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

Humboldt Zone

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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 Humboldt zone, in the 1836 and 1842 Treaty-ceded Territories in Michigan (Fig. 1), is one of the mine zones for which GLIFWC has monitored water quality. The zone is in the watershed of the Middle Branch of the Escanaba River, which flows into Lake Michigan at Escanaba, Michigan. The Humboldt mine was an iron mine that operated between approximately 1954 and 1979 and included an open pit, tailings facilities, and waste rock piles (MIDEQ 2011). The facilities also processed ore for the Ropes gold mine between approximately 1985 and 1990 and discharged tailings from that processing into the old pit lake (MIDEQ 2011). More recently, the underground Eagle copper-nickel mine has been processing ore at the site and depositing tailings into the pit lake since 2014.

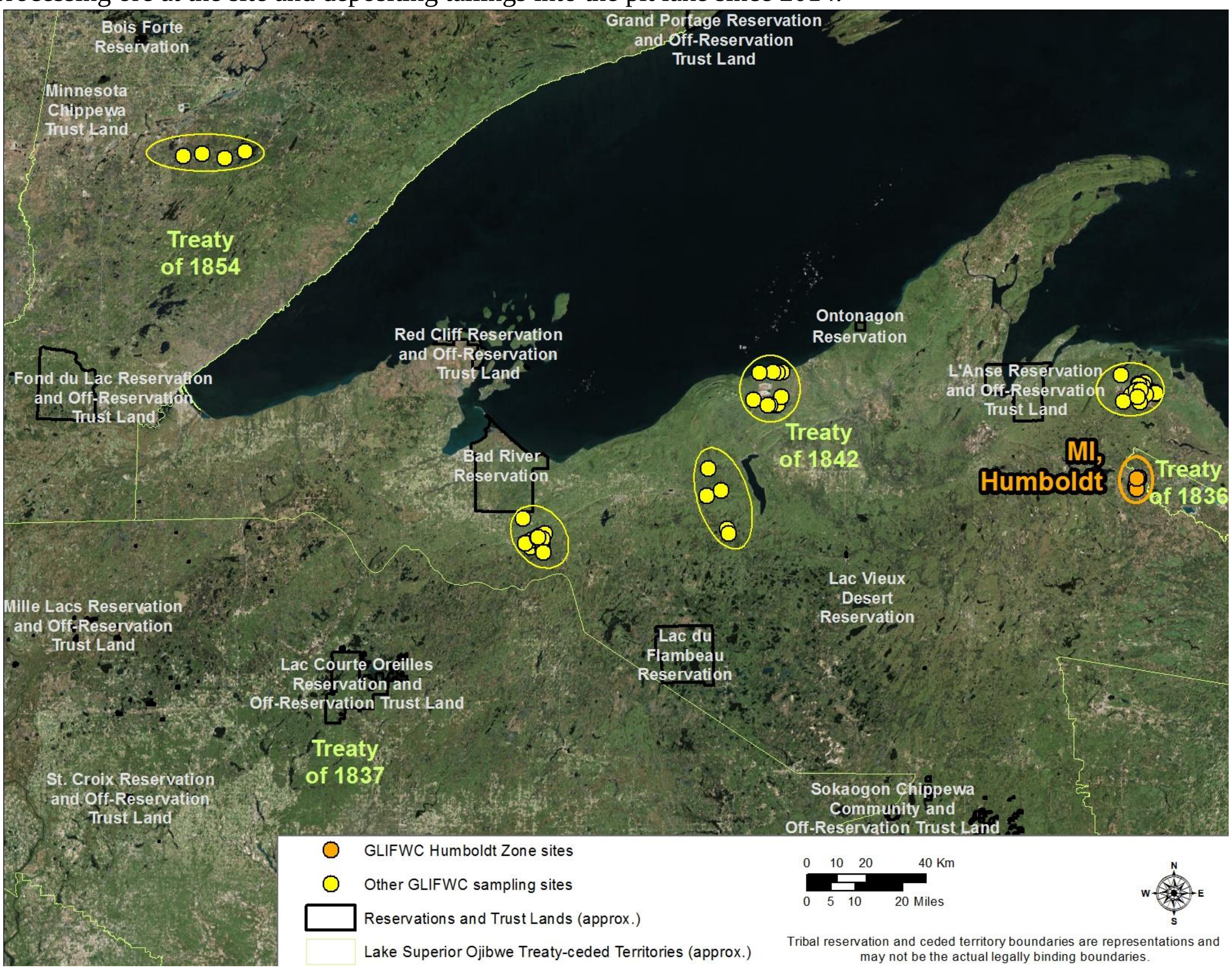

Figure 1. Map of the Humboldt zone water quality monitoring sites relative to other GLIFWC monitoring sites and Reservation and Territories boundaries.

According to state assessments, the Middle Branch of the Escanaba in this zone and the Black River were supporting other indigenous aquatic life and wildlife uses and warm-water fisheries uses but were not assessed for cold-water or warm-water fisheries uses (Fig. 2; MI DEQ 2017). Mercury impaired fish consumption uses in the rivers in this zone (MI DEQ 2017).

The GLIFWC monitoring assessed water quality in the Humboldt zone beginning in 2009 to assess the influence of mine-related waters on surface water quality. 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).

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 one of the samples with the same methods 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. We also used the non-parametric Wilcoxon Mann-Whitney tests and median tests to compare results for northern and southern sites.

[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 five surface water sites (Table 3, Fig. 2). Sampling in this zone began in 2009 and varied in frequency between sites. Monitoring occurred at least yearly at the two most frequently-sampled sites but began in different years (2010 for WBR-003 and 2014 for WLR-3; Table 3, Fig. 2). We did not include in this report data from 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. S = stream.

Site ID	Location	Latitude	Longitude	Type	Number of days of field measure.	Number of samples[1]
FY_culvert	Upstream side of culvert under County FY near Hwy 28	46.496377	-87.896344	S	5	3
Humboldt2Weir1	Upstream side of west culvert under Hwy. 28, near Cty FY	46.49603	-87.89651	S	5	2
WBR-003	Upstream side of culvert of Cty FO @ Black R.	46.47246	-87.902569	S	15	14
WLD-001-SE	Upstream side of CR 601	46.480433	-87.898998	S	3	2
WLR-3	Upstream side of culvert under Cty FX, ~ 0.25 mi N of Hwy. 28	46.49688	-87.88661	S	10	9

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

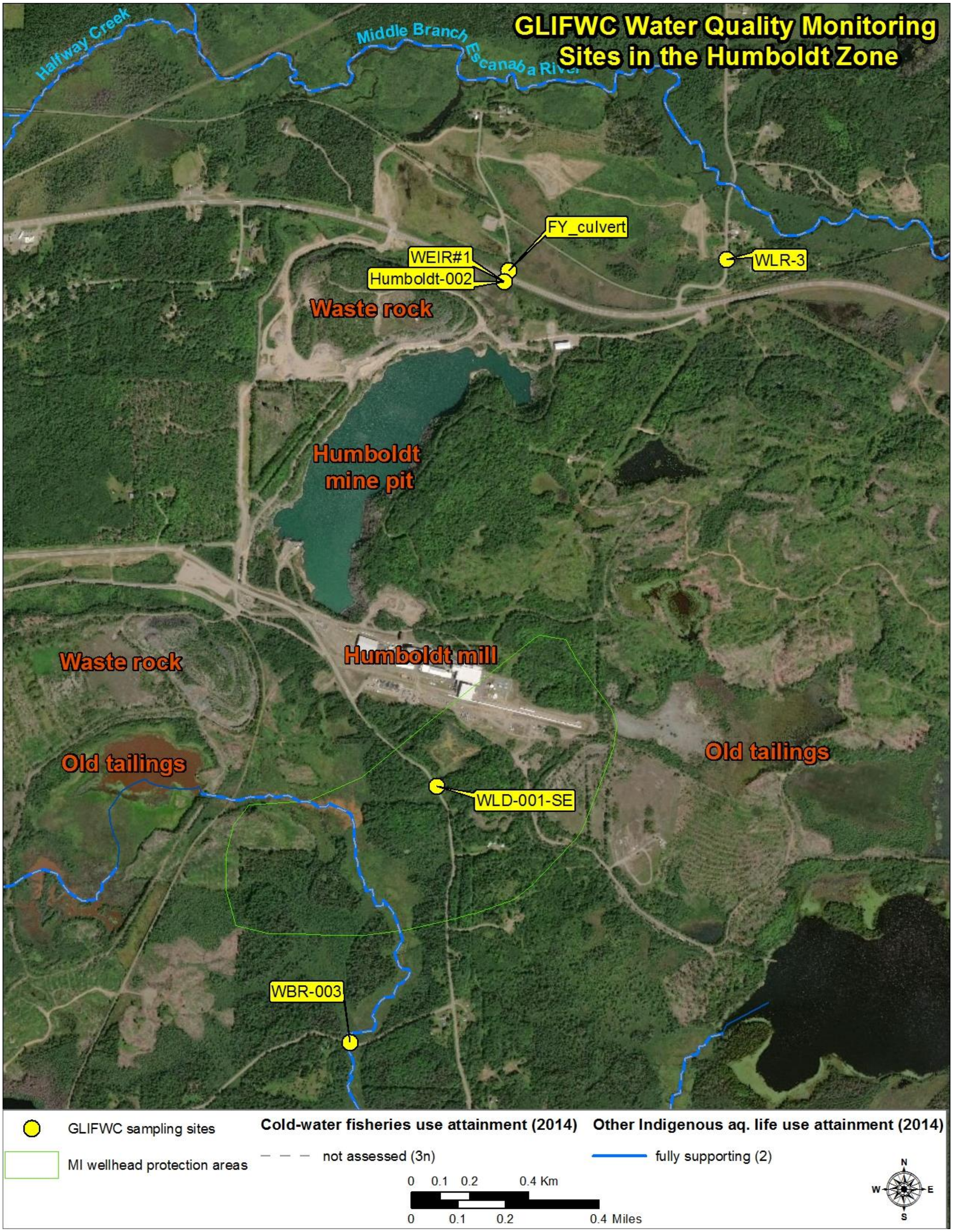

Figure 2. Map of GLIFWC sampling sites and Michigan Department of Environmental Quality select assessments of attainment of designated uses (cold-water fish and other indigenous aquatic life and wildlife) in the Humboldt zone.

