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

Upper St. Louis River Zone

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Administrative Report 19-16
November 2019

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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 Upper St. Louis River zone, in the 1854 Treaty-ceded Territory in Minnesota (Fig. 1), is one of the zones for which GLIFWC has established baseline water quality. The zone is in the headwaters of the St. Louis River, which flows by iron mining zones downstream to the *Gichigami* (Lake Superior). Although some mineral exploration occurred in the headwaters, USGS (2016) records do not indicate that active mining occurred in this zone.

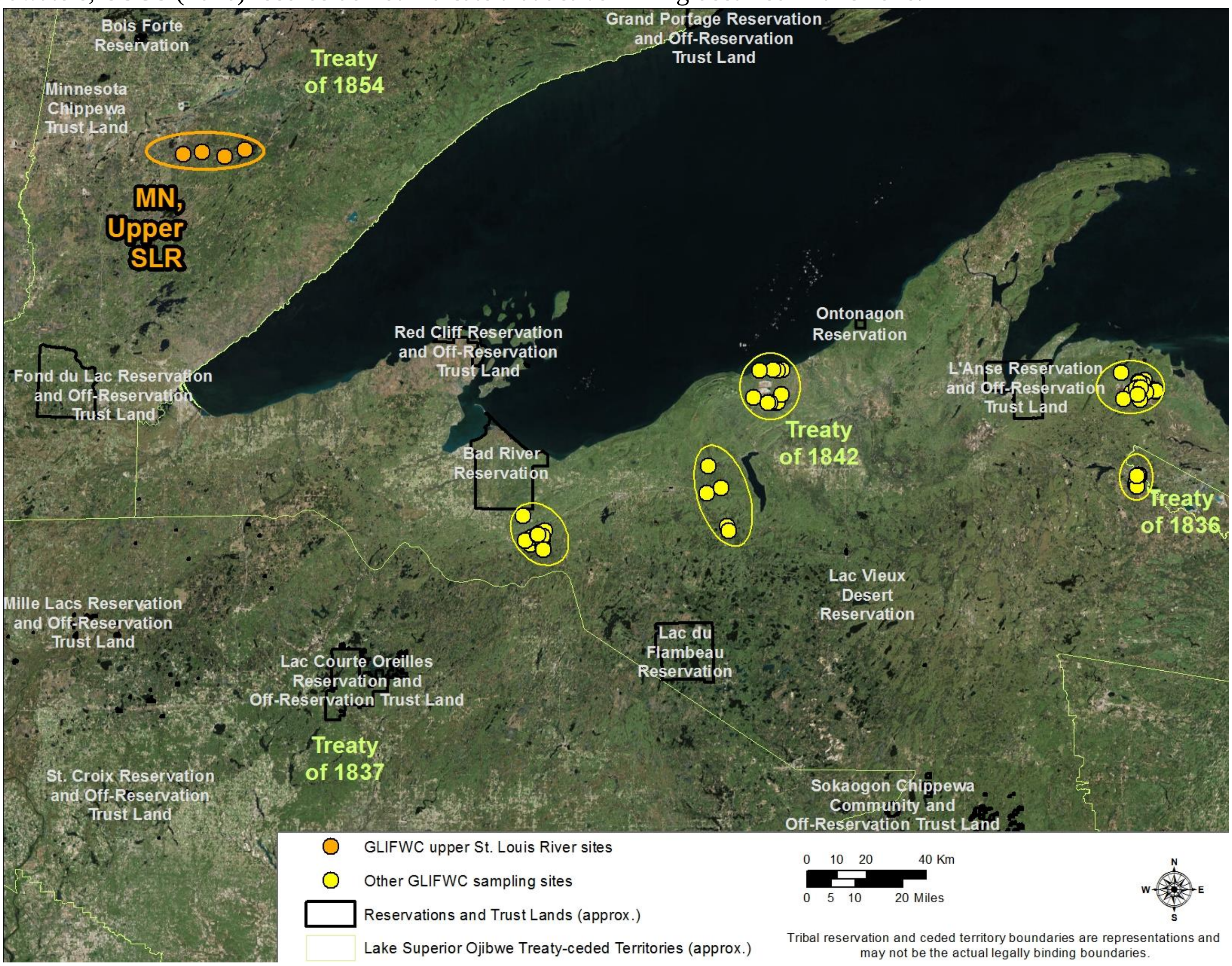

Figure 1. Map of the Upper St. Louis River zone water quality monitoring sites relative to other GLIFWC monitoring sites and Reservation and Territories boundaries.

As part of the Lake Superior Basin, the waters of the St. Louis River are state-classified as Outstanding International Resource Waters. State law protects those waters from degradation from new or expanded discharges of bioaccumulative substances of immediate concern such as polychlorinated biphenyls and mercury (Minn. R. 7052.0300). Minnesota state assessments of the streams of the upper St. Louis River zone have indicated that the River is impaired for mercury in several of the streams (Fig. 2). The River is attaining its designated Aquatic Life and Recreation - General Cold Water Habitat (lakes and streams) use in the lower reaches of the study zone, but data were insufficient to determine attainment in the upper headwaters reach (Fig. 2).

The GLIFWC monitoring assessed water quality in the upper St. Louis 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 9 % of samples and collected field sequential replicates for 22 % 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 four 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 (Minnesota Rules Chapter 7050 chronic standards for class 2 waters unless otherwise noted) 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.

Study sites and frequency

Monitoring included four surface water sites in streams or rivers (Table 3, Fig. 2). Sampling began in 2011 and occurred at least twice per year through 2018, except for single sampling events in 2013 and 2018 at MN-04, and in 2018 at MN-03.

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]
MN-01	St. Louis River at CR 346 (Moose Line Rd.) (FR130)	47.472603	-92.121252	River	17	17
MN-02	St. Louis River at Highway 110 (stream gage location)	47.481121	-92.03985	River	17	16
MN-03	St. Louis River and Skibo Mill landing at FR795	47.4676	-91.93831	River	16	15
MN-04	St. Louis River at railroad near river mile 194	47.491488	-91.845856	River	14	14

