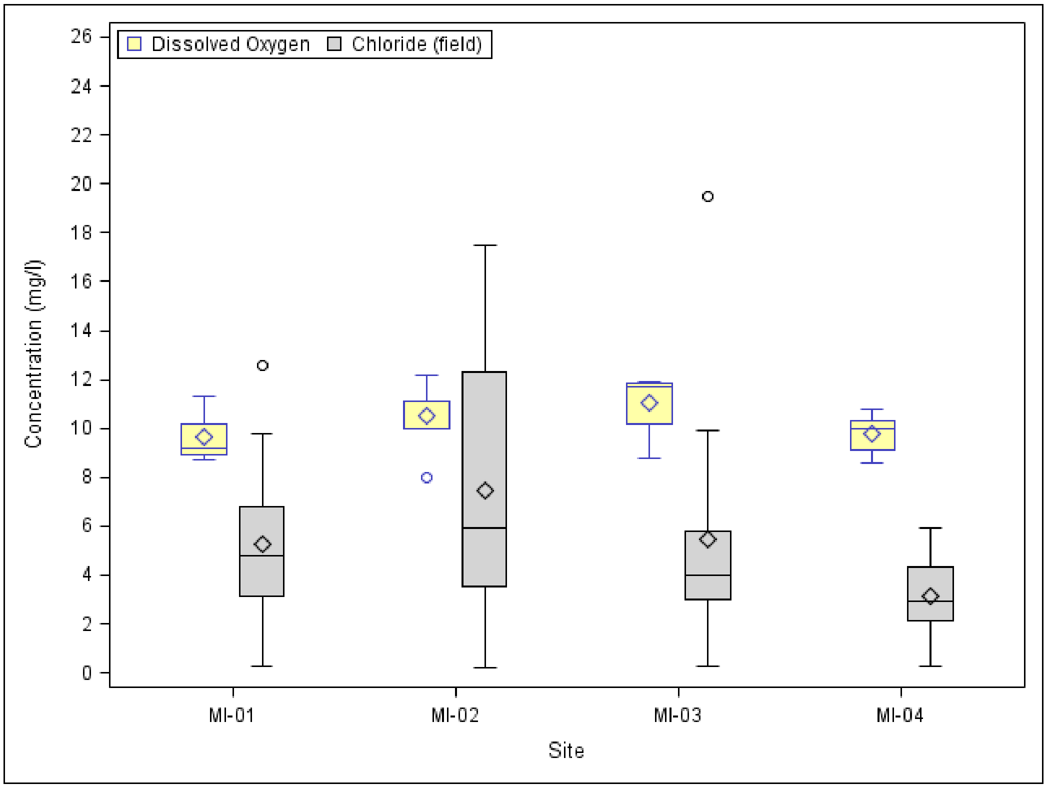

Figure 3. Boxplots of concentrations of dissolved oxygen and chloride from field measurements. Boxplots show medians (-), means (◊), first and third quartiles (box minimum and maximum), maximum and minimum values beyond the quartiles but within 1.5 x the interquartile range (whiskers), and outliers beyond 1.5 x the interquartile range (○).

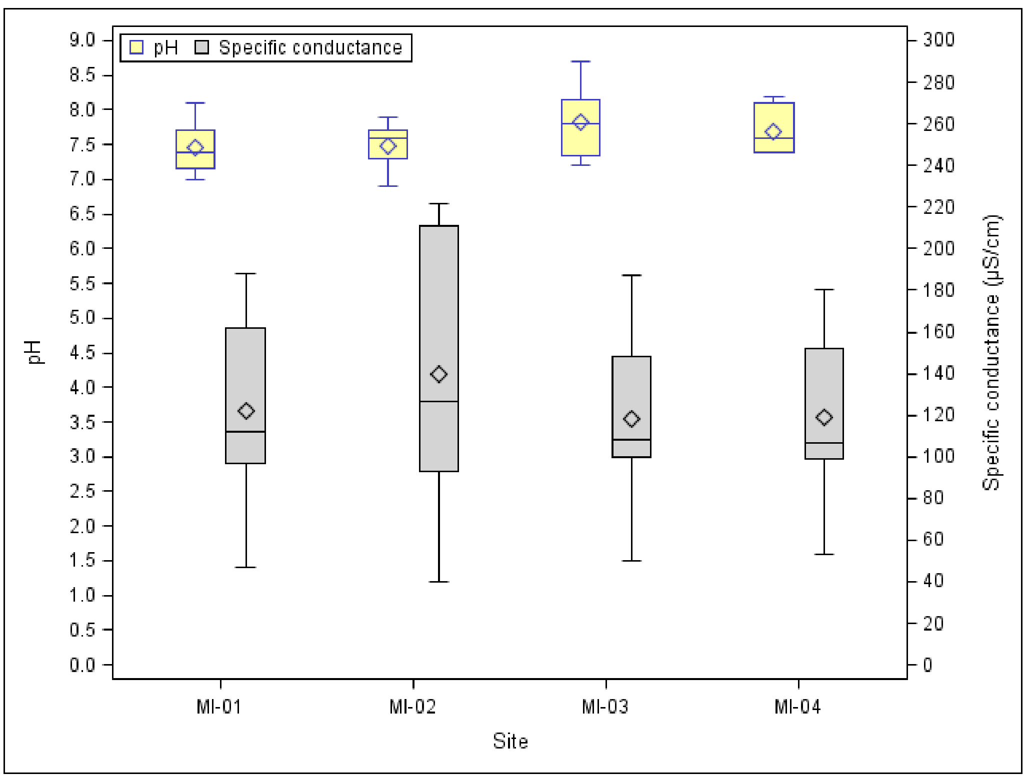

Figure 4. Boxplots of pH and specific conductance from field measurements. Symbols as in Figure 3.

Laboratory results

Most laboratory measurements did not exceed Michigan criteria or USEPA or CCME recommended criteria (Tables 5-9). Mean aluminum and iron concentrations were greater than recommended and state health/secondary/aesthetic criteria at all sites, and manganese was greater than EPA and CCME recommended secondary/aesthetic levels at all sites except MI-02 (Tables 6, 8). Cadmium at MI-01 through MI-03 exceeded USEPA and CCME recommended hardness-based criteria in samples from 26 September 2016 (Table 6), but the measurements (0.5 µg/l) were < 2 * LOD (LOD's of 0.3 µg/l). Cobalt exceeded Canadian hardness-based recommendations at least once at each site (Table 7, Fig. 9). Chromium concentrations were greater than CCME recommendations at three of the sites in 2015-2016 (Table 7, Fig. 8). Copper exceeded CCME recommendations at MI-02 in May 2012 (3 µg/l; Table 7). Lead exceeded the recommended and state hardness-based criteria at MI-04 in May 2015 (183 µg/l).