3. Results

(A) Summary statistics

Field measurements

Dissolved oxygen (DO) means and individual measurements were greater than 6.0 mg/l except for several individual measurements and the mean at WBR-003 (Table 4, Fig. 3). The lowest of those measurements at WBR-003 did not meet state criteria for all waters, even for the warm season (Table 4). Chloride means were greater than 50 mg/l, the state drinking water value, at Humboldt2/Weir1 and WBR-003 (Table 4, Figs. 3, 13). Mean pH measurements were greater than 6.5 except at WBR-003, and individual measurements below 6.0 occurred at a few sites (Table 4, Fig. 4). Mean pH was lowest at the two southern sites (WBR-003 and WLD-001-SE; Table 4). Certain low pH measurements at most sites did not meet state, USEPA, or CCME criteria (Table 4). Specific conductance means were greater than 300 µS/cm at all three northern sites downstream of the pit (FY_culvert, Humboldt2Weir1, and WLR-3), and an individual measurement exceeded 1000 µS/cm at FY_culvert (Table 4, Figs. 4, 13).

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 aesthetic[5])	6.5-9.0	
FY_culvert	**9.1** ± 4.2 (6.5-16.5, 5)	25 ± 21 (4-46, 3)	6.8 ± 0.7 (5.5-7.2, 5)	**793** ± 427 (524-1552, 5)
Humboldt2Weir1	7.1 ± 1.1 (6.3-7.8, 2)	51 ± 28 (24-80, 3)	**7.1** ± 0.1 (7.1-7.2, 3)	555 ± 90 (450-634, 5)
WBR-003	**5.1** ± 2.2 (1.9-7.2, 5)	**57** ± 86 (4-309, 11)	**6.3** ± 0.4 (5.5-7.0, 13)	**186** ± 41 (134-291, 16)
WLD-001-SE		**7** (7-7, 1)	6.6 ± 0.5 (5.8-7.1, 4)	244 ± 48 (207-313, 4)
WLR-3	8.0 ± 1.5 (6-9.6, 5)	44 ± 27 (4-93, 9)	7.0 ± 0.4 (6.4-7.5, 9)	444 ± 163 (120-573, 10)
Entire zone	7.4 ± 3 (1.9-16.5, 17)	46 ± 57 (4-309, 27)	6.7 ± 0.5 (5.5-7.5, 34)	378 ± 266 (120-1552, 40)

[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 criterion

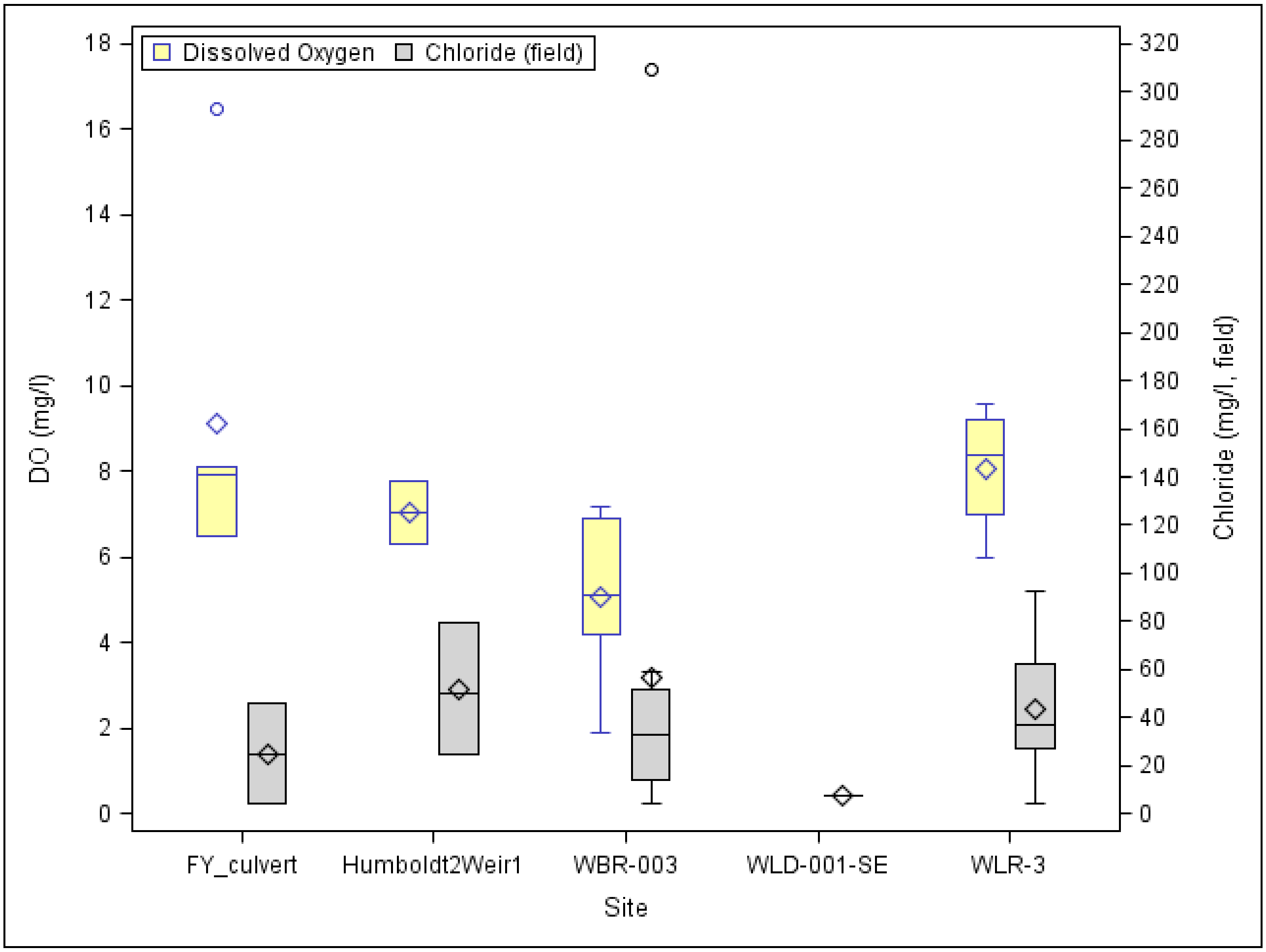

Figure 3. Boxplots of concentrations of dissolved oxygen and chloride from field measurements. Boxplots show medians (-), means (◊), first and third quartiles (box minimum and maximum), maximum and minimum values beyond the quartiles but within 1.5 x the interquartile range (whiskers), and outliers beyond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

