Kawishiwi Watershed Metals Data Summary 2012

Prepared for the Kawishiwi Watershed Protection Project

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Background

The Kawishiwi Watershed is bounded on the south and east by the Laurentian Divide, with water east of the divide flowing east to Lake Superior while water west of the divide flows north to Lake Winnipeg. The southern portion of the Divide includes the Mesabi Iron Range, a geologic feature especially rich in iron compounds, but also biologically active metals such as copper and zinc. The rocks of the Mesabi Range also contain significant concentrations of sulfate compounds.

Residents of the Kawishiwi Watershed have voiced concern about the possibility of potential increases in concentrations of biologically active metals and other compounds in the waters of the watershed through natural erosion and potential runoff from mining operations. The MPCA assisted the Kawishiwi Monitoring Project in 2007 and the Kawishiwi Protection Project in 2012 with metals collection, analysis and assessment. This report summarizes the metals analysis and assessment data.

Research indicated that water column metals sampling were conducted at one site on Birch Lake and one on White Iron from 1977 through 1981 for the Minnesota Regional Copper-Nickel Study. This multi-disciplinary study was developed by the Minnesota Environmental Quality Board, with funding from the Legislative Commission on Minnesota Resources to take a regional examination of all possible regional effects from copper-nickel extraction. One of the goals of the study was, “Collection of baseline data in order to develop a regional perspective as input to predictive impact analysis…”

Overview

Scope

The goal of the 2007 and 2012 metals sampling in Birch and White Iron Lakes is to gather data that will continue to be expanded with future sampling into a database that identifies background conditions for selected metals for both lakes. This Summary provides an overview of the metals sampling project and reports on the progress of the data collection.

The Birch and White Iron Lakes sites established for the 1977 – 1981 Copper-Nickel Study were also sampled in 2007 and 2012. Sampling included water column sampling along with sediment sampling, which was added to provide a more accurate assessment of changes in metals concentrations over time.

All data are archived in the Minnesota Pollution Control Agency’s EQuIS Database.