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

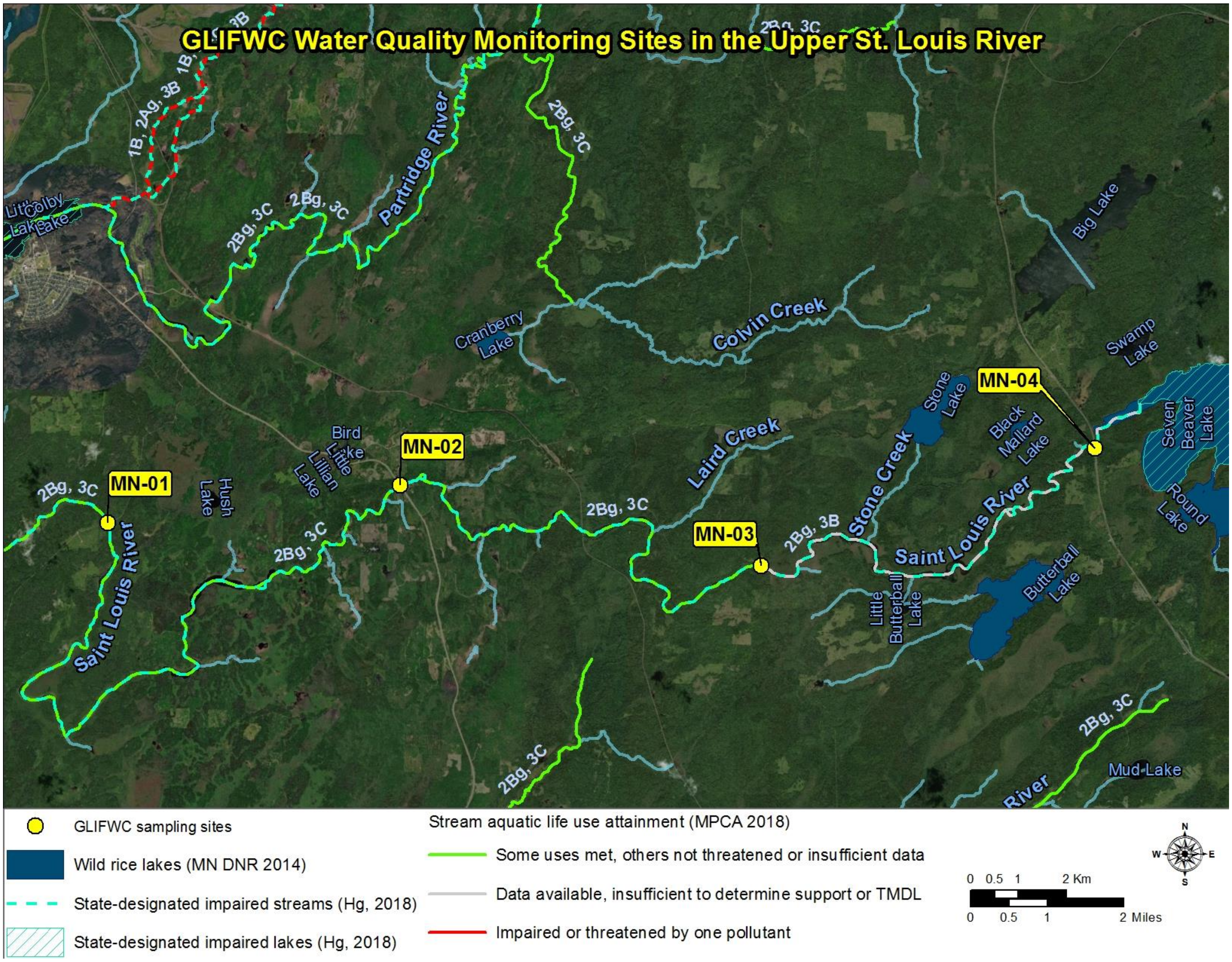

Figure 2. Map of GLIFWC sampling sites and Minnesota Pollution Control Agency designated uses and assessments of water bodies in the upper St. Louis River zone. 1B = Domestic Consumption (requires moderate treatment); 2Ag = Aquatic Life and Recreation - General Cold Water Habitat (lakes and streams); 2B = Aquatic Life and Recreation - Warm Water Habitat (lakes and streams); 2Bg = Aquatic Life and Recreation - General Warm Water Habitat (lakes and streams); 3A = Industrial Consumption (no treatment); 3B = Industrial Consumption (moderate treatment); 3C = Industrial Consumption (heavy treatment).

3. Results

(A) Summary statistics

Field measurements

Dissolved oxygen (DO) means were greater than 6 mg/l and pH means greater than 6.5 at all sampling sites (Table 4, Figs. 3-4). The lowest individual measurements were 5.6 mg/l for DO and 6.0 for chloride. Both of those low measurements were at MN-03 (Table 4, Figs. 3-4). Chloride means were all less than 3 mg/l, and individual measurements did not exceed 7 mg/l (at MN-01; Table 4, Figs. 3, 13). Specific conductance means and individual measurements did not exceed 100 µS/cm (Table 4, Figs. 4, 13). A few individual low measurements of pH (< 6.5) were the only field measurements that did not meet Minnesota state criteria for 2Bg waters, and those measurements were within 10% of the state limit (Table 4).

Table 4. Upper St. Louis River zone 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)
USEPA		230, 250[1]	6.5-9.0	
MN state	5, 7[2]	50, 100, 230, 250[3]	6.0-8.5/9.0, 6.5-8.5[4]	1000[5]
CCME	5.5-9.5[6]	120, 250[7]	6.5-9.0	
MN-01	7.3 ± 0.8 (6.6-8.9, 6)	**2** ± 2 (1-7, 11)	6.8 ± 0.3 (6.3-7.2, 14)	56 ± 14 (34-76, 18)
MN-02	**8.7** ± 0.7 (8.1-9.8, 5)	2 ± 1 (0-3, 11)	**7.0** ± 0.3 (6.4-7.3, 13)	**56** ± 19 (31-90, 17)
MN-03	**6.9** ± 1.3 (5.6-8.6, 4)	1 ± 1 (0-3, 11)	**6.6** ± 0.3 (6.0-7.0, 12)	**49** ± 14 (29-73, 16)
MN-04	8.0 ± 1.1 (6.8-9.4, 4)	**1** ± 1 (1-2, 11)	6.6 ± 0.2 (6.1-6.8, 12)	49 ± 17 (27-78, 15)
Entire zone	7.7 ± 1.1 (5.6-9.8, 19)	2 ± 1 (0-7, 44)	6.8 ± 0.3 (6.0-7.3, 51)	53 ± 16 (27-90, 66)

[1] USEPA secondary drinking water criterion
[2] Criterion is a minimum that depends on water body designation as 2B, 2A, respectively
[3] Criteria represent limits for waters with classifications 3A, 3B, 2A or 2B, and 3C/1 (secondary drinking water criterion), respectively
[4] Criterion is a range that depends on water body designation
[5] Criterion applies to class 4A and 4C waters (all waters unless otherwise listed)
[6] Criterion depends on water temperature class
[7] Canada Health drinking water aesthetic criterion

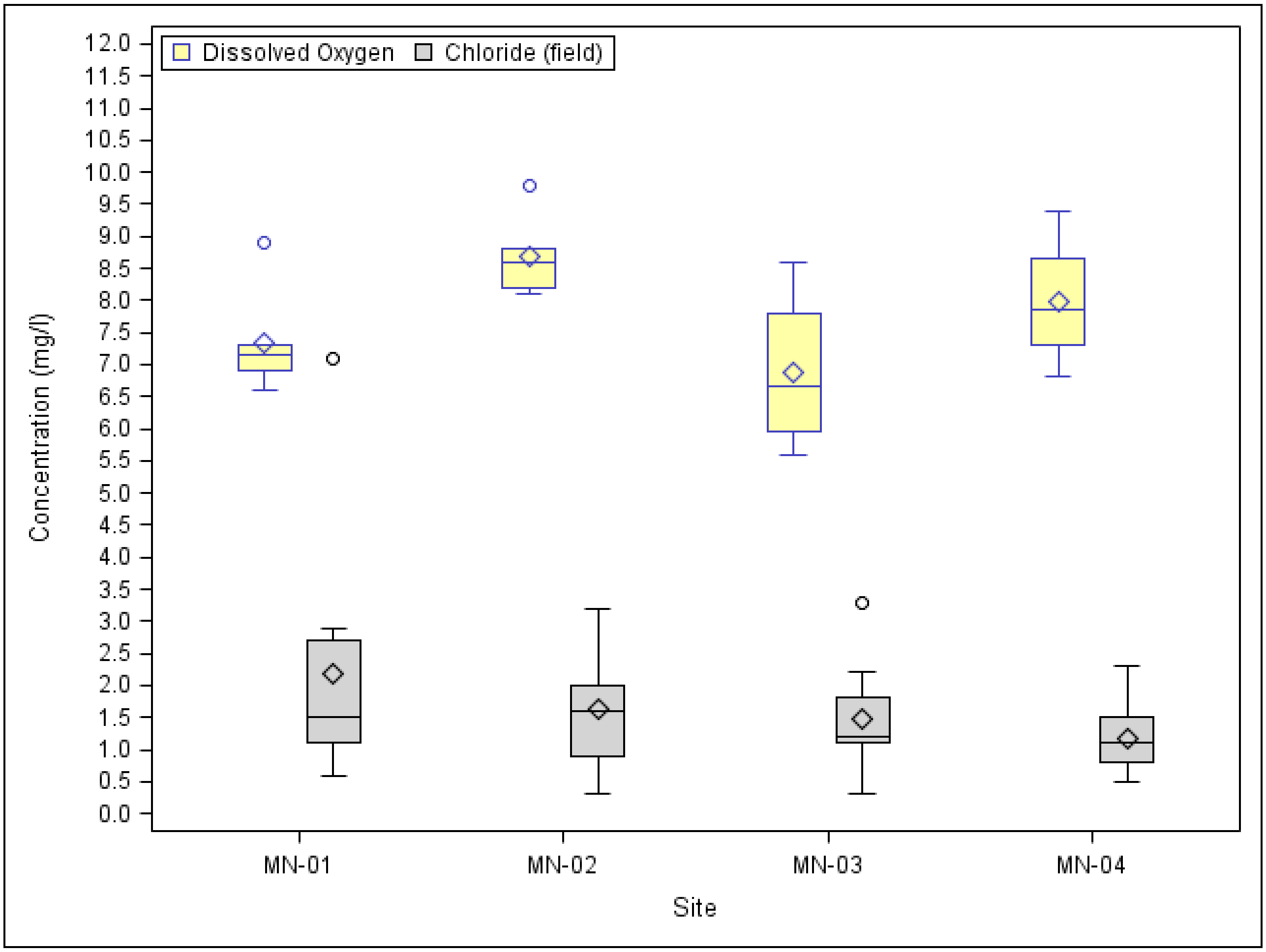

Figure 3. Boxplots of concentrations of dissolved oxygen and chloride from field measurements. Boxplots show medians (-), means (◊), first and third quartiles (box minimum and maximum), maximum and minimum values beyond the quartiles but within 1.5 x the interquartile range (whiskers), and outliers beyond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