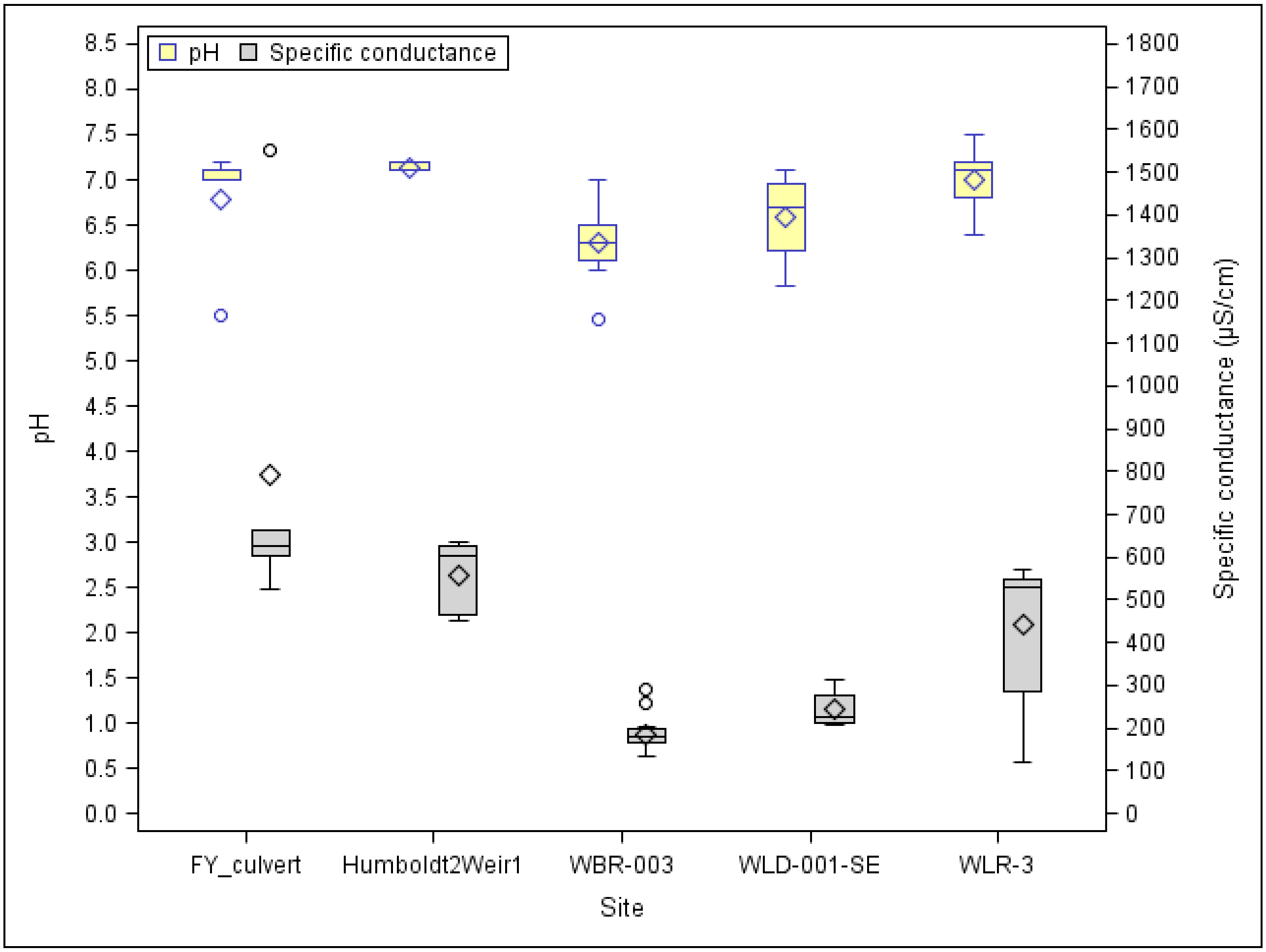

Figure 4. Boxplots of pH and specific conductance from field measurements. Symbols as in Figure 3.

Laboratory results

Some laboratory measurements at several sites exceeded state or recommended criteria. Mean aluminum, iron, and manganese concentrations were greater than recommended and state health/secondary/aesthetic criteria at several sites (Tables 6, 8). Manganese samples that exceeded state hardness-based criterion, or were likely to if hardness had been measured, all had TSS > 6 mg/l. Boron also exceeded state health criterion in one measurement from FY_culvert in October 2018 (Table 6, Fig. 7). Cadmium exceeded recommended criteria on several occasions at WBR-003 (Table 6, Fig. 8). A sample at WBR-003 also demonstrated a chromium concentration greater than the CCME recommendation (Table 7, Fig. 8). Cobalt was greater than Canadian recommendations in at least one sample from most sites (Table 7, Fig. 9), and copper exceeded CCME recommendations in a sample from FY_culvert and from WLR-3 in October 2018 (Table 7, Fig. 9). Nickel reached concentrations up to 17 µg/l at the northern sites, but did not exceed criteria when we had sampled for hardness (Table 8, Fig. 11). Concentrations of zinc exceeded the CCME recommendation in one sample at WBR-003 (Table 9, Fig. 12).

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 – 2.5)	Sulfate (LOD range 0.04 - 5)	TDS (LOD range 2 - 20)	TSS (LOD range 1 - 11)
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 aesthetic[4])	500 (aesthetic)[4]	500 (aesthetic)[4]	
FY_culvert	27.5 ± 5.3 (21.6-31.8, 3)	**168.3** ± 19.1 (153.8-190, 3)	**365** ± 37 (322-390, 3)	2 ± 0 (2-2, 3)
Humboldt2Weir1	12.5 ± 1.4 (11.5-13.5, 2)	111.7 ± 5.7 (107.7-115.8, 2)	301 ± 10 (294-308, 2)	**1** (1-1, 1)
WBR-003	29.9 ± 9.6 (0.1-38.4, 14)	2.6 ± 1.1 (1.5-5.6, 14)	149 ± 47 (95-234, 14)	10 ± 10 (1-32, 14)
WLD-001-SE	**1.8** ± 0.4 (1.5-2.1, 2)	**2.0** ± 0.6 (1.6-2.4, 2)	**143** ± 16 (132-154, 2)	**18** ± 11 (10-25, 2)
WLR-3	**34.5** ± 13.2 (9.1-54.1, 9)	99.4 ± 49.2 (10.4-141.8, 9)	285 ± 99 (82-356, 9)	3 ± 2 (1-6, 9)
Entire zone	28.0 ± 13.1 (0.1-54.1, 30)	55.5 ± 66.1 (1.5-190, 30)	221 ± 103 (82-390, 30)	7 ± 8 (1-32, 29)

[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 criterion

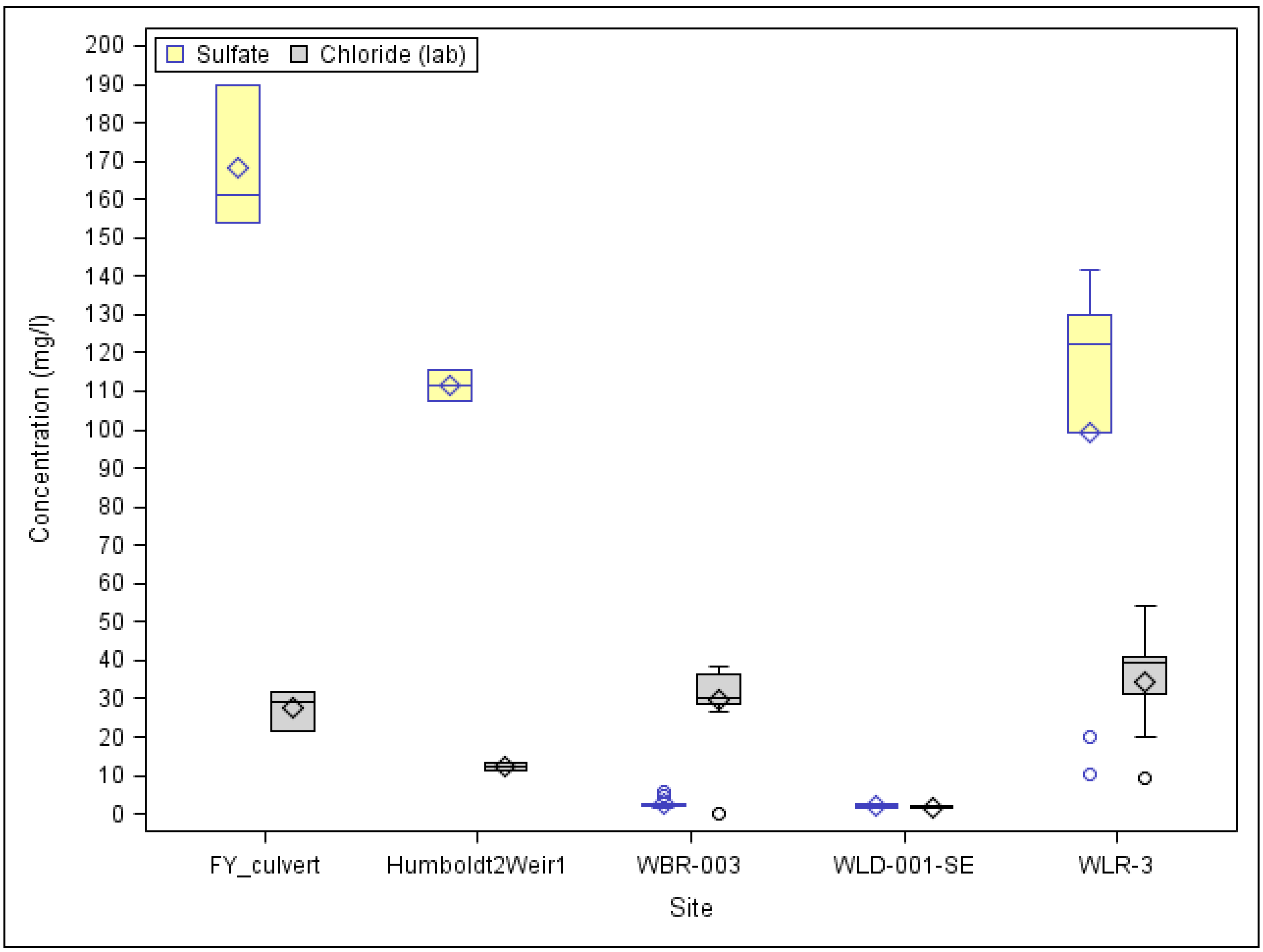

Figure 5. Boxplot of concentrations of sulfate and chloride from lab measurements. Symbols as in Figure 3.

