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

Humboldt Zone

By
John Coleman¹ and Scott Cardiff²
¹Great Lakes Indian Fish and Wildlife Commission
²Nelson Institute for Environmental Studies, University of Wisconsin-Madison

Administrative Report 19-11
November 2019

GREAT LAKES INDIAN FISH
& WILDLIFE COMMISSION
Biological Services Division
P.O. Box 9
Odanah, WI  54861
(715) 682-6619
www.glifwc.org
Report on
Great Lakes Indian Fish and Wildlife Commission
Water Sampling in the Humboldt Zone

John Coleman and Scott Cardiff
November 2019
## Contents

1. Introduction ............................................................................................................................................................ 1

2. Methods ................................................................................................................................................................. 2
   - Field methods ......................................................................................................................................................... 2
     - Field measurements ........................................................................................................................................... 2
     - Sample collection ............................................................................................................................................... 2
   - Laboratory analyses ................................................................................................................................................ 2
   - Statistical analyses .................................................................................................................................................. 3
   - Study sites and frequency ...................................................................................................................................... 4

3. Results .................................................................................................................................................................... 6
   - (A) Summary statistics ...................................................................................................................................... 6
     - Field measurements ........................................................................................................................................... 6
     - Laboratory results ............................................................................................................................................... 8
   - (B) Relation between sites ............................................................................................................................... 17
     - Principal Components Analysis ....................................................................................................................... 17
     - Cluster analysis ................................................................................................................................................ 18
     - Differences between site groups ..................................................................................................................... 19

4. Discussion ............................................................................................................................................................ 19

5. Acknowledgements ............................................................................................................................................. 20

6. References ........................................................................................................................................................... 20
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.](image-url)
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>
<thead>
<tr>
<th>Field measurement</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>YSI Pro Plus, YSI ProDSS</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>YSI Pro Plus, YSI ProDSS</td>
</tr>
<tr>
<td>pH</td>
<td>YSI 556, YSI Pro Plus, YSI ProDSS (also checked with pH paper)</td>
</tr>
<tr>
<td>Specific conductance</td>
<td>YSI 556, YSI Pro Plus, YSI ProDSS (and checked with Hanna Instruments 98311)</td>
</tr>
<tr>
<td>Water temperature</td>
<td>YSI 556, YSI Pro Plus, YSI ProDSS</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Analysis category</th>
<th>Analytes</th>
<th>Analysis type</th>
<th>Laboratory method</th>
<th>Field sampling bottle type</th>
<th>Field preservation</th>
</tr>
</thead>
<tbody>
<tr>
<td>General characteristics &amp; major anions</td>
<td>Alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Total hardness Chloride Sulfate</td>
<td>Titration (alkalinity, hardness), gravimetry (TDS and TSS), various</td>
<td>SM2320B (alkalinity), SM2540C (TDS), SM2540D (TSS), SM2340C (hardness) SM4500 Cl E or G (Cl) EPA 200.7 (sulfate)</td>
<td>High Density Polyethylene (HDPE) 500 ml</td>
<td>&lt; 6 °C</td>
</tr>
<tr>
<td>Metals &amp; other trace elements</td>
<td>Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Zn</td>
<td>Inductively-coupled plasma optical emission spectroscopy</td>
<td>EPA 200.7</td>
<td>High Density Polyethylene (HDPE) 250 ml</td>
<td>&lt; 6 °C, acidified with HNO₃</td>
</tr>
</tbody>
</table>

**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 values¹ 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](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.

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

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.