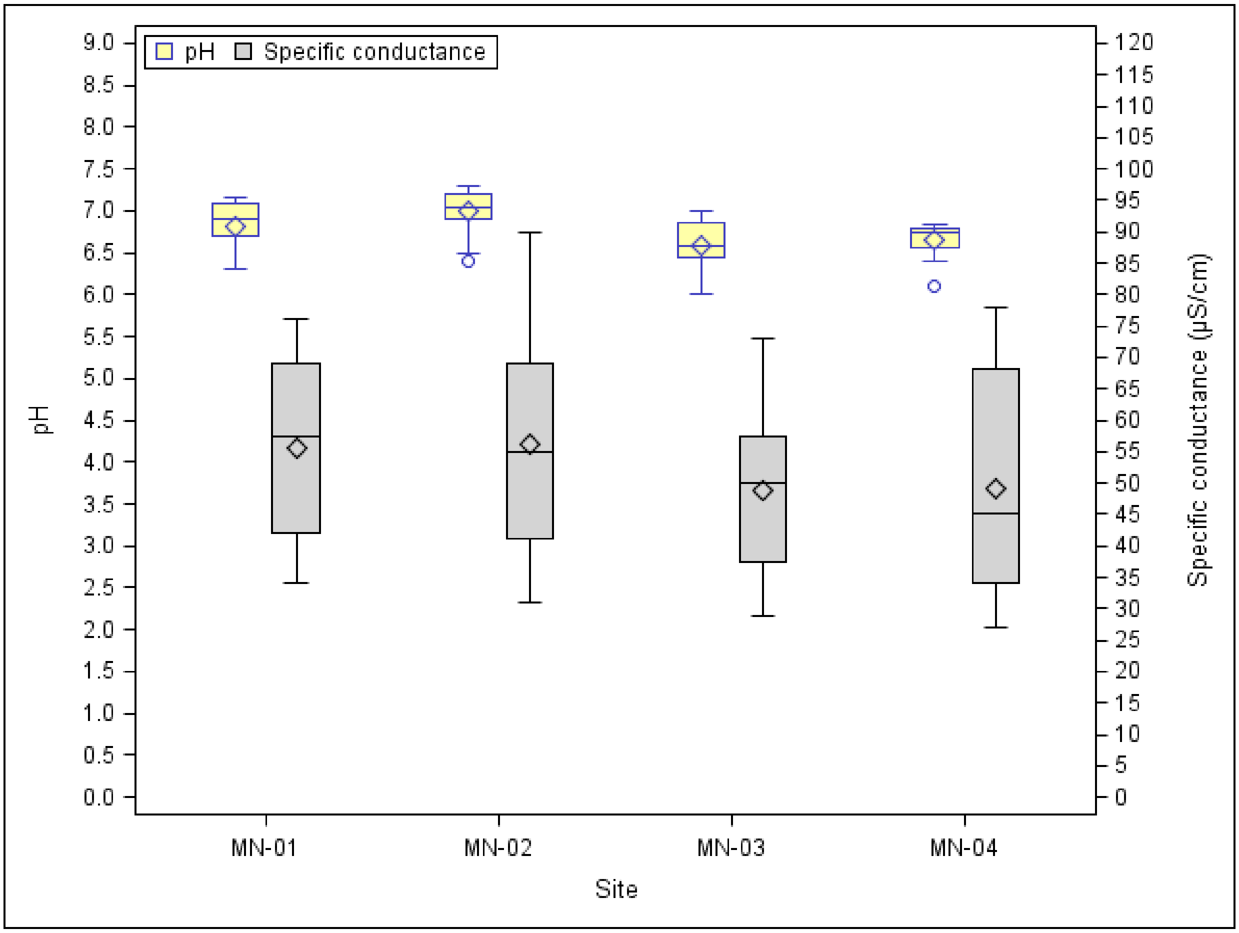

Figure 4. Boxplots of pH and specific conductance from field measurements. Symbols as in Figure 3.

Laboratory results

Most measurements did not exceed Minnesota criteria or USEPA or CCME recommended criteria (Tables 5-9). Sulfate concentrations were all less than 6 mg/l (Table 5, Fig. 5). Mean aluminum, iron, and manganese exceeded recommended and state criteria at all sites, though those criteria were mostly health/secondary/aesthetic criteria (Table 6, 8). Cadmium exceeded all three hardness-based criteria in samples from 26 September 2016 (Table 6), but the measurements (0.5-0.6 µg/l) were < 3 * LOD (LOD's of 0.3 µg/l). The concentration of chromium was greater than the CCME recommendation at MN-04 in September 2016 (17.3 µg/l; Table 7, Fig. 8). Copper exceeded CCME recommendations at each site at least once (Table 7). Those measurements were all 2-3 µg/l except for one measurement that also exceeded state criteria (26 µg/l at MN-01 in May of 2016; Table 7, Fig. 9). Lead exceeded the recommended and state hardness-based criteria at each site at least once (1-6 µg/l), but in all but one case those results were equal to or within 50 % of the LOD. Finally, zinc concentrations did not exceed criteria except at MN-03 in May of 2012 (49 µg/l; Table 9, Fig. 12).

Quality control samples were mostly within acceptable measurement ranges. Fourteen sequential replicate samples from four sites had results (45 total) for some analytes (alkalinity, Al, Be, Cd, Cr, Cu, Pb, Ni, P, K, Na, sulfate, TDS, TSS, total hardness, 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 –	Sulfate (LOD range 0.04 - 0.4)	TDS (LOD range 2 - 20)	TSS (LOD range 2 - 4)
US EPA	230, 250[1]	250[1]	500[1]	
MN state	50, 100, 230, 250[2]	10, 250[3]	700, 500[4]	
CCME	120, 250[5]	500[5]	500[5]	
MN-01	1.7 ± 0.5 (0.4-2.7, 17)	2.4 ± 0.9 (1.5-5.2, 17)	91 ± 19 (60-130, 17)	3 ± 2 (1-8, 17)
MN-02	**1.6** ± 0.6 (0.1-2.8, 16)	**2.6** ± 1.0 (1.4-4.9, 16)	**88** ± 19 (57-126, 16)	3 ± 2 (1-8, 16)
MN-03	1.7 ± 0.8 (0.1-3.8, 15)	**2.2** ± 0.8 (1.3-4.5, 16)	90 ± 29 (38-152, 15)	**3** ± 2 (1-6, 15)
MN-04	**1.7** ± 0.8 (0.1-3.9, 15)	2.3 ± 0.8 (1.3-4.3, 15)	**92** ± 27 (52-160, 15)	**4** ± 3 (1-11, 15)
Entire Zone	1.7 ± 0.7 (0.1-3.9, 63)	2.4 ± 0.9 (1.3-5.2, 64)	90 ± 23 (38-160, 63)	3 ± 2 (1-11, 63)

[1] USEPA secondary drinking water criterion

[2] Criteria represent limits for waters with classifications 3A, 3B, 2A or 2B, and 3C/1 (secondary drinking water criterion), respectively

[3] Criteria represent limits for 4A wild rice waters and for class 1 waters (secondary drinking water criterion), respectively

[4] Criteria represent limits for 4A waters and for class 1waters (secondary drinking water criterion), respectively