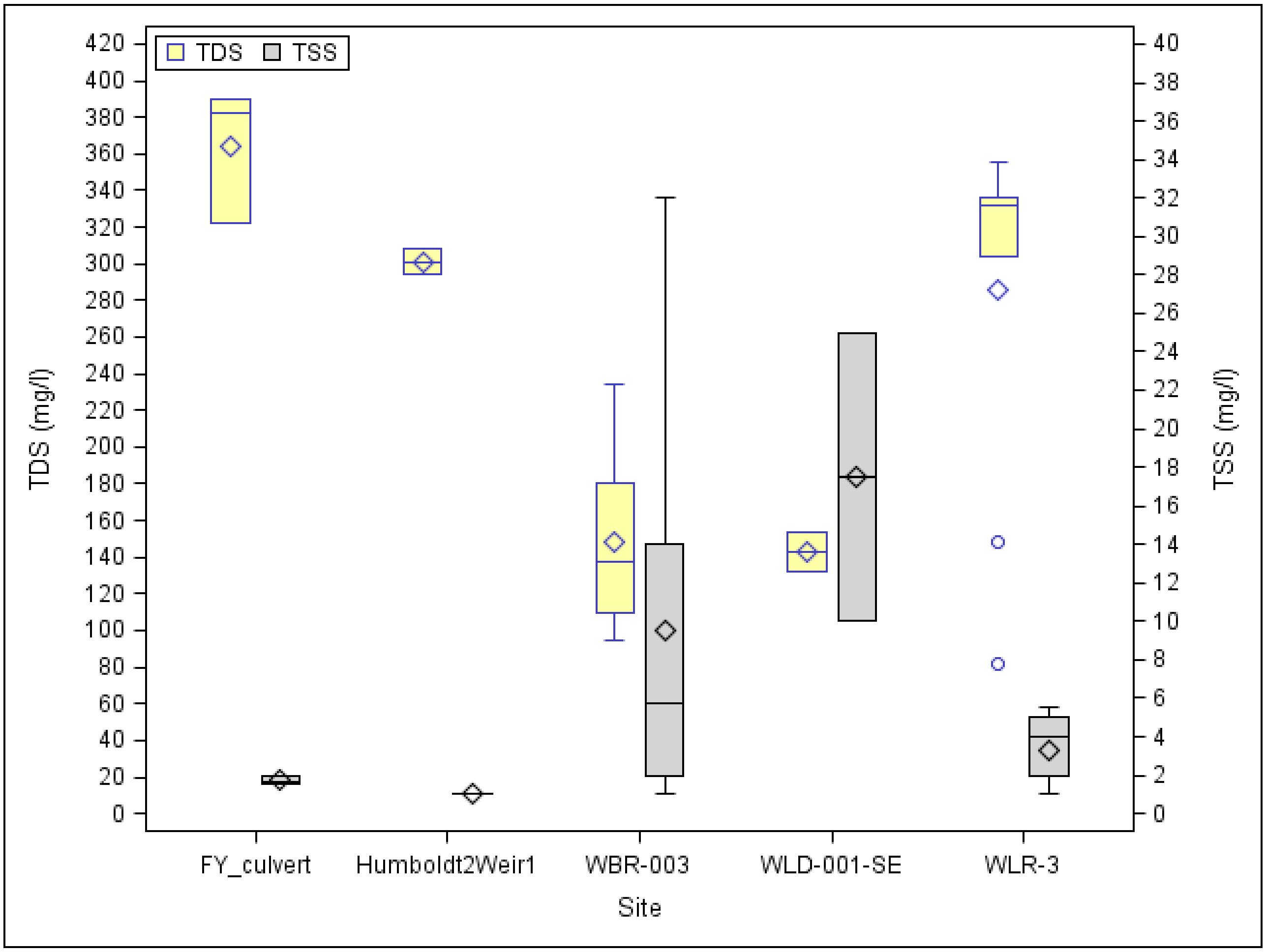

Figure 6. Boxplot of concentrations of TDS and TSS. Symbols as in Figure 3.

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 - 0.025)	Boron (LOD range 0.0008 - 0.026)	Cadmium (LOD range 0.00014 - 0.0007)
US EPA	0.087	6.0[1]	0.00031-0.00150[2]
MI state	0.050 (health)	7.2 (0.5 for health)	0.00098-0.0046[2]
CCME	0.100	1.5	0.00006-0.00031[2]
FY_culvert	0.039 ± 0.023 (0.013-0.052, 3)	**0.246** ± 0.240 (0.095-0.522, 3)	0.0001 ± 0.0001 (0.0001-0.0002, 3)
Humboldt2Weir1	**0.031** ± 0.026 (0.012-0.049, 2)	0.068 ± 0.009 (0.062-0.075, 2)	0.0001 ± 0 (0.0001-0.0002, 2)
WBR-003	0.091 ± 0.040 (0.036-0.188, 14)	**0.014** ± 0.003 (0.009-0.019, 14)	**0.0003** ± 0.0003 (0.0001-0.001, 14)
WLD-001-SE	0.062 ± 0.030 (0.041-0.083, 2)	0.057 ± 0.002 (0.055-0.058, 2)	**0.0001** ± 0 (0.0001-0.0001, 2)
WLR-3	**0.100** ± 0.027 (0.050-0.143, 9)	0.061 ± 0.021 (0.022-0.084, 9)	0.0002 ± 0.0001 (0.0001-0.0004, 9)
Entire Zone	0.083 ± 0.039 (0.012-0.188, 30)	0.058 ± 0.093 (0.009-0.522, 30)	0.0002 ± 0.0002 (0.0001-0.001, 30)

[1] USEPA Health advisory lifetime level

[2] Criterion is hardness-dependent

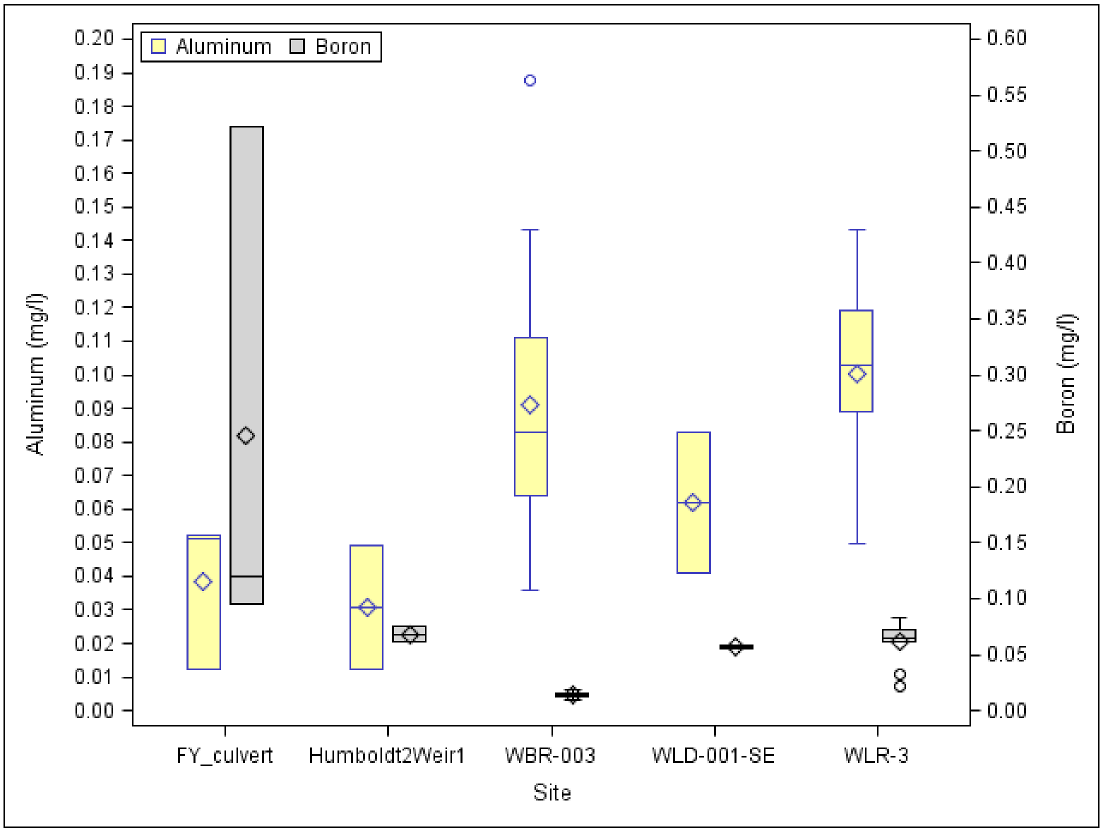

Figure 7. Boxplot of aluminum and boron concentrations. Symbols as in Figure 3.