Quality control samples were mostly within acceptable measurement ranges. Fourteen sequential replicate samples from four sites had results (37 total) for some analytes (Al, B, chloride, Cr, Co, Cu, Fe, P, Na, TDS, TSS, and Zn) that were > 20% different from the original.

Table 5. Chloride (lab measurements), sulfate, TDS, and TSS means ± standard deviation (minimum - maximum, *n*) and regulatory or recommended criteria, in mg/l. Bold font indicates greatest and smallest mean measurements.

Criterion source / site code	Chloride (LOD range 0.2 – 0.5)	Sulfate (LOD range 0.04 - 0.33)	TDS (LOD range 2 - 20)	TSS (LOD range 2 - 5)
US EPA	230, 250[1]	250[1]	500[1]	
MI state	150 (50, 125, 250 health[2])	370 (250 health)	500, 750[3]	
CCME	120, 250[4]	500[4]	500[4]	
MI-01	3.2 ± 1.1 (1.1-4.9, 15)	2.6 ± 1.0 (1.6-5.6, 15)	97 ± 17 (62-124, 15)	**3** ± 2 (1-7, 15)
MI-02	**4.4** ± 1.4 (2.4-6.5, 15)	**3.8** ± 1.7 (1.8-8.9, 15)	**110** ± 23 (74-144, 15)	**2** ± 2 (1-7, 15)
MI-03	3.1 ± 1.1 (0.9-5.3, 15)	2.4 ± 0.8 (1.6-4.2, 15)	94 ± 17 (64-130, 15)	2 ± 1 (1-5, 15)
MI-04	**2.1** ± 0.7 (0.1-3.2, 15)	**2.3** ± 0.7 (1.5-4.0, 15)	**87** ± 16 (63-124, 15)	2 ± 1 (1-5, 15)
Entire Zone	3.2 ± 1.3 (0.1-6.5, 60)	2.8 ± 1.2 (1.5-8.9, 60)	97 ± 20 (62-144, 60)	2 ± 2 (1-7, 60)

[1] USEPA secondary drinking water criterion
[2] Criteria in parentheses apply to drinking water, public water supply, and health-based limits, respectively
[3] Criteria represent chronic and instantaneous criteria, respectively
[4] Canada Health drinking water aesthetic criterion

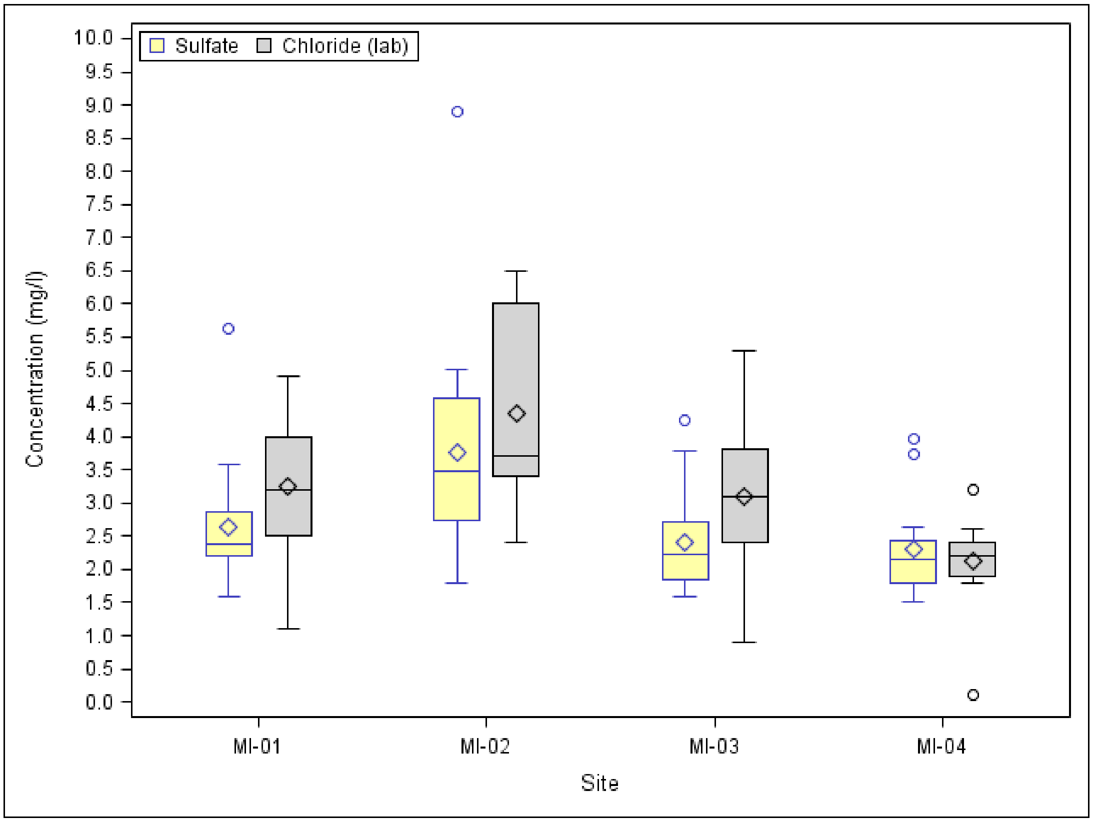

Figure 5. Boxplot of concentrations of sulfate and chloride from lab measurements. Symbols as in Figure 3.