[5] Canada Health drinking water aesthetic criterion

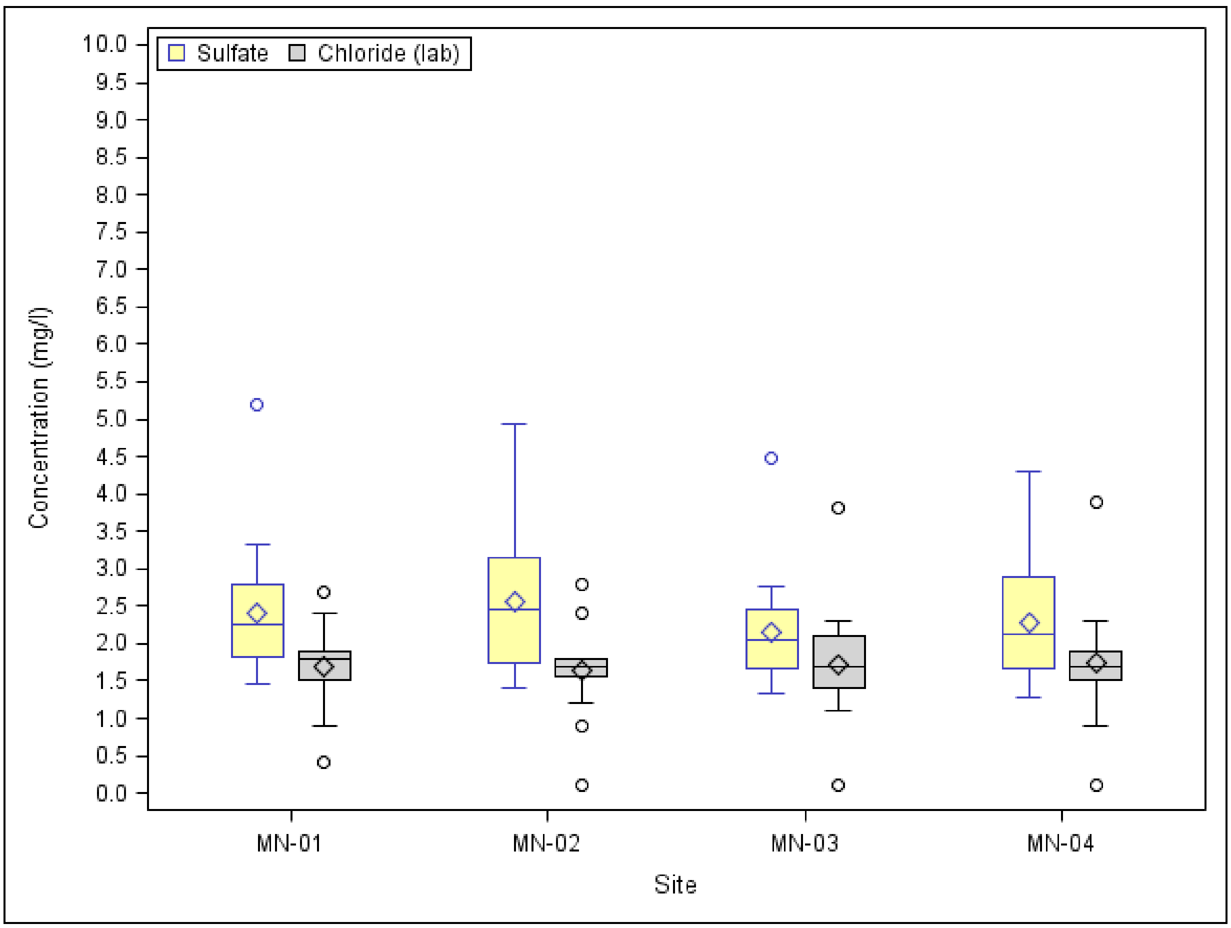

Figure 5. Boxplot of concentrations of sulfate and chloride from lab measurements. Symbols as in Figure 3.

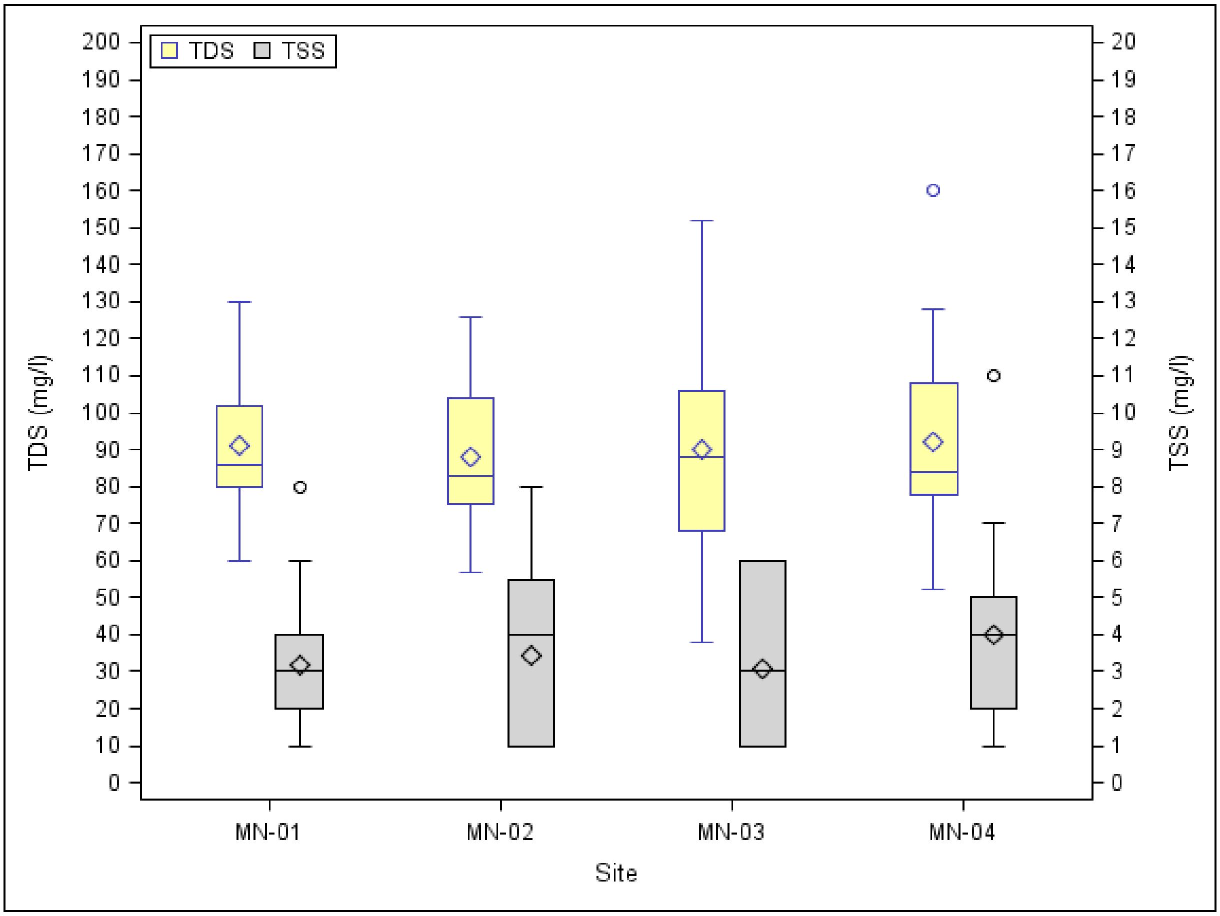

Figure 6. Boxplot of concentrations of TDS and TSS. Symbols as in Figure 3.

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 - 0.2)	Boron (LOD range 0.002 - 0.026)	Cadmium (LOD range 0.0002 - 0.0007)
US EPA	0.087	6.0[1]	0.00020-0.00058 [2]
MN state	0.087, 0.125, 0.050-0.200[3]	0.5[4]	0.00030-0.00084[2]
CCME	0.100	1.5	0.00004-0.00012[2]
MN-01	0.232 ± 0.095 (0.084-0.479, 17)	**0.015** ± 0.015 (0.001-0.060, 17)	0.0002 ± 0.0001 (0.0001-0.0006, 17)
MN-02	**0.216** ± 0.092 (0.050-0.335, 16)	0.012 ± 0.009 (0.002-0.034, 16)	**0.0002** ± 0.0001 (0.0001-0.0005, 16)
MN-03	0.271 ± 0.150 (0.082-0.733, 16)	0.011 ± 0.006 (0.002-0.020, 16)	**0.0002** ± 0.0001 (0.0001-0.0006, 16)
MN-04	**0.296** ± 0.145 (0.083-0.717, 15)	**0.009** ± 0.005 (0.001-0.015, 15)	**0.0002** ± 0.0001 (0.0001-0.0005, 15)
Entire Zone	0.253 ± 0.124 (0.050-0.733, 64)	0.012 ± 0.010 (0.001-0.060, 64)	0.0002 ± 0.0001 (0.0001-0.0006, 64)

[1] USEPA Health advisory lifetime level
[2] Criterion is hardness-dependent
[3] Criteria represent limits for waters with classifications 2A, 2B, and 1 (secondary drinking water criterion), respectively
[4] Criterion applies to class 4A waters (all waters unless otherwise listed)

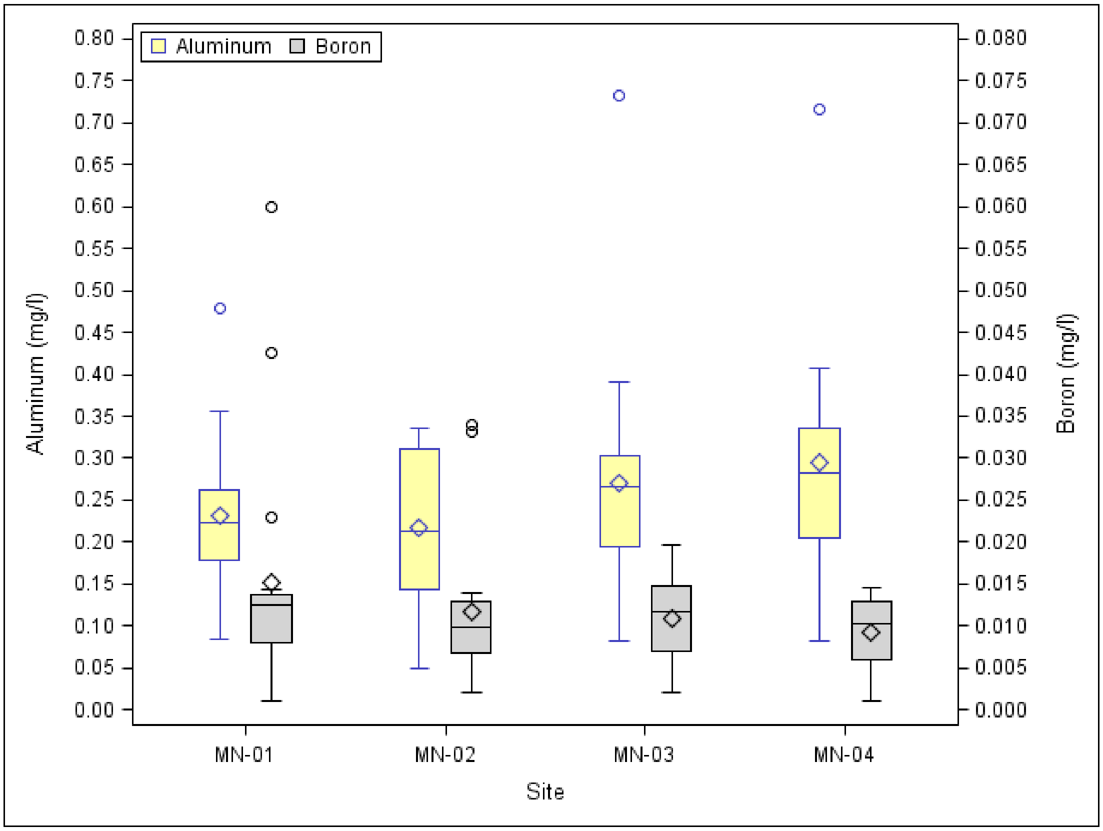

Figure 7. Boxplot of aluminum and boron concentrations. Symbols as in Figure 3.