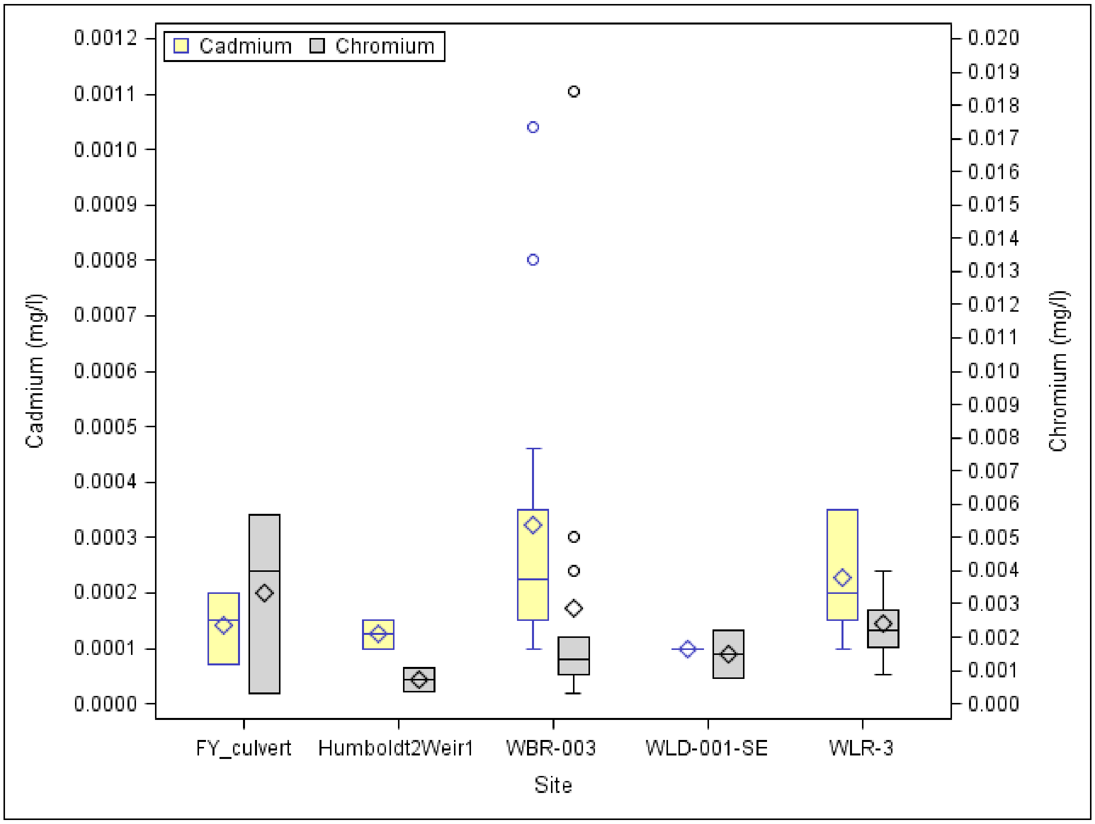

Figure 8. Boxplot of cadmium and chromium concentrations. Symbols as in Figure 3.

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 0.0002 - 0.0013)
US EPA	0.033-0.169[1, 2]		Biotic Ligand Model
MI state	0.033-0.169[1, 2]	0.100 (0.040 residential health)	0.003-0.019[2]
CCME / CFEQG	0.0089[1]	0.0006-0.0014[2]	0.002-0.004[2]
FY_culvert	**0.0033** ± 0.0027 (0.0003-0.0057, 3)	**0.0024** ± 0.0005 (0.002-0.0029, 3)	0.0018 ± 0.0011 (0.0009-0.003, 3)
Humboldt2Weir1	**0.0007** ± 0.0005 (0.0004-0.0011, 2)	0.0023 ± 0.0003 (0.002-0.0025, 2)	**0.0024** ± 0.0001 (0.0023-0.0024, 2)
WBR-003	0.0029 ± 0.0047 (0.0003-0.0184, 14)	0.0004 ± 0.0003 (0.0001-0.0013, 14)	**0.0008** ± 0.0004 (0.0003-0.0017, 14)
WLD-001-SE	0.0015 ± 0.0010 (0.0008-0.0022, 2)	**0.0002** ± 0 (0.0002-0.0003, 2)	0.0011 ± 0.0008 (0.0005-0.0017, 2)
WLR-3	0.0024 ± 0.0011 (0.0009-0.0040, 9)	0.0011 ± 0.0007 (0.0003-0.0022, 9)	0.0016 ± 0.0004 (0.0011-0.0021, 9)
Entire Zone	0.0025 ± 0.0033 (0.0003-0.0184, 30)	0.0009 ± 0.0008 (0.0001-0.0029, 30)	0.0012 ± 0.0007 (0.0003-0.003, 30)

[1] Criterion for chromium (III)

[2] Criterion is hardness-dependent

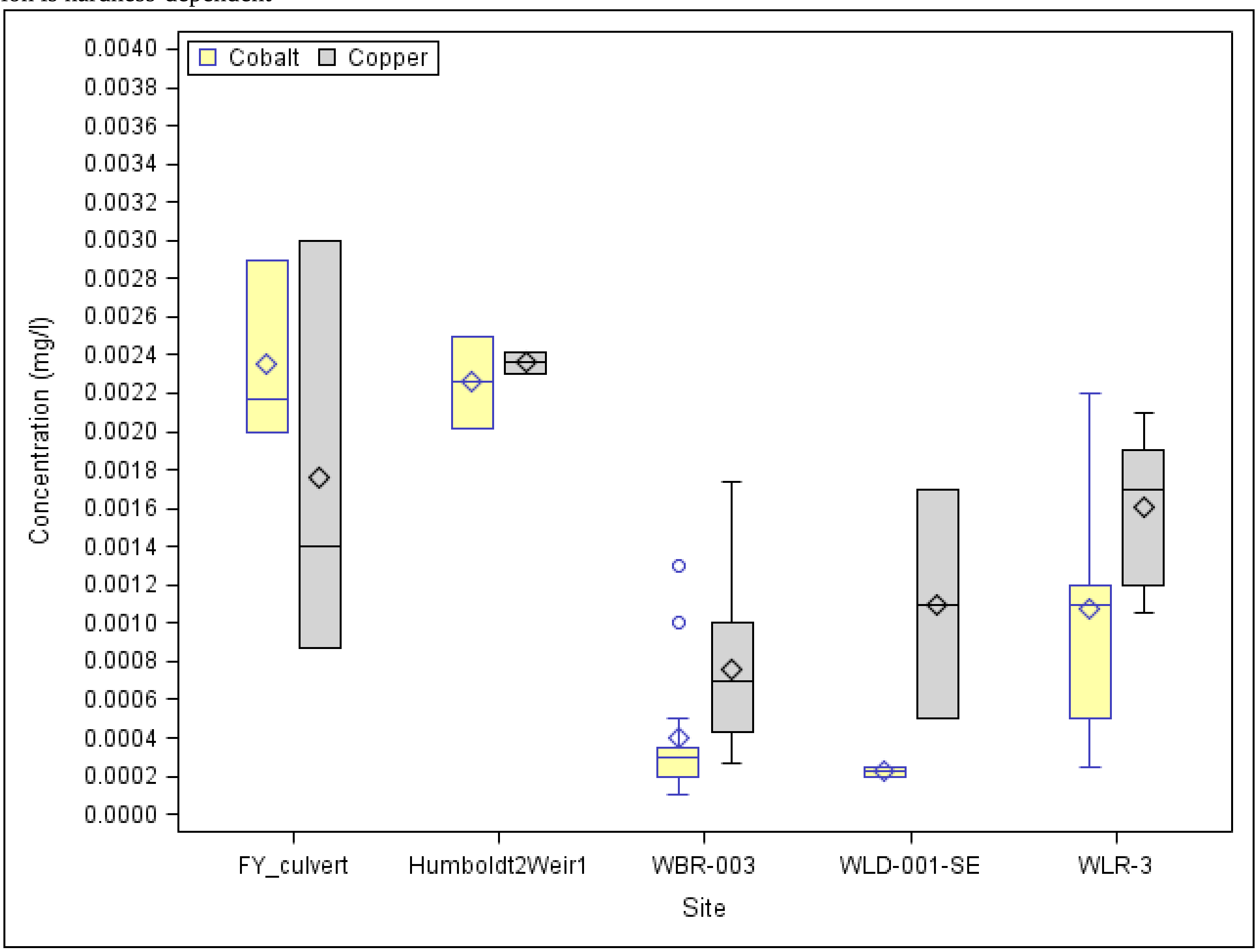

Figure 9. Boxplot of cobalt and copper concentrations. Symbols as in Figure 3.