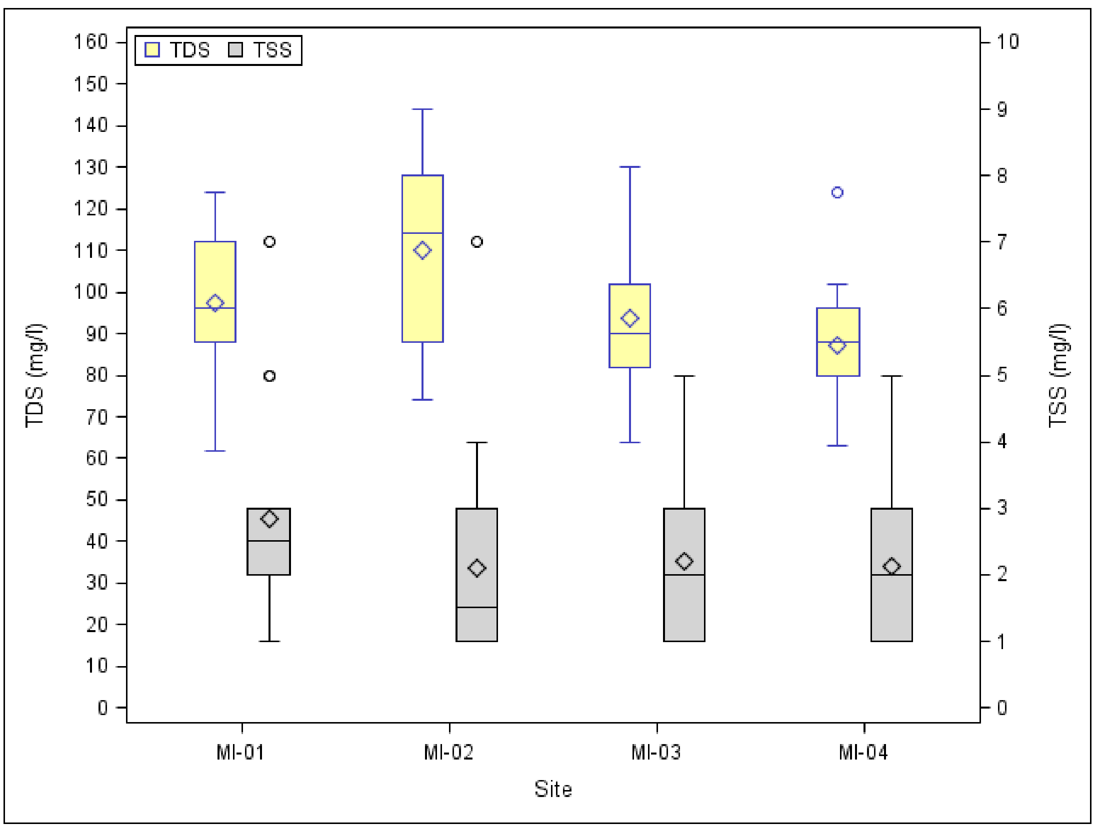

Figure 6. Boxplot of concentrations of TDS and TSS. Symbols as in Figure 3.

Table 6. Aluminum, boron, and cadmium means ± standard deviation (minimum - maximum, *n*) and regulatory or recommended criteria, in mg/l. Bold font indicates greatest and smallest mean measurements.

Criterion source / site code	Aluminum (LOD range 0.002 - 0.02)	Boron (LOD range 0.002 - 0.026)	Cadmium (LOD range 0.0002 - 0.0007)
US EPA	0.087	6.0[1]	0.00033-0.00089 [2]
MI state	0.050 (health)	7.2 (0.5 for health)	0.0010-0.0028[2]
CCME	0.100	1.5	0.00006-0.00018[2]
MI-01	0.121 ± 0.048 (0.058-0.248, 15)	**0.013** ± 0.006 (0.001-0.027, 15)	0.0002 ± 0.0001 (0.0001-0.0005, 15)
MI-02	**0.138** ± 0.073 (0.026-0.295, 15)	0.013 ± 0.005 (0.005-0.022, 15)	**0.0002** ± 0.0001 (0.0001-0.0006, 15)
MI-03	0.104 ± 0.067 (0.023-0.267, 15)	0.013 ± 0.005 (0.001-0.019, 15)	0.0002 ± 0.0001 (0.0001-0.0005, 15)
MI-04	**0.090** ± 0.068 (0.012-0.281, 15)	**0.012** ± 0.004 (0.002-0.018, 15)	**0.0002** ± 0.0001 (0.0001-0.0004, 15)
Entire Zone	0.113 ± 0.066 (0.012-0.295, 60)	0.013 ± 0.005 (0.001-0.027, 60)	0.0002 ± 0.0001 (0.0001-0.0006, 60)

[1] USEPA Health advisory lifetime level

[2] Criterion is hardness-dependent

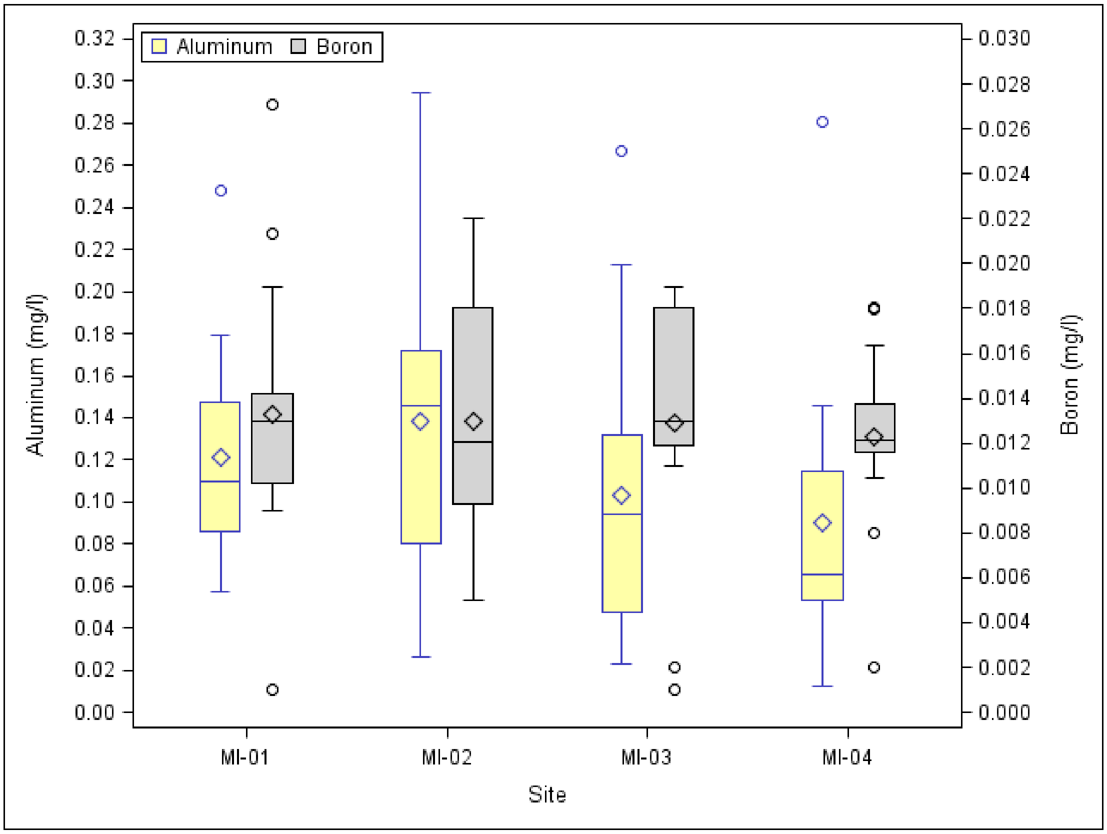

Figure 7. Boxplot of aluminum and boron concentrations. Symbols as in Figure 3.