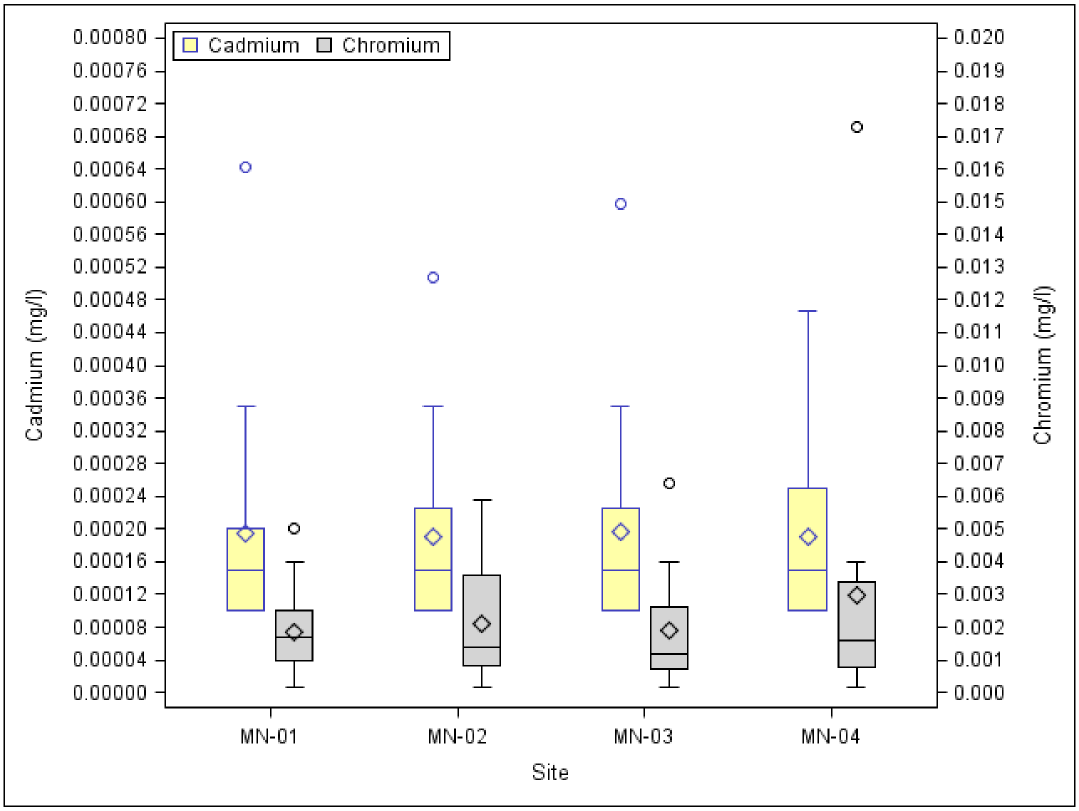

Figure 8. Boxplot of cadmium and chromium concentrations. Symbols as in Figure 3.

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	0.021-0.063[1, 2]		Biotic Ligand Model
MN state	0.051-0.151[1, 2]	0.0028, 0.005[3]	0.0034-0.0077[2]
CCME / CFEQG	0.0089[1]	0.0005-0.0009[2]	0.002[2]
MN-01	**0.0019** ± 0.0013 (0.0002-0.0050, 17)	**0.0003** ± 0.0002 (0.0001-0.001, 17)	**0.0030** ± 0.0060 (0.0010-0.0262, 17)
MN-02	0.0021 ± 0.0017 (0.0002-0.0059, 16)	0.0003 ± 0.0002 (0.0001-0.001, 16)	0.0014 ± 0.0008 (0.0006-0.0034, 16)
MN-03	0.0019 ± 0.0017 (0.0002-0.0064, 16)	**0.0003** ± 0.0002 (0.0001-0.001, 16)	**0.0011** ± 0.0005 (0.0005-0.0025, 16)
MN-04	**0.0030** ± 0.0042 (0.0002-0.0173, 15)	0.0003 ± 0.0002 (0.0001-0.001, 15)	0.0013 ± 0.0005 (0.0005-0.0024, 15)
Entire Zone	0.0022 ± 0.0024 (0.0002-0.0173, 64)	0.0003 ± 0.0002 (0.0001-0.001, 64)	0.0017 ± 0.0032 (0.0005-0.0262, 64)

[1] Criterion for chromium (III)

[2] Criterion is hardness-dependent

[3] Criteria represent limits for class 2A/2Bd and other 2B waters, respectively

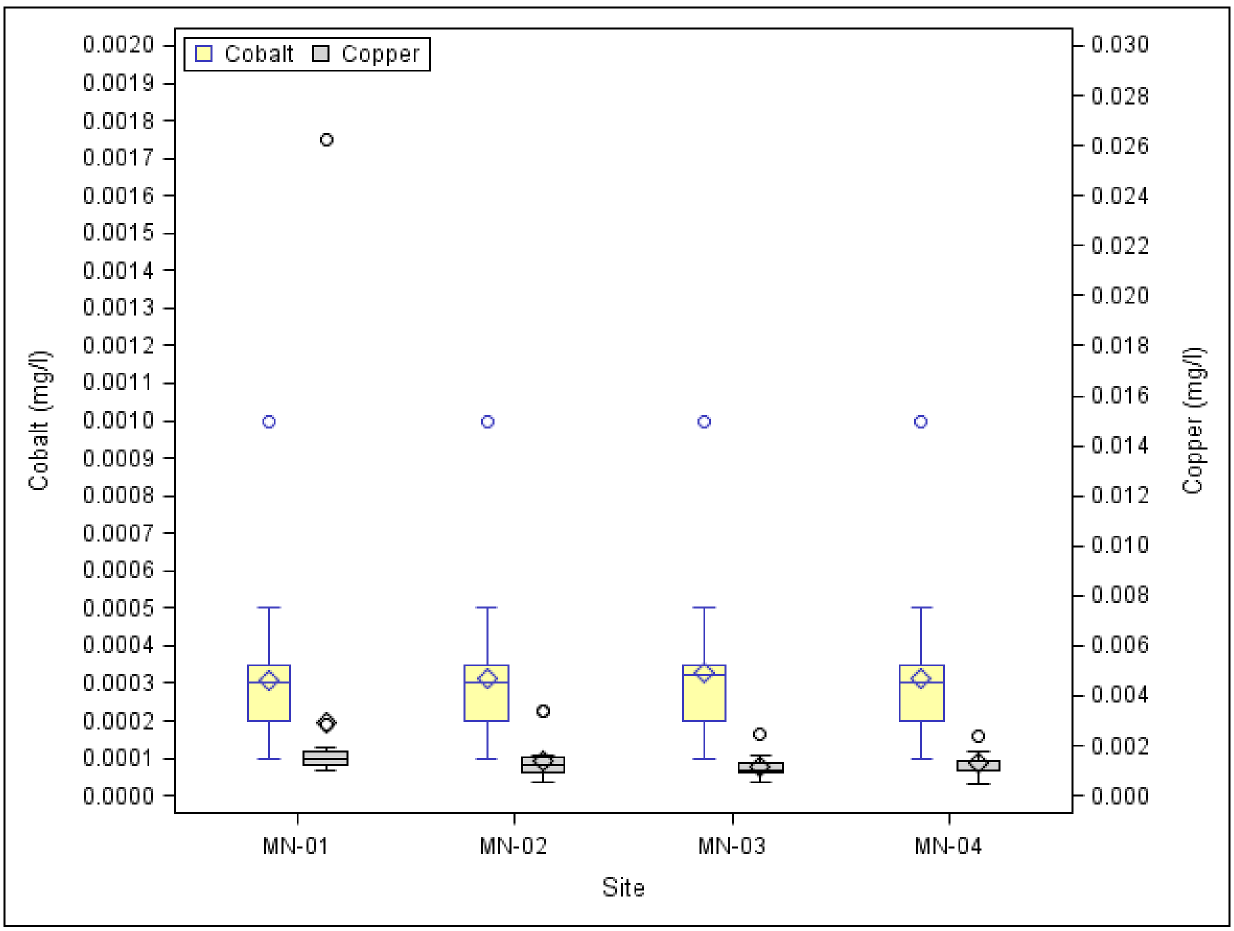

Figure 9. Boxplot of cobalt and copper concentrations. Symbols as in Figure 3.