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 0.00005 - 0.002)	Nickel (LOD range 0.0006 - 0.004)
US EPA	1.000, 0.300[1]	0.050[1], 0.300[2]	0.019-0.103[3]
MI state	0.300 (health)	0.703-3.992[3]	0.019-0.103[3]
CCME	0.300 (aesthetic)[4]	0.120 (0.050 aesthetic)[4]	0.025-0.150[3]
FY_culvert	0.359 ± 0.497 (0.028-0.931, 3)	0.047 ± 0.056 (0.01-0.111, 3)	**0.012** ± 0.005 (0.007-0.017, 3)
Humboldt2Weir1	**0.059** ± 0.022 (0.043-0.074, 2)	**0.026** ± 0.023 (0.01-0.042, 2)	0.012 ± 0.007 (0.007-0.017, 2)
WBR-003	7.881 ± 5.305 (2.801-21.7, 14)	0.705 ± 0.692 (0.043-2.404, 14)	0.002 ± 0.001 (0-0.003, 14)
WLD-001-SE	**8.882** ± 3.632 (6.313-11.45, 2)	**2.239** ± 0.086 (2.178-2.3, 2)	**0.0003** ± 0 (0.0003-0.0003, 2)
WLR-3	0.831 ± 0.420 (0.145-1.339, 9)	0.125 ± 0.077 (0.025-0.218, 9)	0.009 ± 0.004 (0.005-0.017, 9)
Entire Zone	4.559 ± 5.224 (0.028-21.7, 30)	0.522 ± 0.725 (0.01-2.404, 30)	0.006 ± 0.005 (0-0.017, 30)

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

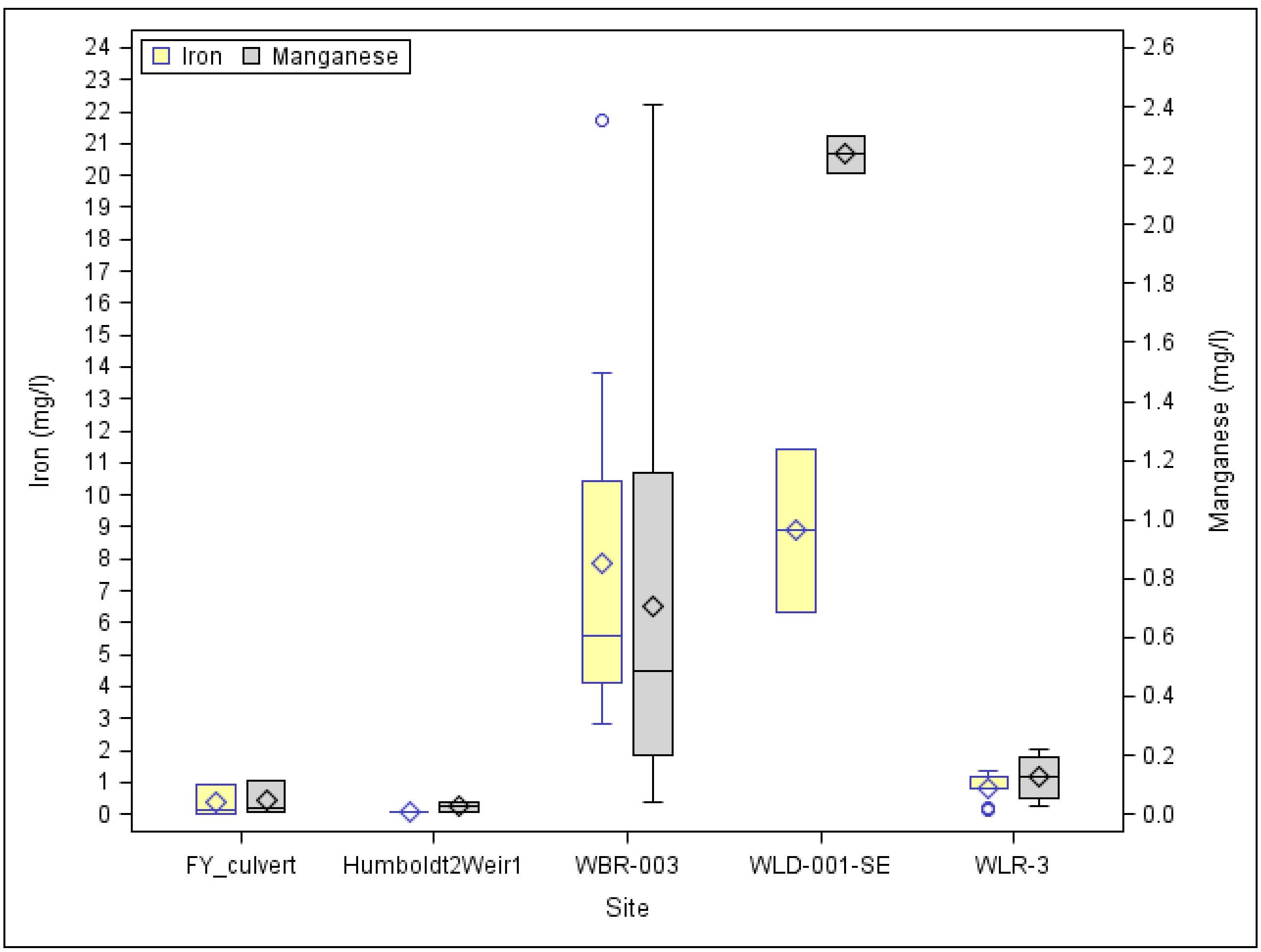

Figure 10. Boxplot of iron and manganese concentrations. Symbols as in Figure 3.

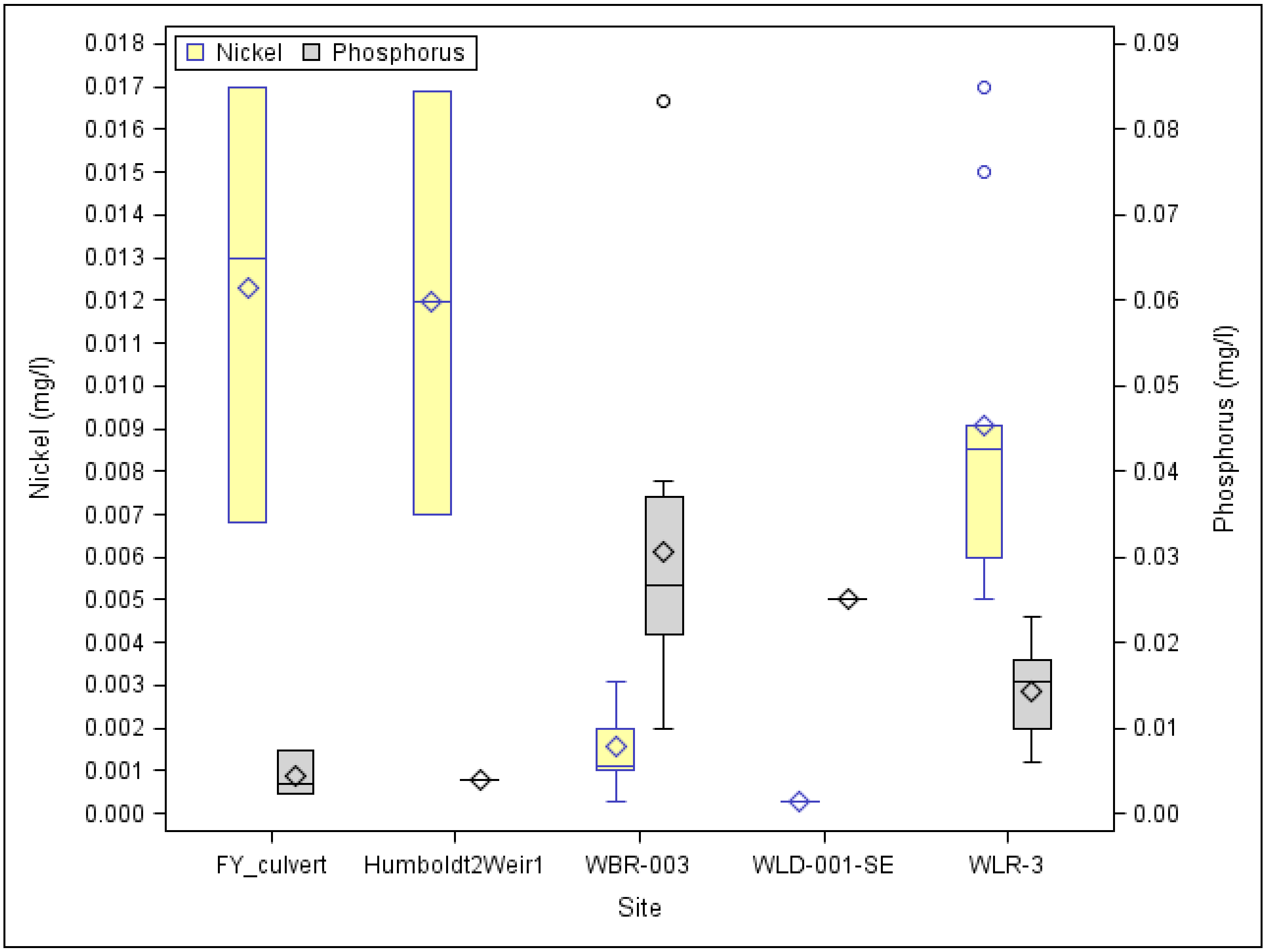

Figure 11. Boxplot of nickel and phosphorus concentration. Symbols as in Figure 3.