<table>
<thead>
<tr>
<th>Criterion source/site code</th>
<th>Dissolved oxygen (mg/l)</th>
<th>Chloride (mg/l)</th>
<th>pH</th>
<th>Specific conductance (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US EPA</td>
<td>230, 2501</td>
<td></td>
<td>6.5-9.0</td>
<td></td>
</tr>
<tr>
<td>MI</td>
<td>4.72</td>
<td>150 (50, 125, 250 health3)</td>
<td>6.5-9.0</td>
<td></td>
</tr>
<tr>
<td>CCME</td>
<td>5.5-9.54</td>
<td>120 (250 aesthetic5)</td>
<td>6.5-9.0</td>
<td></td>
</tr>
<tr>
<td>FY_culvert</td>
<td>9.1 ± 4.2 (6.5-16.5, 5)</td>
<td>25 ± 21 (4-46, 3)</td>
<td>6.8 ± 0.7 (5.5-7.2, 5)</td>
<td>793 ± 427 (524-1552, 5)</td>
</tr>
<tr>
<td>Humboldt2Weir1</td>
<td>7.1 ± 1.1 (6.3-7.8, 2)</td>
<td>51 ± 28 (24-80, 3)</td>
<td>7.1 ± 0.1 (7.1-7.2, 3)</td>
<td>555 ± 90 (450-634, 5)</td>
</tr>
<tr>
<td>WBR-003</td>
<td>5.1 ± 2.2 (1.9-7.2, 5)</td>
<td>57 ± 86 (4-309, 11)</td>
<td>6.3 ± 0.4 (5.5-7.0, 13)</td>
<td>186 ± 41 (134-291, 16)</td>
</tr>
<tr>
<td>WLD-001-SE</td>
<td>7 (7-7, 1)</td>
<td>6.6 ± 0.5 (5.8-7.1, 4)</td>
<td>244 ± 48 (207-313, 4)</td>
<td></td>
</tr>
<tr>
<td>WLR-3</td>
<td>8.0 ± 1.5 (6-9.6, 5)</td>
<td>44 ± 27 (4-93, 9)</td>
<td>7.0 ± 0.4 (6.4-7.5, 9)</td>
<td>444 ± 163 (120-573, 10)</td>
</tr>
<tr>
<td>Entire zone</td>
<td>7.4 ± 3 (1.9-16.5, 17)</td>
<td>46 ± 57 (4-309, 27)</td>
<td>6.7 ± 0.5 (5.5-7.5, 34)</td>
<td>378 ± 266 (120-1552, 40)</td>
</tr>
</tbody>
</table>

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 (○).
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.

<table>
<thead>
<tr>
<th>Criterion source / site code</th>
<th>Chloride (LOD range 0.2 – 2.5)</th>
<th>Sulfate (LOD range 0.04 - 5)</th>
<th>TDS (LOD range 2 - 20)</th>
<th>TSS (LOD range 1 - 11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US EPA</td>
<td>230, 250¹</td>
<td>250¹</td>
<td>500¹</td>
<td></td>
</tr>
<tr>
<td>MI state</td>
<td>150 (50, 125, 250 health²)</td>
<td>370 (250 health)</td>
<td>500, 750¹</td>
<td></td>
</tr>
<tr>
<td>CCME</td>
<td>120 (250 aesthetic⁴)</td>
<td>500 (aesthetic⁴)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FY_culvert</td>
<td>27.5 ± 5.3 (21.6-31.8, 3)</td>
<td><strong>168.3 ± 19.1</strong> (153.8-190, 3)</td>
<td><strong>365 ± 37</strong> (322-390, 3)</td>
<td>2 ± 0 (2-2, 3)</td>
</tr>
<tr>
<td>Humboldt2Weir1</td>
<td>12.5 ± 1.4 (11.5-13.5, 2)</td>
<td>111.7 ± 5.7 (107.7-115.8, 2)</td>
<td>301 ± 10 (294-308, 2)</td>
<td><strong>1</strong> (1-1, 1)</td>
</tr>
<tr>
<td>WBR-003</td>
<td>29.9 ± 9.6 (0.1-38.4, 14)</td>
<td>2.6 ± 1.1 (1.5-5.6, 14)</td>
<td>149 ± 47 (95-234, 14)</td>
<td>10 ± 10 (1-32, 14)</td>
</tr>
<tr>
<td>WLD-001-SE</td>
<td><strong>1.8 ± 0.4</strong> (1.5-2.1, 2)</td>
<td><strong>2.0 ± 0.6</strong> (1.6-2.4, 2)</td>
<td><strong>143 ± 16</strong> (132-154, 2)</td>
<td><strong>18 ± 11</strong> (10-25, 2)</td>
</tr>
<tr>
<td>WLR-3</td>
<td><strong>34.5 ± 13.2</strong> (9.1-54.1, 9)</td>
<td>99.4 ± 49.2 (10.4-141.8, 9)</td>
<td>285 ± 99 (82-356, 9)</td>
<td>3 ± 2 (1-6, 9)</td>
</tr>
<tr>
<td>Entire zone</td>
<td>28.0 ± 13.1 (0.1-54.1, 30)</td>
<td>55.5 ± 66.1 (1.5-190, 30)</td>
<td>221 ± 103 (82-390, 30)</td>
<td>7 ± 8 (1-32, 29)</td>
</tr>
</tbody>
</table>

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

---

![Boxplot of concentrations of sulfate and chloride from lab measurements. Symbols as in Figure 3.](image-url)

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.

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

<sup>1</sup> USEPA Health advisory lifetime level
<sup>2</sup> 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).