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]	0.012-0.038[3]
MN state	0.300[4]	0.050[4]	0.037-0.114[3]
CCME	0.300 (aesthetic)[5]	0.120[4], 0.050 (aesthetic)[5]	0.025-0.071[3]
MN-01	**1.914** ± 0.876 (0.704-3.559, 17)	**0.100** ± 0.035 (0.044-0.168, 17)	**0.002** ± 0.001 (0-0.003, 17)
MN-02	**1.458** ± 0.526 (0.715-2.453, 16)	**0.067** ± 0.024 (0.019-0.112, 16)	**0.001** ± 0.001 (0-0.003, 16)
MN-03	1.848 ± 1.011 (0.719-4.143, 16)	0.071 ± 0.032 (0.025-0.132, 16)	0.001 ± 0.001 (0-0.004, 16)
MN-04	1.602 ± 1.149 (0.638-4.587, 15)	0.070 ± 0.082 (0.019-0.358, 15)	0.001 ± 0.001 (0-0.005, 15)
Entire Zone	1.711 ± 0.913 (0.638-4.587, 64)	0.077 ± 0.049 (0.019-0.358, 64)	0.001 ± 0.001 (0-0.005, 64)

[1] USEPA drinking water secondary criterion
[2] USEPA health advisory lifetime level
[3] Criterion is hardness-dependent
[4] Criterion is for class 1 waters (secondary drinking water criterion)
[5] Canada Health drinking water criterion

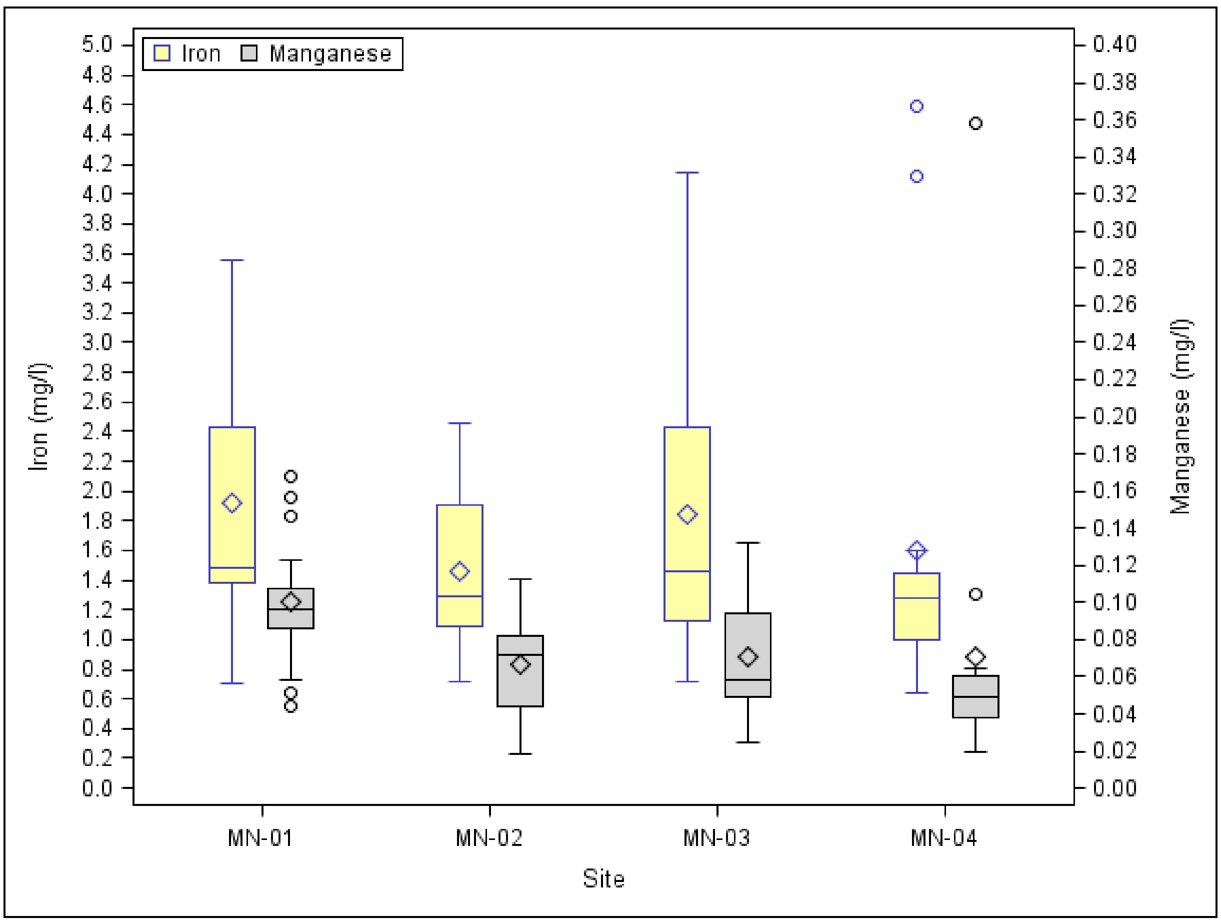

Figure 10. Boxplot of iron and manganese concentrations. Symbols as in Figure 3.

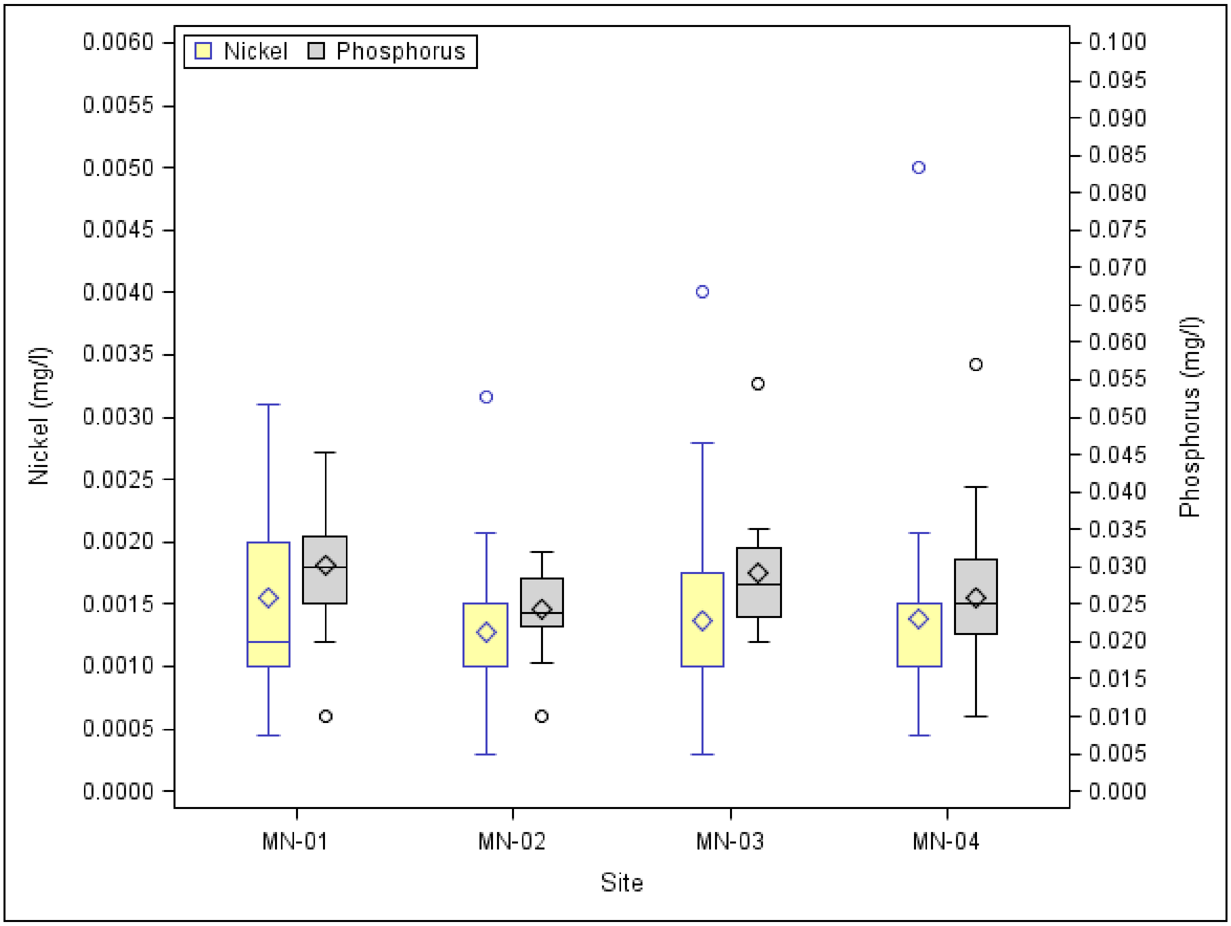

Figure 11. Boxplot of nickel and phosphorus concentration. Symbols as in Figure 3.