Sample Collection

Site Locations

- Birch Lake 69-0003 – 00-101
- White Iron Lake 69-0004-00-103

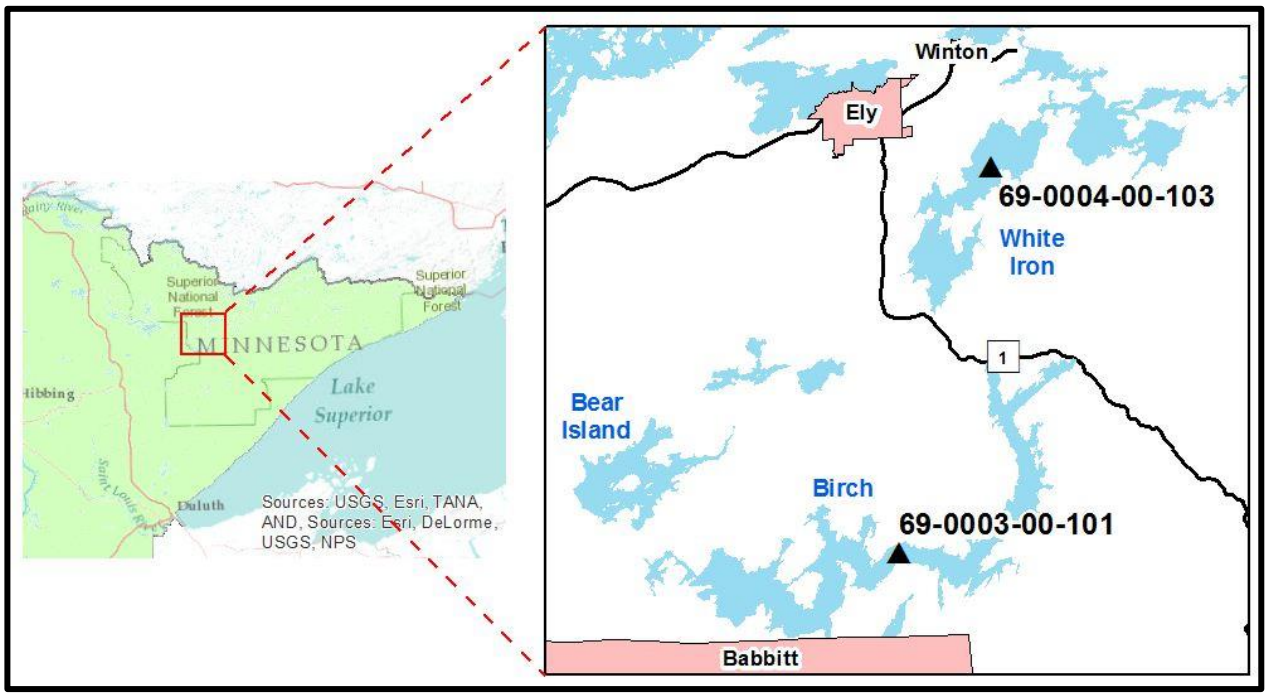


Image 1 – Site Locator Map

Site Parameters

The Iron Range Metals Suite 2012 is composed of twenty-one (21) biologically active metals determined most likely to be found in the Mesabi Range deposit based on data from previous sampling and analysis of metals in waters of the Kawishiwi Watershed. A complete listing of all parameters can be found in Attachment A – Iron Range Metals Suite 2012.

Surface Water Sample Collection, Handling and Laboratory Analysis

Samples were collected on October 16, 2012. Water was collected at 18 inches below the surface in a two liter container supplied by the analysis laboratory. The water was then decanted into laboratory supplied 500 ml sample bottles using "clean hands/dirty hands" techniques. Metals were stabilized with nitric acid and nutrients were stabilized with sulfuric acid.

Ten (10) sample bottles and ten (10) sample blank bottles filled with de-ionized water (for quality assurance/quality control) from each site were labeled, placed in ice filled containers along with the necessary paperwork and were shipped to the Minnesota Department of Health (MDH) Environmental Laboratory in St. Paul for analysis.

The MDH Lab analyzed the samples and sample blanks for total concentrations of all twenty-one metals and six chemical parameters and submitted the analysis report to the MPCA on November 19, 2012.

The 2007 water column samples were collected at 18 inches with a suction pump and analyzed by the MDH Environmental Laboratory.

There were no data available regarding collection methodology for the 1977-81 data.

Sediment Sample Collection, Handling and Laboratory Analysis

Samples were collected on October 16, 2012. Collectors wore Nitrile gloves. Sediment was collected with a clean Ekman dredge in approximately 25 feet of water. The sediment was then spooned into laboratory supplied 1 liter sample bottles using "clean hands/dirty hands" techniques. The target depth for sediment removal was 7.5 cm.

Two (2) sample bottles from each site were labeled, placed in ice filled containers along with the necessary paperwork and were shipped to Pace Analytical Services in Minneapolis for analysis.

Pace Analytical analyzed the samples for total concentrations for all twenty-one metals and submitted the analysis report to the MPCA on November 9, 2012.

The 2007 sediment samples were collected via the same methods as the 2012 data, but the sediment analysis was performed by the MDH Environmental Laboratory.

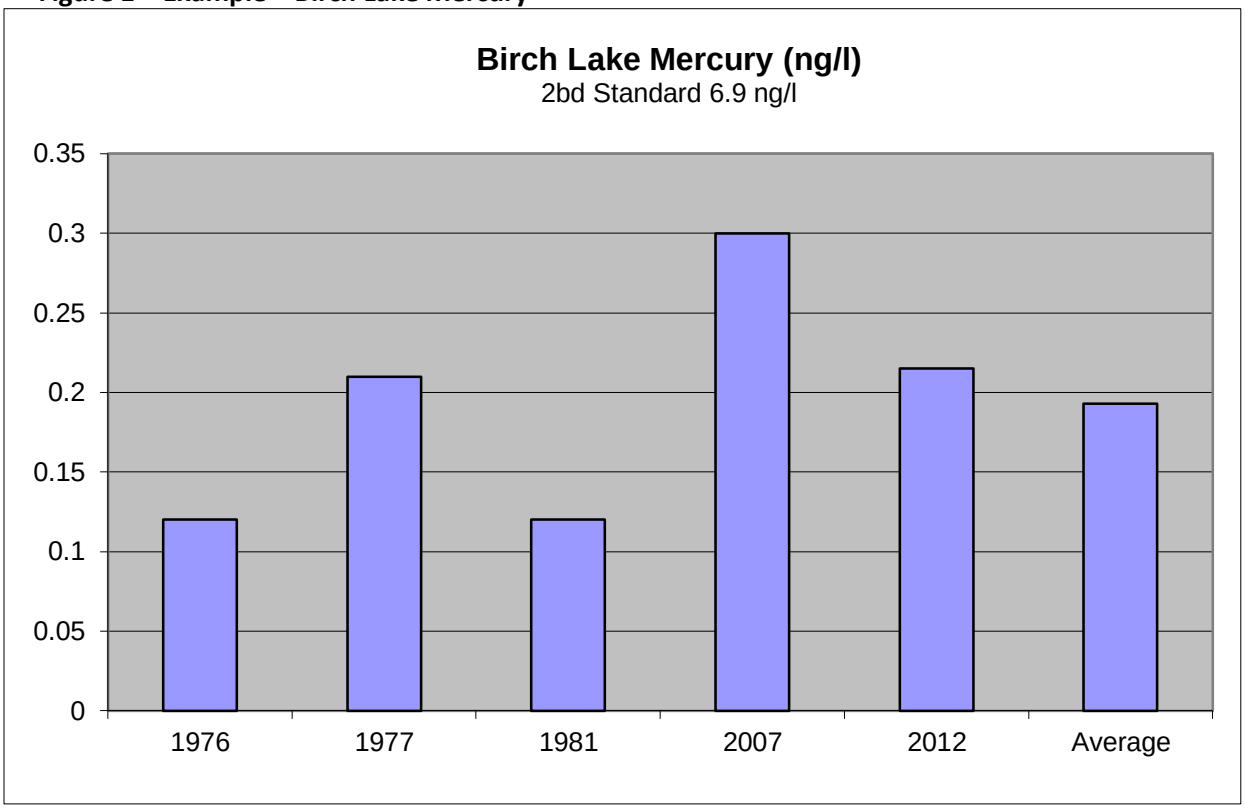
There is no record of any sediment sampling performed concurrent with the 1977-81 water column sampling events.