<table>
<thead>
<tr>
<th>Criterion source / site code</th>
<th>Chromium (LOD range 0.00015 - 0.008)</th>
<th>Cobalt (LOD range 0.0002 - 0.002)</th>
<th>Copper (LOD range 0.0002 - 0.0013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US EPA</td>
<td>0.033-0.169¹,²</td>
<td>0.100 (0.040 residential health)</td>
<td>0.003-0.019²</td>
</tr>
<tr>
<td>MI state</td>
<td>0.033-0.169¹,²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCME / CFEQG</td>
<td>0.0089¹</td>
<td>0.0006-0.0014²</td>
<td>0.002-0.004²</td>
</tr>
<tr>
<td>FY_culvert</td>
<td><strong>0.0033 ± 0.0027</strong> (0.0003-0.0057, 3)</td>
<td><strong>0.0024 ± 0.0005</strong> (0.002-0.0029, 3)</td>
<td>0.0018 ± 0.0011 (0.0009-0.003, 3)</td>
</tr>
<tr>
<td>Humboldt2Weir1</td>
<td><strong>0.0007 ± 0.0005</strong> (0.0004-0.0011, 2)</td>
<td>0.0023 ± 0.0003 (0.002-0.0025, 2)</td>
<td><strong>0.0024 ± 0.0001</strong> (0.0023-0.0024, 2)</td>
</tr>
<tr>
<td>WBR-003</td>
<td>0.0029 ± 0.0047 (0.0003-0.0184, 14)</td>
<td>0.0004 ± 0.0003 (0.0001-0.0013, 14)</td>
<td><strong>0.0008 ± 0.0004</strong> (0.0003-0.0017, 14)</td>
</tr>
<tr>
<td>WLD-001-SE</td>
<td>0.0015 ± 0.0010 (0.0008-0.0022, 2)</td>
<td><strong>0.0002 ± 0</strong> (0.0002-0.0003, 2)</td>
<td>0.0011 ± 0.0008 (0.0005-0.0017, 2)</td>
</tr>
<tr>
<td>WLR-3</td>
<td>0.0024 ± 0.0011 (0.0009-0.0040, 9)</td>
<td>0.0011 ± 0.0007 (0.0003-0.0022, 9)</td>
<td>0.0016 ± 0.0004 (0.0011-0.0021, 9)</td>
</tr>
<tr>
<td>Entire Zone</td>
<td>0.0025 ± 0.0033 (0.0003-0.0184, 30)</td>
<td>0.0009 ± 0.0008 (0.0001-0.0029, 30)</td>
<td>0.0012 ± 0.0007 (0.0003-0.003, 30)</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Criterion source / site code</th>
<th>Iron (LOD range 0.001 - 0.05)</th>
<th>Manganese (LOD range 0.00005 - 0.002)</th>
<th>Nickel (LOD range 0.0006 - 0.004)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US EPA 1.000, 0.300</td>
<td>0.050(^1), 0.300(^2)</td>
<td>0.019-0.103(^3)</td>
<td></td>
</tr>
<tr>
<td>MI state 0.300 (health)</td>
<td>0.703-3.992(^3)</td>
<td>0.019-0.103(^3)</td>
<td></td>
</tr>
<tr>
<td>CCME 0.300 (aesthetic)(^4)</td>
<td>0.120 (0.050 aesthetic)(^4)</td>
<td>0.025-0.150(^3)</td>
<td></td>
</tr>
<tr>
<td>FY_culvert 0.359 ± 0.497 (0.028-0.931, 3)</td>
<td>0.047 ± 0.056 (0.01-0.111, 3)</td>
<td>\textbf{0.012 ± 0.005} (0.007-0.017, 3)</td>
<td></td>
</tr>
<tr>
<td>Humboldt2Weir1 \textbf{0.059 ± 0.022 (0.043-0.074, 2)}</td>
<td>\textbf{0.026 ± 0.023 (0.01-0.042, 2)}</td>
<td>0.012 ± 0.007 (0.007-0.017, 2)</td>
<td></td>
</tr>
<tr>
<td>WBR-003 7.881 ± 5.305 (2.801-21.7, 14)</td>
<td>0.705 ± 0.692 (0.043-2.404, 14)</td>
<td>0.002 ± 0.001 (0-0.003, 14)</td>
<td></td>
</tr>
<tr>
<td>WLD-001-SE \textbf{8.882 ± 3.632 (6.313-11.45, 2)}</td>
<td>\textbf{2.239 ± 0.086 (2.178-2.3, 2)}</td>
<td>\textbf{0.0003 ± 0} (0.0003-0.0003, 2)</td>
<td></td>
</tr>
<tr>
<td>WLR-3 0.831 ± 0.420 (0.145-1.339, 9)</td>
<td>0.125 ± 0.077 (0.025-0.218, 9)</td>
<td>0.009 ± 0.004 (0.005-0.017, 9)</td>
<td></td>
</tr>
<tr>
<td>Entire Zone 4.559 ± 5.224 (0.028-21.7, 30)</td>
<td>0.522 ± 0.725 (0.01-2.404, 30)</td>
<td>0.006 ± 0.005 (0-0.017, 30)</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) 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.