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			0.028-0.086[1]
MN state	0.012-0.090 (lakes)[2]	60% of cations[3]	0.025-0.076[1]
CCME		200[4]	0.030[5]
MN-01	**0.03** ± 0.01 (0.01-0.05, 17)	1 ± 0 (1-2, 17)	**0.008** ± 0.007 (0.001-0.027, 17)
MN-02	**0.02** ± 0.01 (0.01-0.03, 16)	**1** ± 0 (1-2, 16)	**0.004** ± 0.002 (0.001-0.008, 16)
MN-03	0.03 ± 0.01 (0.02-0.05, 16)	**1** ± 0 (1-1, 16)	0.008 ± 0.011 (0.001-0.049, 16)
MN-04	0.03 ± 0.01 (0.01-0.06, 15)	1 ± 0 (1-2, 15)	0.005 ± 0.002 (0.001-0.009, 15)
Entire Zone	0.03 ± 0.01 (0.01-0.06, 64)	1 ± 0 (1-2, 64)	0.006 ± 0.007 (0.001-0.049, 64)

[1] Criterion is hardness-dependent

[2] Criteria apply to lakes and depend on ecoregion, designation class (2A/2Bd/2B), and designation as trout lake

[3] Criterion applies to class 4A waters (all waters unless otherwise listed)

[4] Canada Health drinking water aesthetic criterion

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

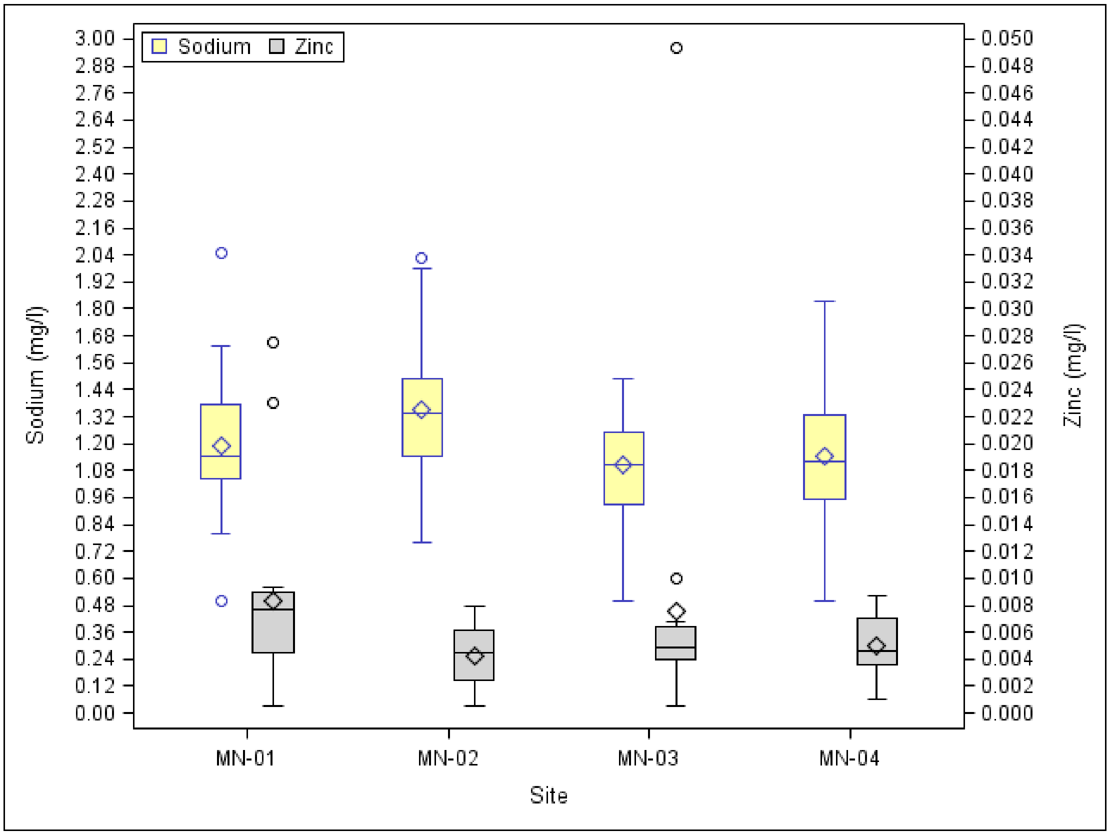

Figure 12. Boxplot of sodium and zinc concentrations. Symbols as in Figure 3.

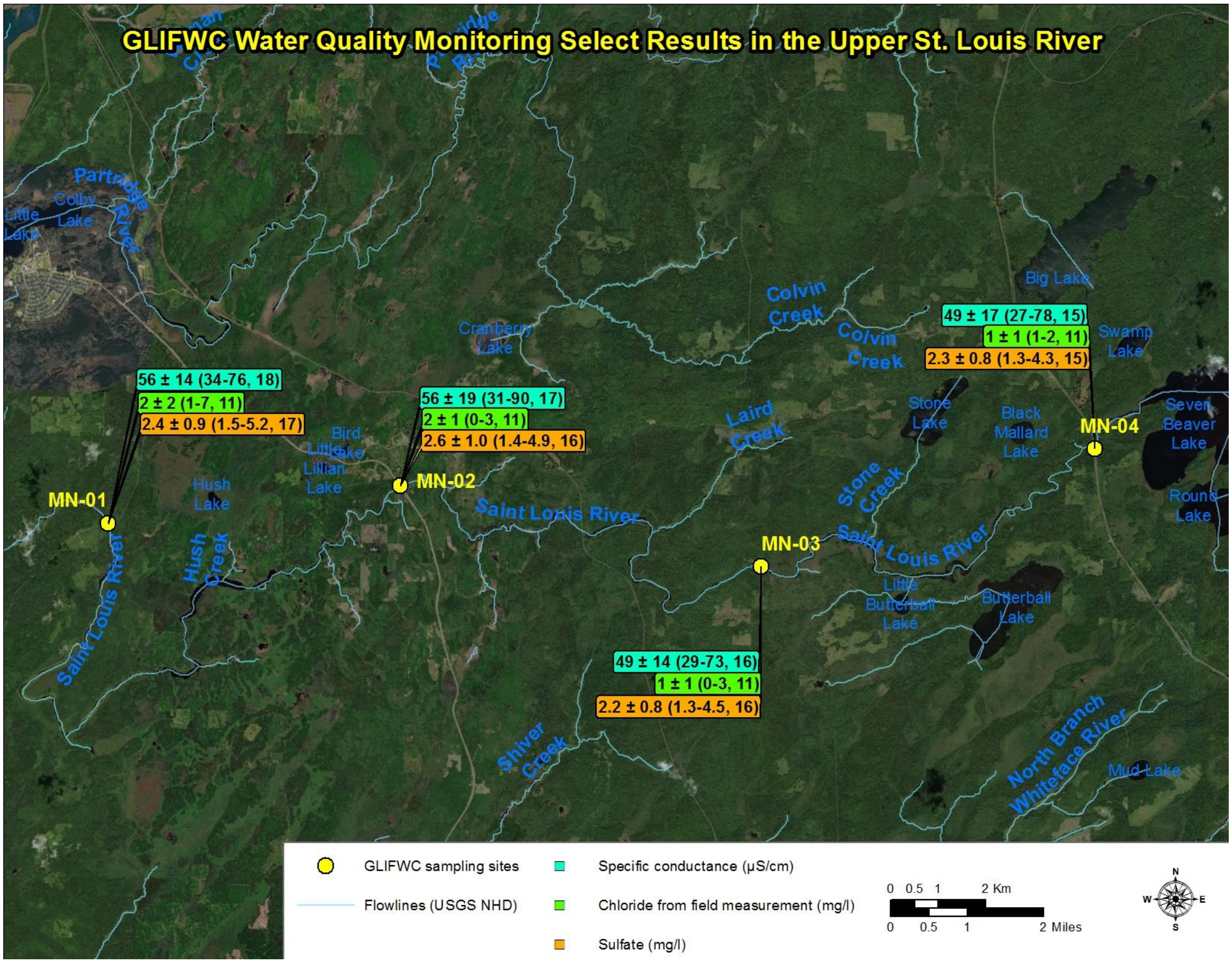

Figure 13. Specific conductance, chloride, and sulfate results from the upper St. Louis River zone. Results are means ± standard deviation (minimum – maximum, *n*).

(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 upper St. Louis River sites and other GLIFWC study sites on the first and second principal components indicated that the upper St. Louis River sites were closer to each other than to other sites, with the exception of one upstream, reference site in the White Pine zone of Michigan (Fig. 14).