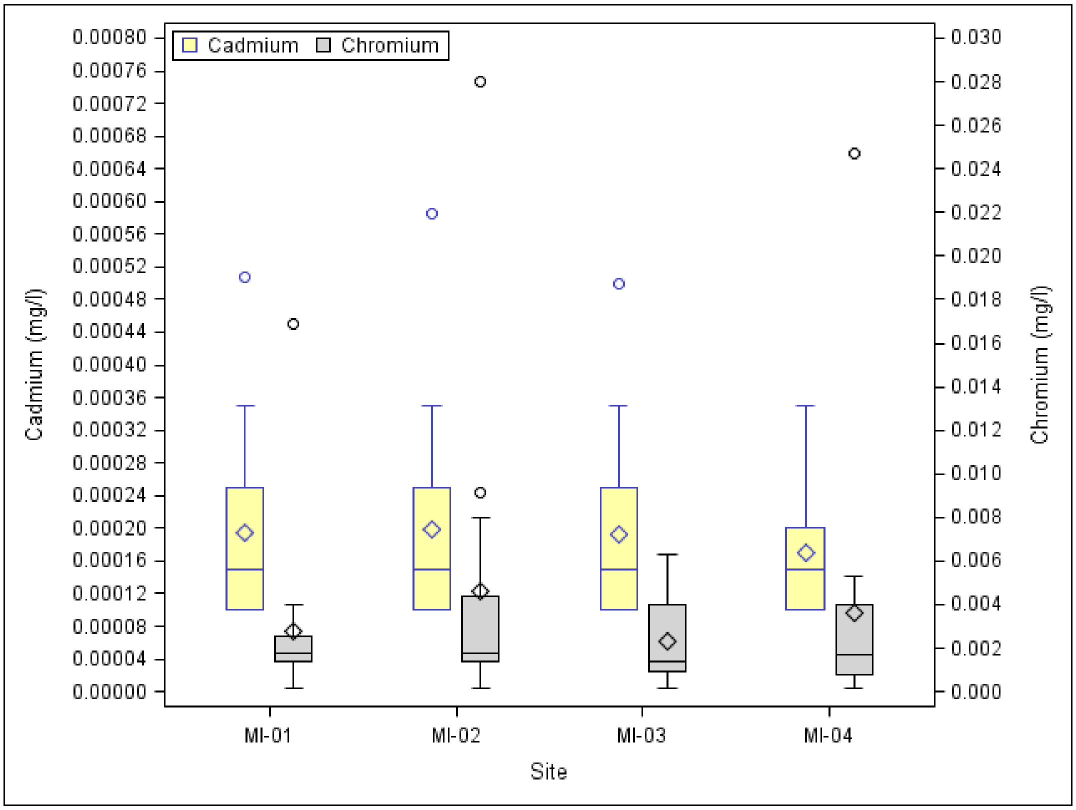

Figure 8. Boxplot of cadmium and chromium concentrations. Symbols as in Figure 3.

Table 7. Chromium, cobalt, and copper means ± standard deviation (minimum - maximum, *n*) and regulatory or recommended criteria, in mg/l. Bold font indicates greatest and smallest mean measurements. CFEQG = Canadian Federal Environmental Quality Guidelines (for cobalt).

Criterion source / site code	Chromium (LOD range 0.00015 - 0.008)	Cobalt (LOD range 0.0002 - 0.002)	Copper (LOD range 0.0004 - 0.0011)
US EPA	0.036-0.097[1, 2]		Biotic Ligand Model
MI state	0.036-0.097[1, 2]	0.100 (0.040 residential health)	0.0037-0.0106[2]
CCME / CFEQG	0.0089[1]	0.0006-0.00114[2]	0.002-0.003[2]
MI-01	0.0028 ± 0.004 (0.0002-0.0169, 15)	0.0007 ± 0.0005 (0.0001-0.0020, 15)	0.0012 ± 0.0004 (0.0005-0.0018, 15)
MI-02	**0.0046** ± 0.007 (0.0002-0.0280, 15)	0.0006 ± 0.0007 (0.0001-0.0025, 15)	**0.0014** ± 0.0008 (0.0004-0.0033, 15)
MI-03	**0.0023** ± 0.002 (0.0002-0.0063, 15)	**0.0007** ± 0.0008 (0.0001-0.0026, 15)	0.0010 ± 0.0003 (0.0005-0.0015, 15)
MI-04	0.0036 ± 0.006 (0.0002-0.0247, 15)	**0.0005** ± 0.0005 (0.0001-0.0015, 15)	**0.0009** ± 0.0004 (0.0004-0.0019, 15)
Entire Zone	0.0033 ± 0.005 (0.0002-0.0280, 60)	0.0006 ± 0.0006 (0.0001-0.0026, 60)	0.0011 ± 0.0005 (0.0004-0.0033, 60)

[1] Criterion for chromium (III)