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 0.0004 - 0.009)
US EPA			0.044-0.237[1]
MI state	1.00	120, 350 (health)[2]	0.044-0.237[1]
CCME		200 (aesthetic)[3]	0.030[4]
FY_culvert	0.004 ± 0 (0-0.01, 3)	**49** ± 33 (28-87, 3)	0.005 ± 0.003 (0.003-0.008, 3)
Humboldt2Weir1	**0.004** (0-0, 1)	10 (10-10, 1)	**0.002** ± 0.001 (0.001-0.003, 2)
WBR-003	**0.03** ± 0.02 (0.01-0.08, 13)	14 ± 3 (6-18, 13)	0.011 ± 0.014 (0.001-0.052, 14)
WLD-001-SE	0.03 (0.03-0.03, 1)	**2** (2-2, 1)	**0.013** ± 0.007 (0.008-0.018, 2)
WLR-3	0.01 ± 0.01 (0.01-0.02, 9)	27 ± 9 (11-38, 9)	0.006 ± 0.003 (0.003-0.012, 9)
Entire Zone	0.02 ± 0.02 (0-0.08, 27)	21 ± 16 (2-87, 27)	0.008 ± 0.01 (0.001-0.052, 30)

[1] Criterion is hardness-dependent
[2] Criteria represent residential health-based and non-residential health-based limits, respectively
[3] Canada Health drinking water criterion
[4] CCME criterion prior to publication in 2018 of criterion dependent on hardness, pH, and DOC

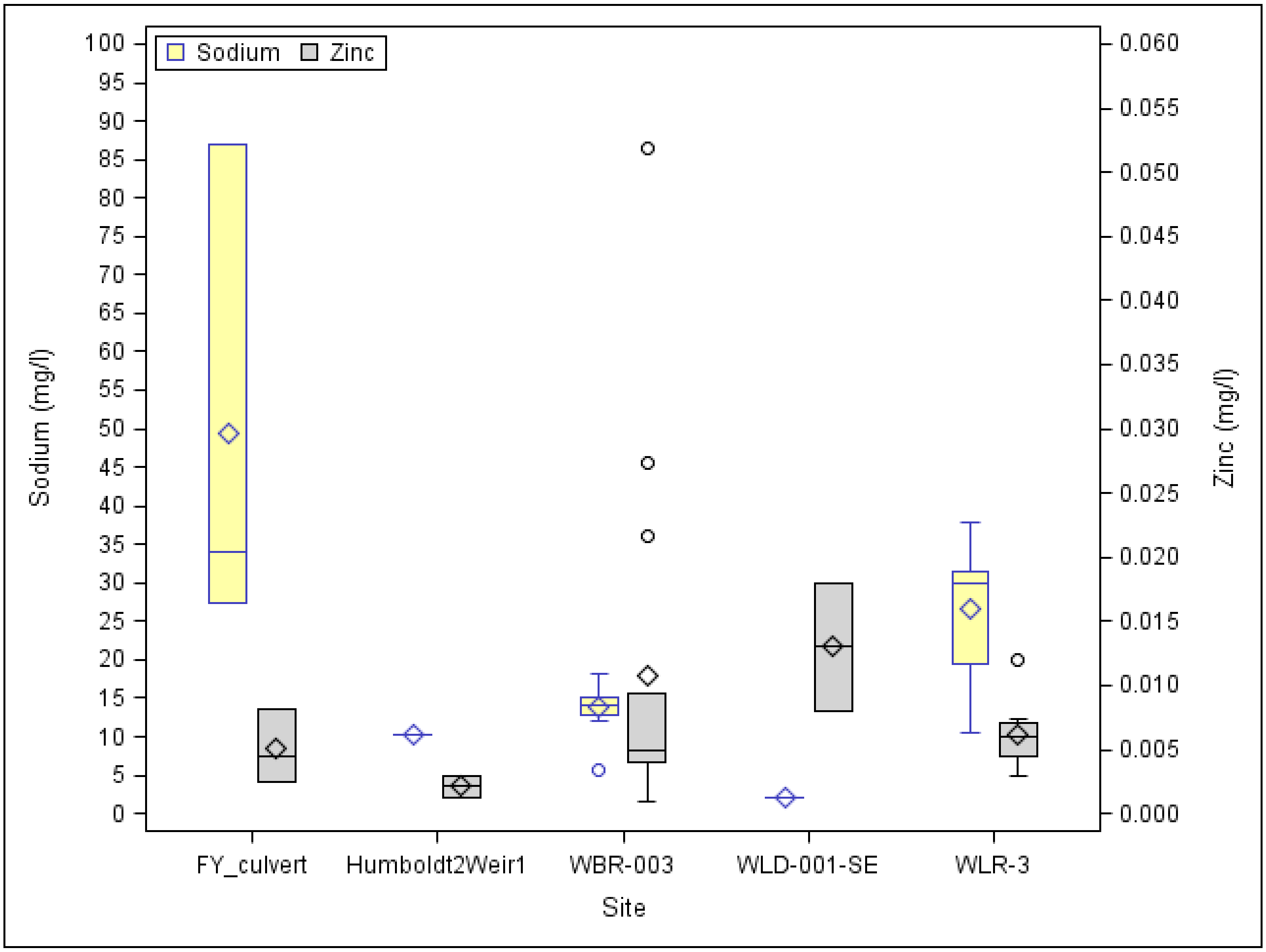

Figure 12. Boxplot of sodium and zinc concentrations. Symbols as in Figure 3.

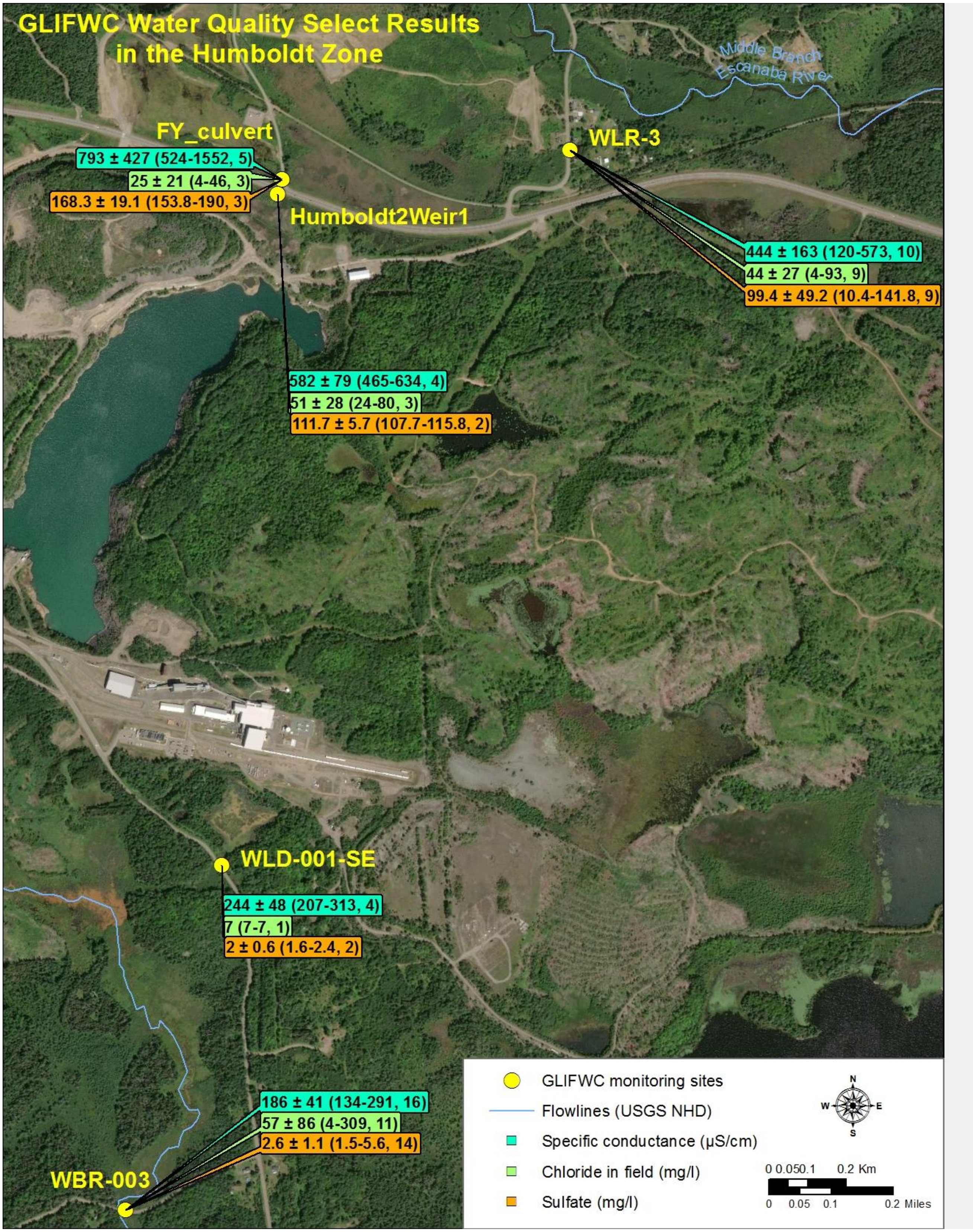

Figure 13. Specific conductance, chloride, and sulfate results from the Humboldt zone. Results are means ± standard deviation (minimum – maximum, *n*).