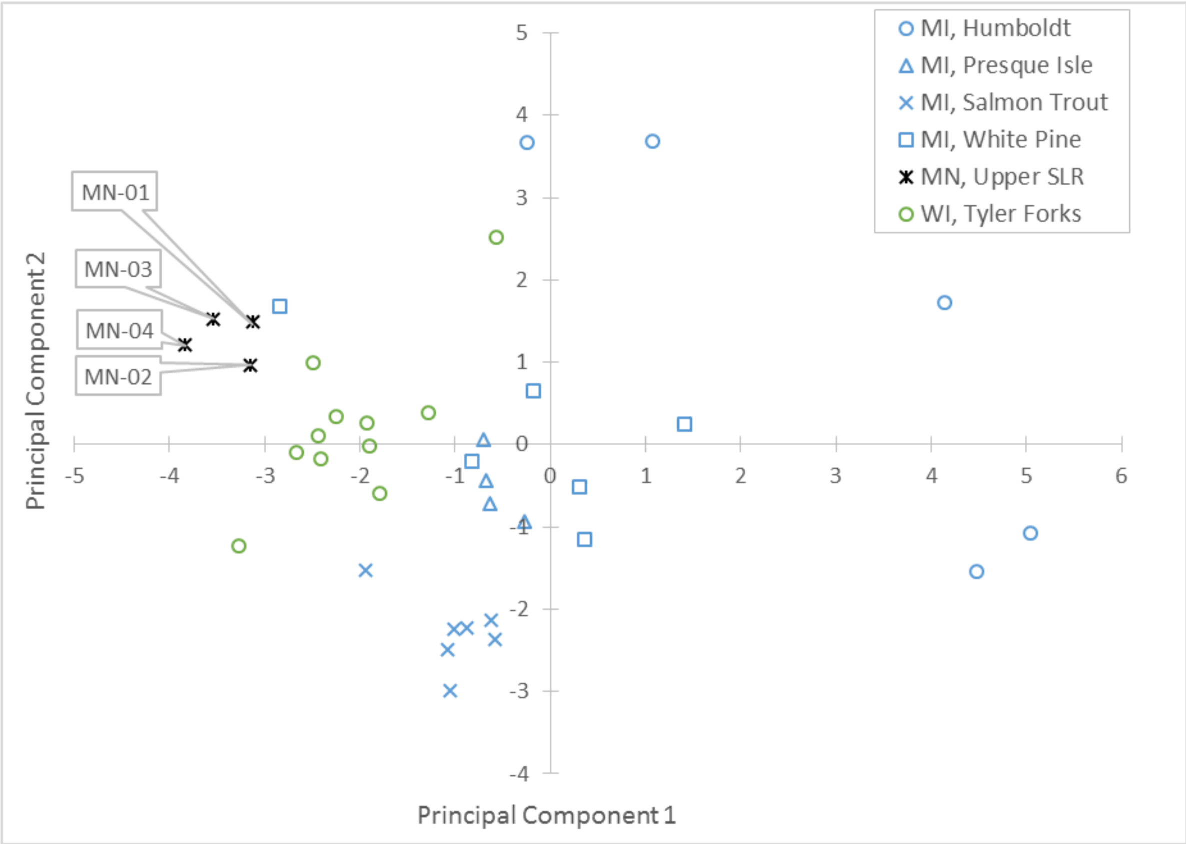

Figure 14. Principal Components Analysis (PCA) of all sites using log-transformed site median values of characteristics with non-detects < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, phosphorus, potassium, sodium, TDS, and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

Cluster analysis

Cluster analysis indicated that MN-01 and MN-02 formed a cluster distinct from a second cluster of MN-03 and MN-04 (Fig. 15). The means and medians of the upstream cluster sites (MN-03 and MN-04) were smaller than the downstream cluster sites (MN-01 and MN-02) for specific conductance, pH, and sulfate, and the means and medians were greater for aluminum (Tables 4-6). Means values of alkalinity, calcium, and total hardness were also lower at MN-03 and MN-04 than at the other two sites.

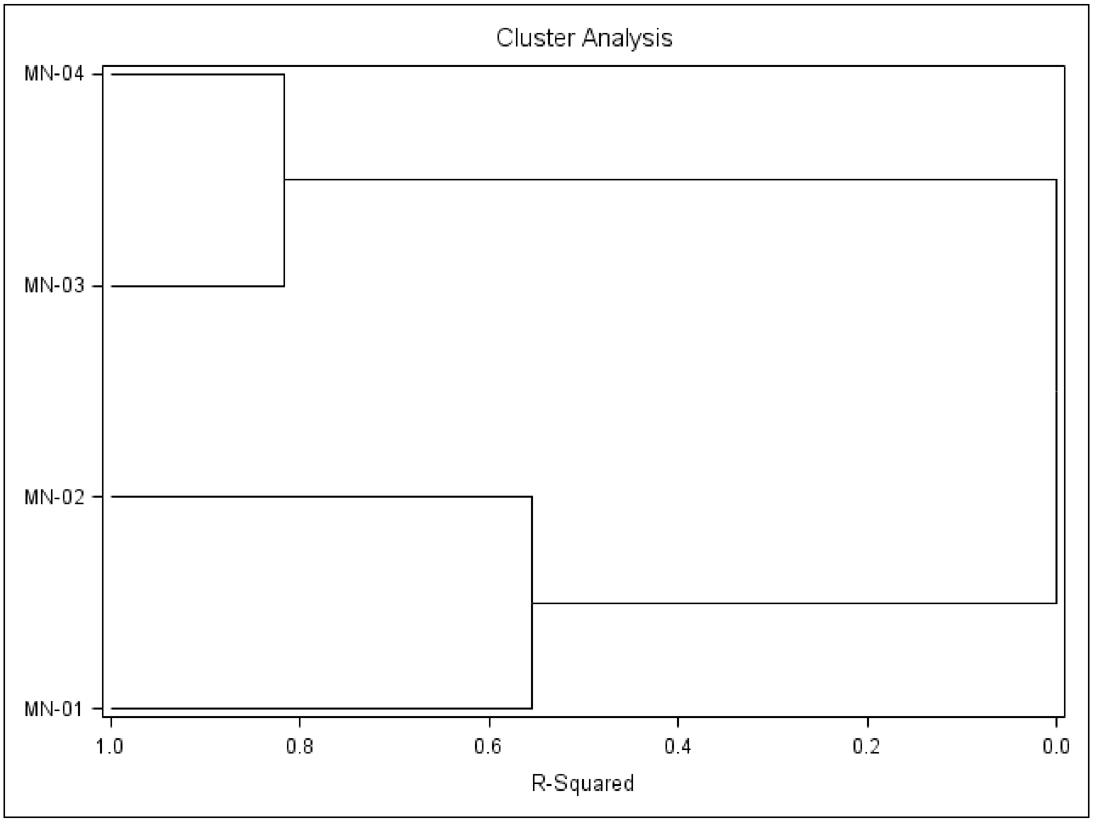

Figure 15. Cluster analysis of upper St. Louis River sites using log-transformed site median values of characteristics with non-detects < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium,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

4. Discussion

GLIFWC water quality monitoring in the upper St. Louis River watershed indicated that constituents of potential concern were generally within state criteria during the sampling in 2011 – 2018. Aluminum, iron, and manganese exceeded criteria, but those could relate to natural factors such as turbidity and organic carbon. Several pH measurements that were slightly below 6.5 could also be the result of naturally acidic waters. Copper and zinc exceeded state criteria in one sample each, but all the other samples were within state criteria for those metals. Water sample results were mostly within USEPA and CCME recommended criteria if ignoring sample results relatively close to the LOD.

Comparisons between sites suggest that the upper St. Louis River water quality characteristics are different from other sampled zones, and that the downstream two sites are different from the upstream two sites. Those differences between upstream and downstream may relate to specific conductance, pH, sulfate, and aluminum, but differences were relatively minor. Causes of the differences could relate to one or more of the following factors: inputs from streams (Laird Creek and 3 unnamed streams), roads, or a railroad between the two groups of sites; differences in riparian vegetation, watershed land cover, or geology between the groups of sites; and the attenuation or dilution of characteristics of the upstream lake and wetland waters.

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

5. Acknowledgements

We would like to recognize the substantial contributions made by others to this data collection and analysis effort. Dawn White of GLIFWC provided data collection support, and Dara J. Olson Unglaube, also of GLIFWC, provided database management support that was essential to the storage, retrieval and analysis of the data. The Water and Environmental Analysis Laboratory at University of Wisconsin – Stevens Point analyzed our water samples. We would also like to acknowledge Steve Ventura and the University of Wisconsin's Land Information and Computer Graphics Facility for their support of GLIFWC at the U.W.'s Madison campus. That support has enabled our staff to conduct this and other environmental projects in support of the Lake Superior Ojibwe. And finally, we would like to thank natural resources department of the Fond du Lac Band of the Lake Superior Chippewa for their assistance in identifying suitable sampling locations.

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