[2] Criterion is hardness-dependent

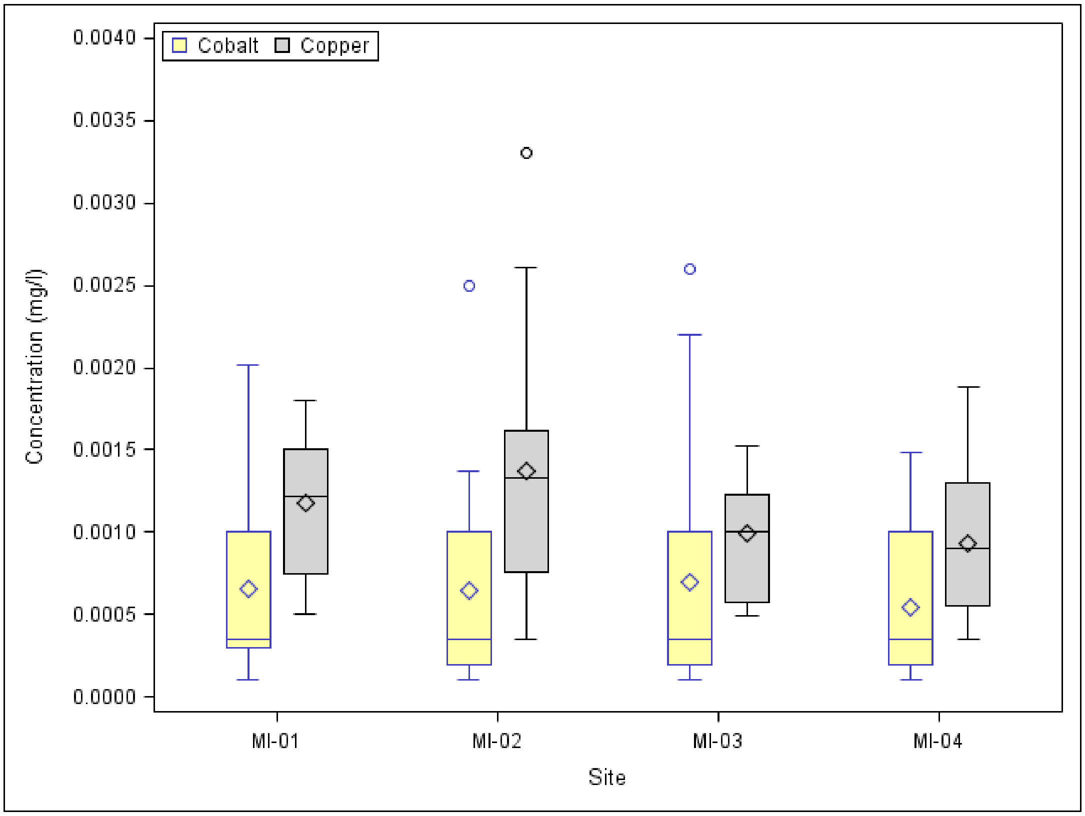

Figure 9. Boxplot of cobalt and copper concentrations. Symbols as in Figure 3.

Table 8. Iron, manganese, and nickel means ± standard deviation (minimum - maximum, *n*) and regulatory or recommended criteria, in mg/l. Bold font indicates greatest and smallest mean measurements.

Criterion source / site code	Iron (LOD range 0.001 - 0.05)	Manganese (LOD range 0.0002 - 0.002)	Nickel (LOD range 0.00059 - 0.004)
US EPA	1.000, 0.300[1]	0.050[1], 0.300[2]	0.021-0.059[3]
MI state	0.300 (health)	0.762-2.240[3]	0.021-0.059[3]
CCME	0.300 (aesthetic)[4]	0.120, 0.050 (aesthetic)[4]	0.025-0.107[3]
MI-01	**0.479** ± 0.144 (0.315-0.824, 15)	0.073 ± 0.026 (0.040-0.142, 15)	0.001 ± 0.001 (0-0.002, 15)
MI-02	0.415 ± 0.173 (0.221-0.912, 15)	**0.022** ± 0.007 (0.014-0.038, 15)	0.001 ± 0.001 (0-0.003, 15)
MI-03	**0.393** ± 0.174 (0.145-0.690, 15)	0.065 ± 0.024 (0.027-0.109, 15)	**0.001** ± 0.001 (0-0.004, 15)
MI-04	0.401 ± 0.160 (0.149-0.647, 15)	**0.082** ± 0.034 (0.038-0.169, 15)	**0.001** ± 0 (0-0.002, 15)
Entire Zone	0.422 ± 0.163 (0.145-0.912, 60)	0.061 ± 0.033 (0.014-0.169, 60)	0.001 ± 0.001 (0-0.004, 60)

[1] USEPA drinking water secondary criterion
[2] USEPA health advisory lifetime level
[3] Criterion is hardness-dependent
[4] Canada Health drinking water criterion

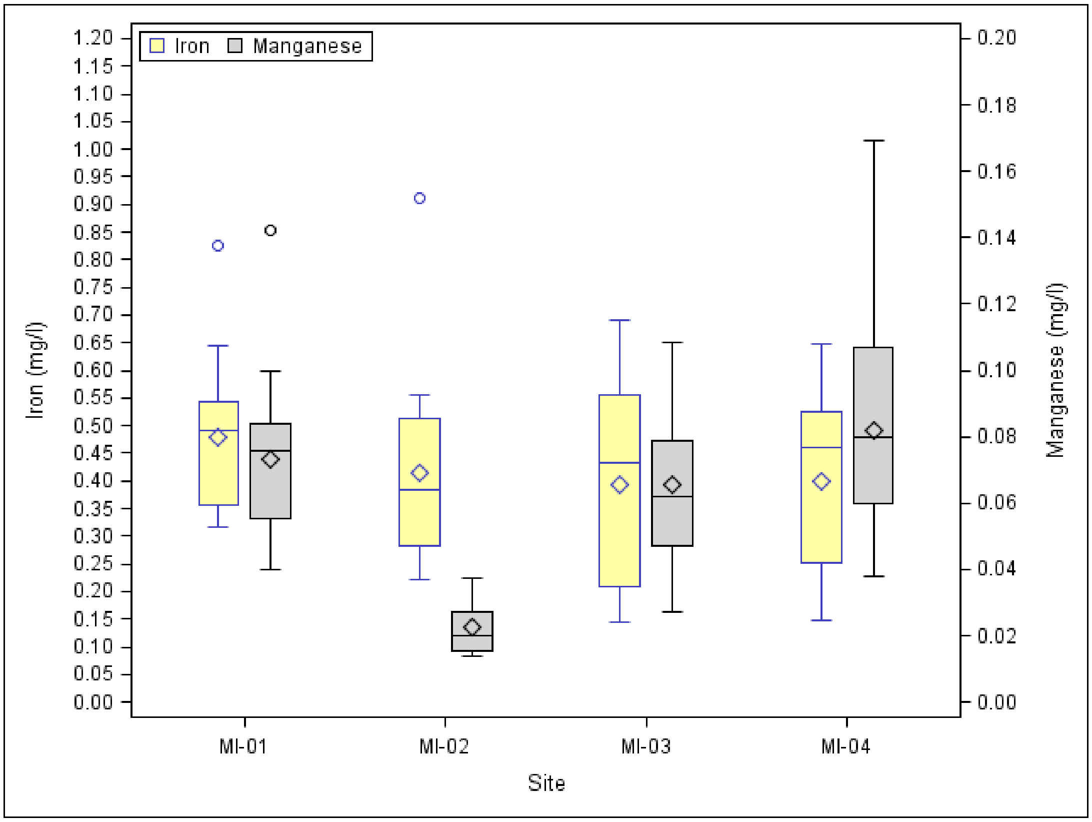

Figure 10. Boxplot of iron and manganese concentrations. Symbols as in Figure 3.