<table>
<thead>
<tr>
<th>Criterion source / site code</th>
<th>Phosphorus (LOD range 0.003 - 0.02)</th>
<th>Sodium (LOD range 0.08 - 1)</th>
<th>Zinc (LOD range 0.0004 - 0.009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>US EPA</td>
<td></td>
<td></td>
<td>0.044-0.237&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>MI state</td>
<td>1.00</td>
<td>120, 350 (health)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.044-0.237&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>CCME</td>
<td>200 (aesthetic)&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
<td>0.030&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>FY_culvert</td>
<td>0.004 ± 0 (0.01, 3)</td>
<td>49 ± 33 (28-87, 3)</td>
<td>0.005 ± 0.003 (0.003-0.008, 3)</td>
</tr>
<tr>
<td>Humboldt2Weir1</td>
<td>0.004 (0-0, 1)</td>
<td>10 (10-10, 1)</td>
<td>0.002 ± 0.001 (0.001-0.003, 2)</td>
</tr>
<tr>
<td>WBR-003</td>
<td>0.03 ± 0.02 (0.01-0.08, 13)</td>
<td>14 ± 3 (6-18, 13)</td>
<td>0.011 ± 0.014 (0.001-0.052, 14)</td>
</tr>
<tr>
<td>WLD-001-SE</td>
<td>0.03 (0.03-0.03, 1)</td>
<td>2 (2-2, 1)</td>
<td>0.013 ± 0.007 (0.008-0.018, 2)</td>
</tr>
<tr>
<td>WLR-3</td>
<td>0.01 ± 0.01 (0.01-0.02, 9)</td>
<td>27 ± 9 (11-38, 9)</td>
<td>0.006 ± 0.003 (0.003-0.012, 9)</td>
</tr>
<tr>
<td>Entire Zone</td>
<td>0.02 ± 0.02 (0-0.08, 27)</td>
<td>21 ± 16 (2-87, 27)</td>
<td>0.008 ± 0.01 (0.001-0.052, 30)</td>
</tr>
</tbody>
</table>

<sup>1</sup> Criterion is hardness-dependent
<sup>2</sup> Criteria represent residential health-based and non-residential health-based limits, respectively
<sup>3</sup> Canada Health drinking water criterion
<sup>4</sup> 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).

<table>
<thead>
<tr>
<th>Component number</th>
<th>Eigenvalue</th>
<th>Proportion of variance</th>
<th>Cumulative proportion of variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.123</td>
<td>0.537</td>
<td>0.537</td>
</tr>
<tr>
<td>2</td>
<td>2.791</td>
<td>0.164</td>
<td>0.701</td>
</tr>
<tr>
<td>3</td>
<td>1.627</td>
<td>0.096</td>
<td>0.797</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Eigenvectors by principal component.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>0.0976</td>
</tr>
<tr>
<td>Specific conductance</td>
<td>0.3252</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0.2359</td>
</tr>
<tr>
<td>Aluminum</td>
<td>-0.1913</td>
</tr>
<tr>
<td>Barium</td>
<td>0.1728</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.3116</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.2669</td>
</tr>
<tr>
<td>Copper</td>
<td>-0.0514</td>
</tr>
<tr>
<td>Iron</td>
<td>-0.0750</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.3105</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.0039</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>-0.1294</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.3035</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.2977</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.2951</td>
</tr>
<tr>
<td>TDS</td>
<td>0.3158</td>
</tr>
<tr>
<td>Hardness</td>
<td>0.3247</td>
</tr>
</tbody>
</table>

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).

![Graph showing principal components analysis of site data](image)

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).
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.
5. Acknowledgements

We would like to recognize the substantial contributions made by others to this data collection and analysis effort. Both Dawn White and Esteban Chiriboga of GLIFWC provided data collection support and helped develop the sampling plans and quality assurance documents. Without their early and ongoing efforts, this water quality characterization could not take place. 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. Finally, we would like to thank the Natural Resources Department of the Keweenaw Bay Indian Community and the Yellow Dog Watershed Preserve for their assistance in identifying suitable sampling locations.

6. References


MIDEQ (Michigan Department of Environmental Quality). 2017. Water quality and pollution control in Michigan, 2016 Sections 303(d), 305(b), and 314 Integrated Report. MI/DEQ/WRD-16/001.