Report Approach and Caveats

- The 1977-81 data may not be directly comparable to the 2007 and 2012 data. Field protocols and laboratory methods have undergone significant changes designed to improve accuracy.
- Water column samples may not provide an accurate picture of metals concentrations in a given lake. For example 2007 and 2012 were both drought years. Generally droughts result in decreased flows and lower water levels which result in in increased concentrations in the water column. The limited number of water column data points for Birch and White Iron do not allow for statistical analysis. This report compares the water column concentrations to Minnesota State 2bd Standards when a standard is available. While comparison to a standard is not as desirable as a trend analysis it does provide perspective for the reader.
- There are no Minnesota standards for sediment concentrations and very little data available for lake sediments downstream of the Mesabi Range deposits. With only two sampling events, there are not enough sediment data points to perform a statistical analysis or to draw any conclusions.
- Many of the 2007 samples were analyzed to parts per trillion (ng/l). Given the very low levels of most metal concentrations and how far concentrations were below State Standards, the 2012 samples were analyzed to parts per billion (µg/l) to reduce costs, except for mercury which was analyzed to parts per trillion and a few others were analyzed to parts per million (mg/l) for consistency. While this reduction in resolution makes it difficult to directly compare some of the metals concentrations for this report it will reduce future costs and still provide adequate detail for assessment and ultimately trend analysis.
- The bar graphs in the Findings section below are scaled to the highest and lowest concentrations for the specific metal. While a change may look very large due to the scale of the graph it may actually be environmentally insignificant. For example, Figure 6 shows is a drop from 0.3 ng/l to 0.21 ng/l amounting to a drop of 0.09 parts per trillion. The Standard, in this case 6.9 ng/l, may

help to provide context. When it was reasonable to show the Standard on the graph, for example Aluminum, the Standard is indicated by a red line.

Figure 1 – Example – Birch Lake Mercury



Findings

Surface Water

Birch Lake

1. <QL indicates a non-detect (the analyte may be present, but it is below the resolution of the analysis method used)
2. There were no exceedances to Minnesota State Standards, please see Table 1 – Birch Lake Water Column Metals Temporal Comparison.