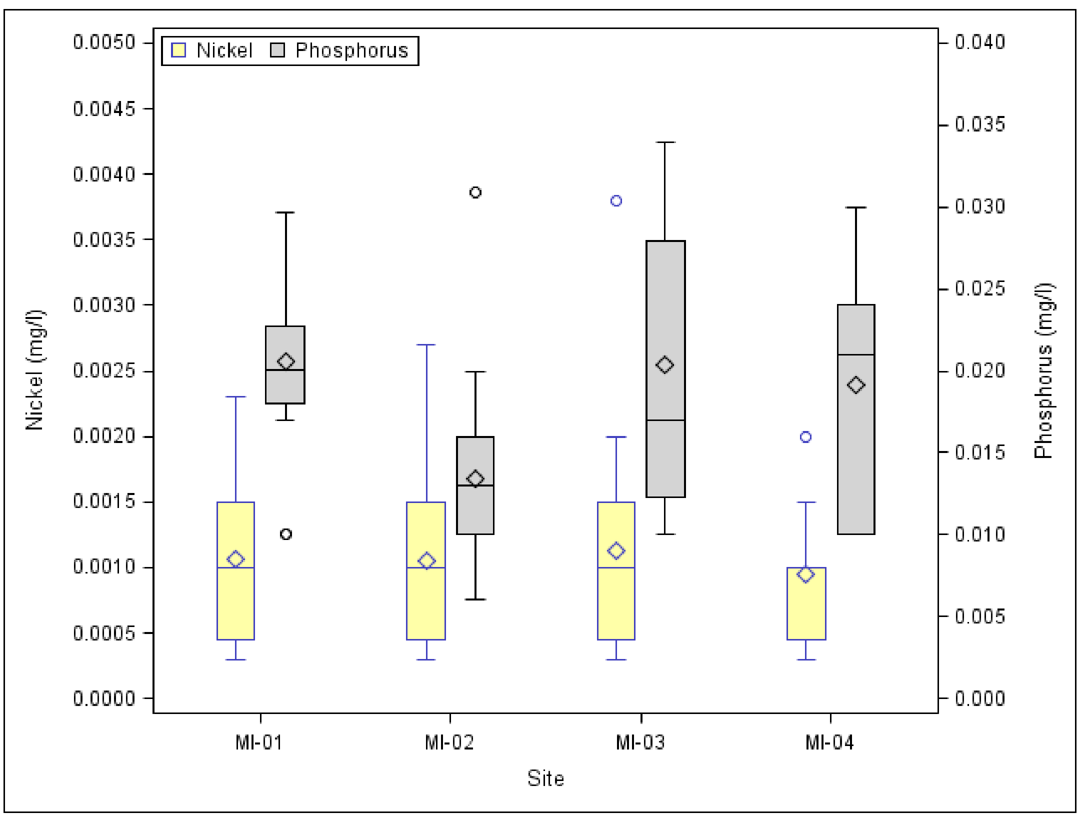

Figure 11. Boxplot of nickel and phosphorus concentration. Symbols as in Figure 3.

Table 9. Phosphorus, sodium, and zinc means ± standard deviation (minimum - maximum, *n*) and regulatory or recommended criteria, in mg/l. Bold font indicates greatest and smallest mean measurements.

Criterion source / site code	Phosphorus (LOD range 0.003 - 0.02)	Sodium (LOD range 0.08 - 1)	Zinc (LOD range 0.001 - 0.009)
US EPA			0.048-0.136[1]
MI state	1.00	120, 350 (health)[2]	0.048-0.136[1]
CCME		200[3]	0.030[4]
MI-01	**0.02** ± 0.01 (0.01-0.03, 15)	2 ± 0 (2-3, 15)	0.004 ± 0.002 (0.001-0.007, 15)
MI-02	**0.01** ± 0.01 (0.01-0.03, 15)	**2** ± 1 (2-3, 15)	0.004 ± 0.002 (0.001-0.008, 15)
MI-03	0.02 ± 0.01 (0.01-0.03, 15)	2 ± 0 (1-3, 15)	**0.003** ± 0.002 (0.001-0.009, 15)
MI-04	0.02 ± 0.01 (0.01-0.03, 15)	**2** ± 0 (1-2, 15)	**0.004** ± 0.003 (0.001-0.013, 15)
Entire Zone	0.02 ± 0.01 (0.01-0.03, 60)	2 ± 0 (1-3, 60)	0.004 ± 0.002 (0.001-0.013, 60)

[1] Criterion is hardness-dependent

[2] Criteria represent residential health-based and non-residential health-based limits, respectively

[3] Canada Health drinking water aesthetic criterion

[4] CCME criterion prior to publication in 2018 of criterion dependent on hardness, pH, and DOC