(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 10 % of variance, and was related primarily to Ba and Cu.

Graphing the Humboldt sites and other GLIFWC study sites on the first and second principal components indicated that the Humboldt sites were in two different groups (Fig. 14). The two southern sites (WBR-003 and WLD-001-SE) plotted closer to certain sites in Wisconsin than to the other Humboldt sites (Fig. 14).

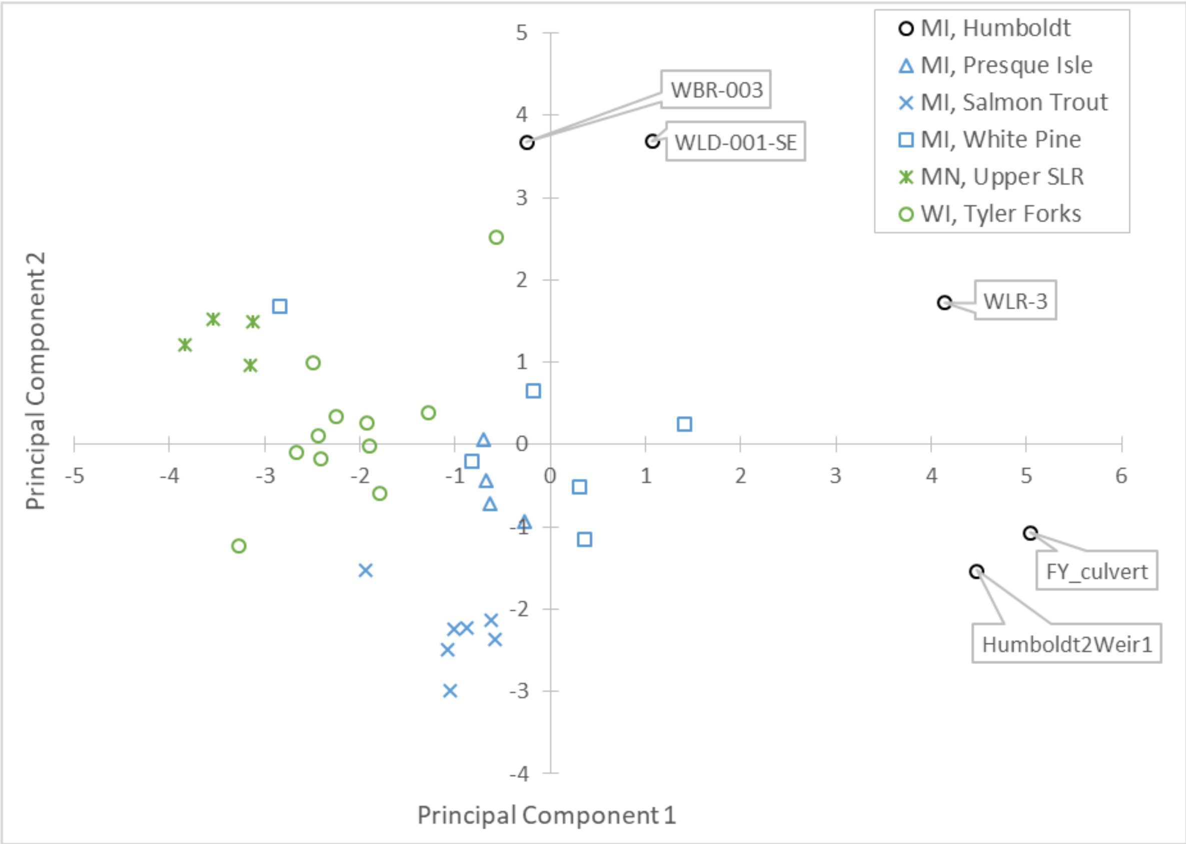

Figure 14. Principal Components Analysis (PCA) of all sites using log-transformed site median values of characteristics with non-detects representing < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, phosphorus, potassium, sodium,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

Cluster analysis

Cluster analysis indicated that the southern two sites downstream of the old iron mining waste rock and tailings (WBR-003 and WLD-001-SE) clustered separately from the northern sites downstream of the active pit lake disposal (Humboldt2Weir1, WLR-3, and FY_culvert; Fig. 15).

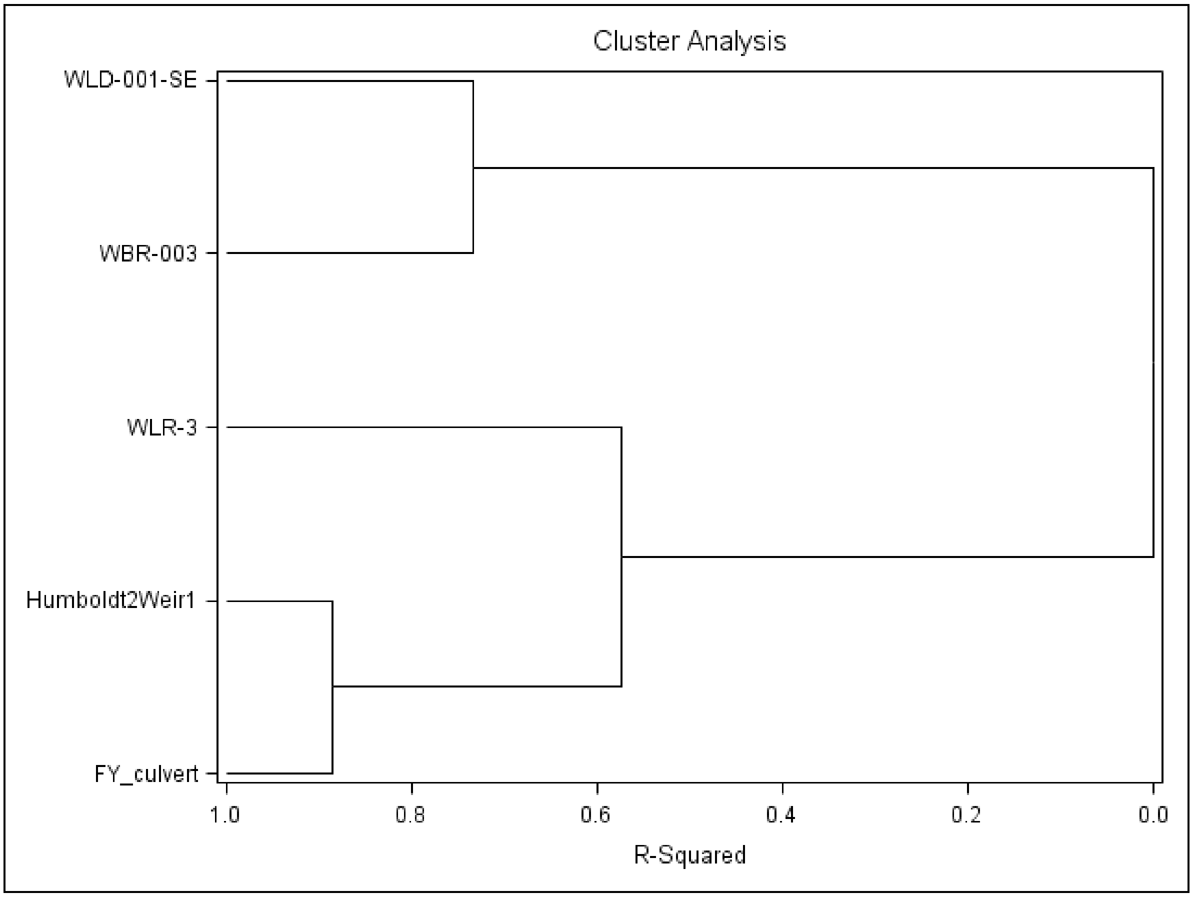

Figure 15. Cluster analysis of Humboldt zone sites using log-transformed site median values of characteristics with non-detects < 10 % of data (specific conductance, pH, alkalinity, chloride, sulfate, aluminum, barium, calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, TDS, and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

Differences between site groups

Testing for significant differences in the distributions and medians between the northern and southern site groups pooled across sites and dates by Wilcoxon Mann-Whitney tests and median tests indicated significant differences for several constituents. Values were greater ($P < 0.05$) at the group of northern sites for specific conductance, pH, boron, calcium, cobalt, copper, magnesium, nickel, potassium, sodium, sulfate, TDS, and hardness. Conversely, values were greater ($P < 0.05$) at the group of southern sites for arsenic, iron, manganese, phosphorus, and TSS. Most arsenic results were below detection limits and all were less than 2 * LOD (LOD range of 1-8 µg/l), but 6 out of 8 samples with detected arsenic were at the southern site WBR-003. Detected arsenic concentrations at WBR-003 ranged from 3 to 7 µg/l (mean 6.1 µg/l, median 6.0 µg/l).

4. Discussion

GLIFWC water quality monitoring in the Humboldt zone indicated that constituents of potential concern were present at high concentrations in the waters downstream of the discharge to the north from the pit lake disposal area. Those characteristics were likely a result of mine discharges and included specific conductance, TDS, sulfate, boron, cobalt, copper, and nickel. For the southern two sites, which are in the Black River watershed and downstream of the historic iron mining waste rock and tailings, iron, manganese, and TSS were at relatively high concentrations.

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