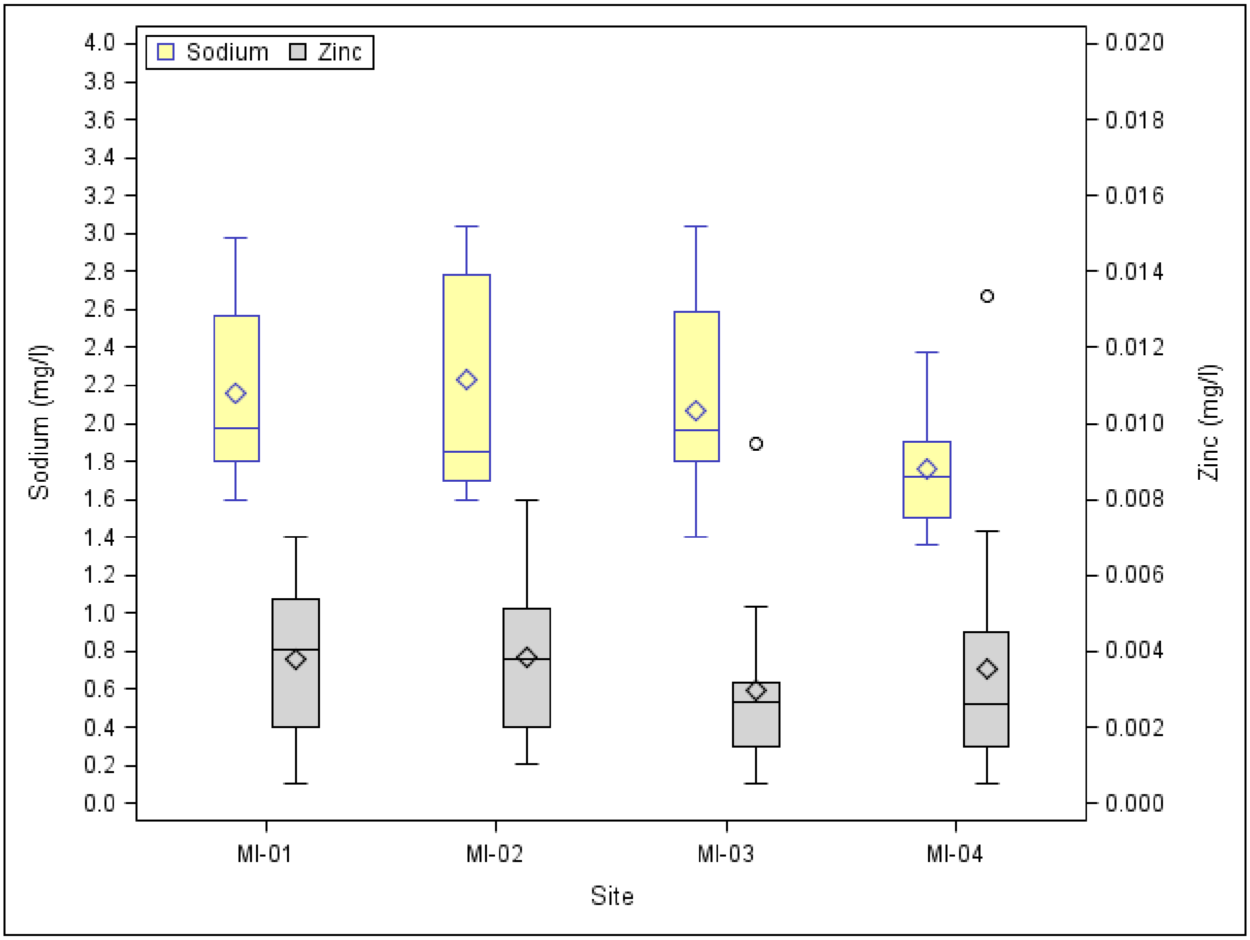

Figure 12. Boxplot of sodium and zinc concentrations. Symbols as in Figure 3.

Figure 13. Specific conductance, chloride, and sulfate results from the Presque Isle River zone. Results are means ± standard deviation (minimum – maximum, *n*).

(B) Relation between sites

Principal Components Analysis

Table 10. Eigenvalues and proportion of variance explained for components 1-3 of the Principal Components Analysis (PCA).

Component number	Eigenvalue	Proportion of variance	Cumulative proportion of variance
1	9.123	0.537	0.537
2	2.791	0.164	0.701
3	1.627	0.096	0.797

Table 11. Eigenvectors for water quality characteristics for components 1-3 of the Principal Components Analysis (PCA).

Characteristic	Eigenvectors by principal component.		
	1	2	3
pH	0.0976	-0.3947	0.2781
Specific conductance	0.3252	-0.0080	-0.0102
Alkalinity	0.2359	0.0717	0.1865
Aluminum	-0.1913	0.2546	0.2366
Barium	0.1728	0.0414	0.5912
Calcium	0.3116	-0.1024	0.0900
Chloride	0.2669	0.1886	-0.0291
Copper	-0.0514	0.1248	0.5931
Iron	-0.0750	0.5425	0.0180
Magnesium	0.3105	0.1024	-0.0978
Manganese	0.0039	0.5174	-0.1507
Phosphorus	-0.1294	0.3180	0.1084
Potassium	0.3035	0.0840	0.1200
Sodium	0.2977	0.1478	-0.0206
Sulfate	0.2951	0.0163	-0.2365
TDS	0.3158	0.0900	-0.0798
Hardness	0.3247	-0.0029	-0.0105

We included in the PCA the following characteristics that had less than 10 % with non-detects: specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, phosphorus, potassium, sodium, TDS, and hardness.

The PCA indicated that a combination of specific conductance, TDS, hardness, and several major elements and ions (Ca, Mg, K, Na, chloride, and sulfate) explained 54 % of the variance of the data as part of the first principal component (Tables 10-11). The second component, which explained 16 % of the variance, consisted primarily of pH (inversely related), Al, Fe, Mn, and P. The third component explained only 9.6 % of variance, and was related primarily to Ba and Cu.

Graphing the Presque Isle River sites and other GLIFWC study sites on the first and second principal components indicated that the Presque Isle River sites were closer to each other than to other sites, with the exception of one downstream site in the White Pine zone of Michigan (Fig. 14).

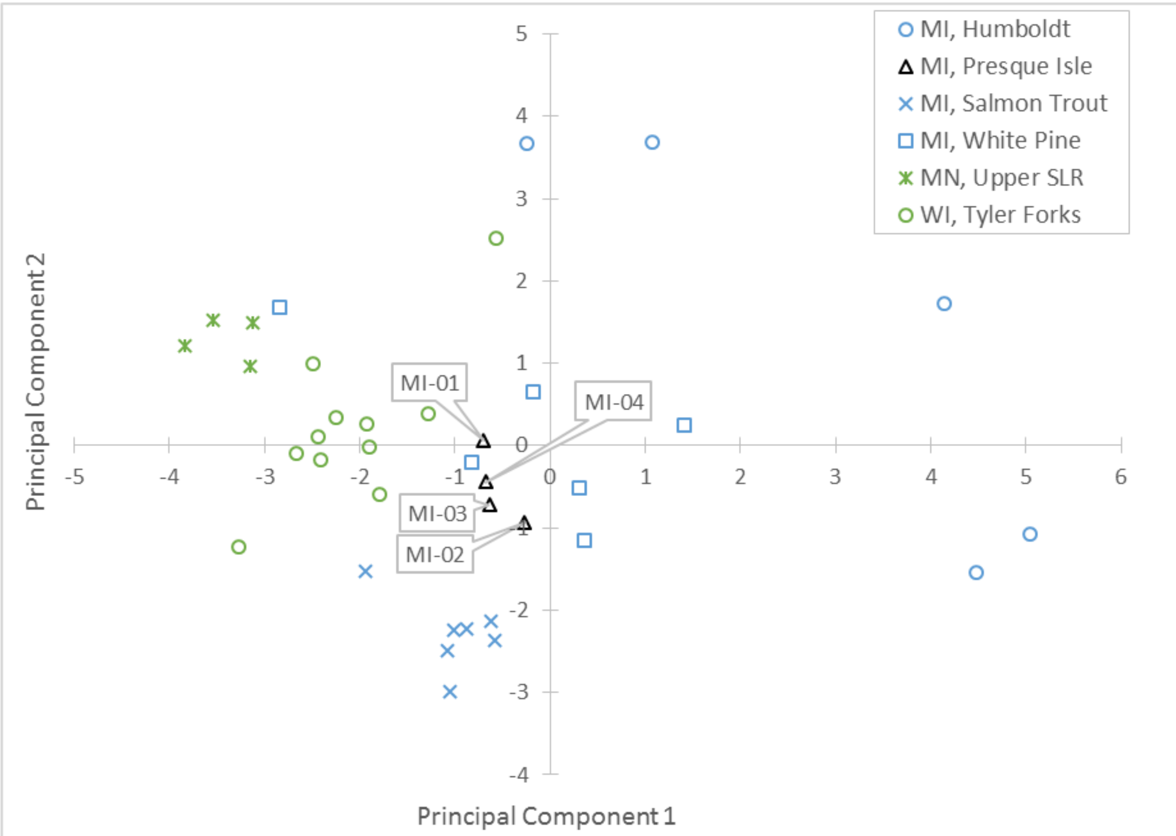

Figure 14. Principal Components Analysis (PCA) of all sites using log-transformed site median values of characteristics with non-detects < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, phosphorus, potassium, sodium, TDS, and hardness).

Cluster analysis

Cluster analysis indicated that MI-02, the site on the Little Presque Isle River, was distinct from a cluster of the other sites (Fig. 15). Within that other cluster, MI-04, the site the furthest upstream, was distinct from two sites further downstream (MI-01 and MI-03; Fig. 15). MI-02 demonstrated mean values of specific conductance, alkalinity, hardness, TDS, chloride, sulfate, aluminum, calcium, copper, and magnesium that were greater than mean values at the other sites, and mean values of iron, manganese, and phosphorus that were lower than at the other sites (Tables 4-9; Figs. 3-7, 9-11).

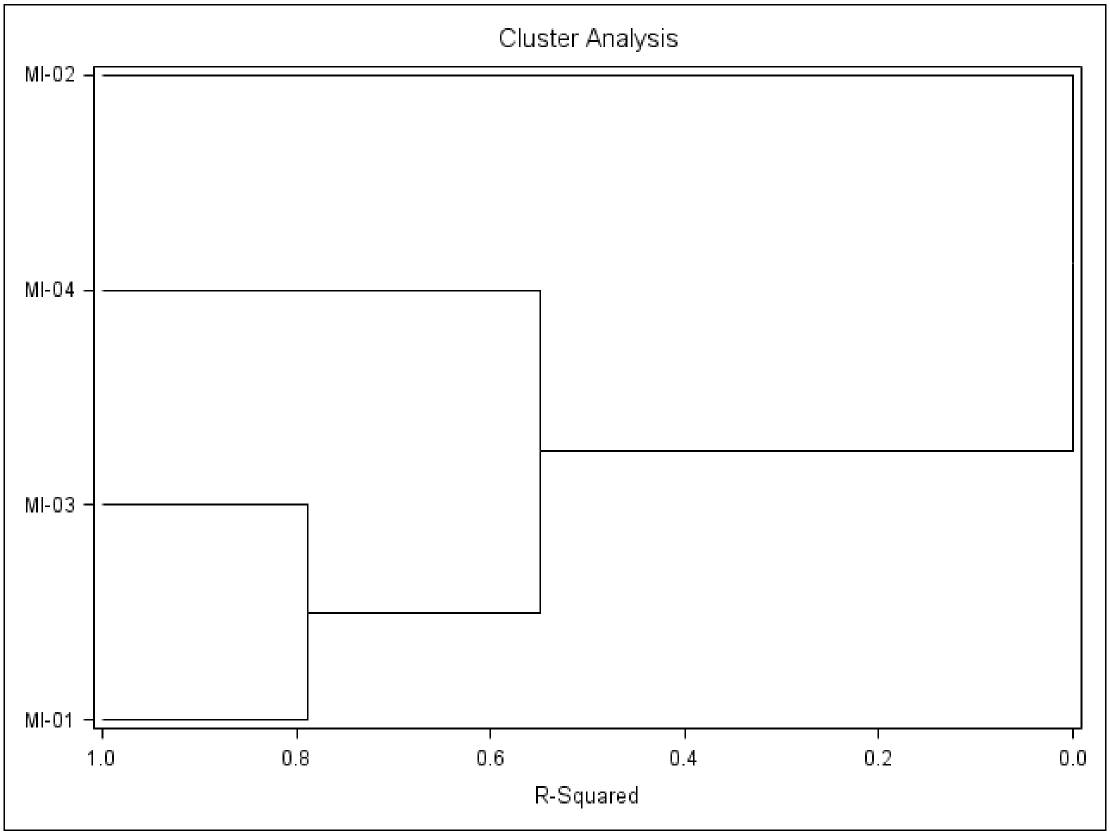

Figure 15. Cluster analysis of upper St. Louis River sites using log-transformed site median values of characteristics with non-detects < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, TDS, and hardness).

4. Discussion

GLIFWC water quality monitoring in the Presque Isle River zone indicated that constituents of potential concern were within state criteria during the sampling in 2011 – 2018. Aluminum, iron, and manganese concentrations were greater than criteria, but the iron and manganese criteria were secondary, aesthetic, or human health for drinking water and the results could relate to natural factors such as turbidity and organic carbon. The measurement of lead at MI-04 in May of 2015 that exceeded state surface water criteria was unusually high (183 µg/l) and could be indicative of a pollution event during high spring flows, or be a result of sample contamination. Similar possibilities could explain the relatively high copper measurement at MI-02 in May 2012. The relatively high cobalt measurements, on the other hand, are more likely to be a geological influence in this watershed since all sites demonstrated at least one large concentration. Water sample results were otherwise within state and USEPA and CCME recommended criteria if ignoring sample results close to LOD values.

Comparisons between sites suggest that the Presque Isle River zone water quality characteristics are different from other sampled zones, and that the Little Presque Isle River site was distinct from the other sites. The distinctiveness of the Little Presque Isle River site may relate to higher specific conductance, alkalinity, hardness, TDS, chloride, sulfate, aluminum, and copper, or lower iron, manganese, and phosphorus. Explanations for such differences could involve differences in geology, point sources of contamination into the river, or land cover in the watersheds at the different sampling sites. The only apparent potential discharge or stormwater runoff sites in the Little Presque Isle River watershed are a gas transmission site, some former gravel pits, septic systems, or roads. It is unclear if those could explain the apparent difference between the Little Presque Isle River site and the other sites.

Results overall suggest that water quality was relatively unimpacted in the upper Presque Isle River zone in 2011-2018.

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