Table 1 – Birch Lake Water Column Temporal Comparison

Parameter	1977-81	2007	2012	Units	Class 2bd Standard
Aluminum	91.12	51.9	63	µg/l	125.0 µg/l
Antimony	*not sampled*	1	<1	µg/l	5.5 µg/l
Arsenic	0.65	0.45	<1	µg/l	2.0 µg/l
Barium	*not sampled*	6.2	7.97	µg/l	*none*
Beryllium	*not sampled*	0.4	<0.4	µg/l	*none*
Boron	*not sampled*	<QL	32.5	µg/l	*none*
Cadmium	0.025	0.07	<0.10	µg/l	1.1 µg/l
Calcium	18.57	11.5	9.83	mg/l	*none*
Chromium	*not sampled*	0.57	0.55	µg/l	207.0 µg/l
Copper	2.46	1.31	1.44	µg/l	9.8 µg/l
Lead	0.29	0.14	<1.0	µg/l	3.2 µg/l
Magnesium	17.94	9.45	6.48	mg/l	*none*
Manganese	74.1	21.33	35.9	µg/l	*none*
Mercury	0.21	0.3	0.52	ng/l	6.9 ng/l
Molybdenum	*not sampled*	1	<1	µg/l	*none*
Nickel	2.05	1.74	2.72	µg/l	158.0 µg/l
Phosphorus as P	*not sampled*	0.02	0.016	mg/l	0.030µg/l
Selenium	*not sampled*	1	<1	µg/l	5.0 µg/l
Silver	*not sampled*	<QL	<0.2	µg/l	1.0 µg/l
Thallium	*not sampled*	1	<1	µg/l	0.028 µg/l
Titanium	*not sampled*	<QL	<1	µg/l	*none*
Zinc	1.75	1.2	<10	µg/l	106.0 µg/l

3. Some water column metals have a slight increase in concentration for the 2012 sampling event; however all metals with adequate 2012 resolution - except for mercury and nickel - indicate a decrease since the 1977-81 sampling. See Figures 1 – 7 below.

Figure 2 – Birch Lake Aluminum

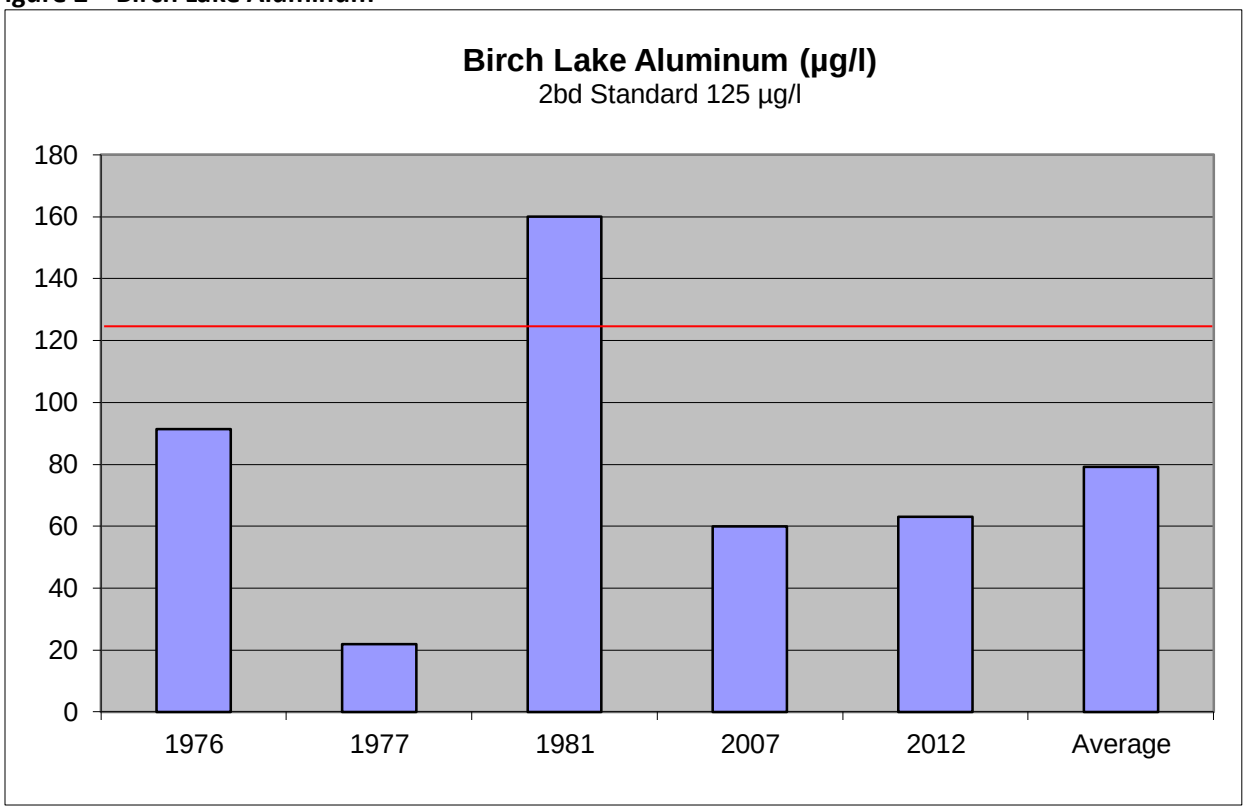


Figure 3 – Birch Lake Calcium

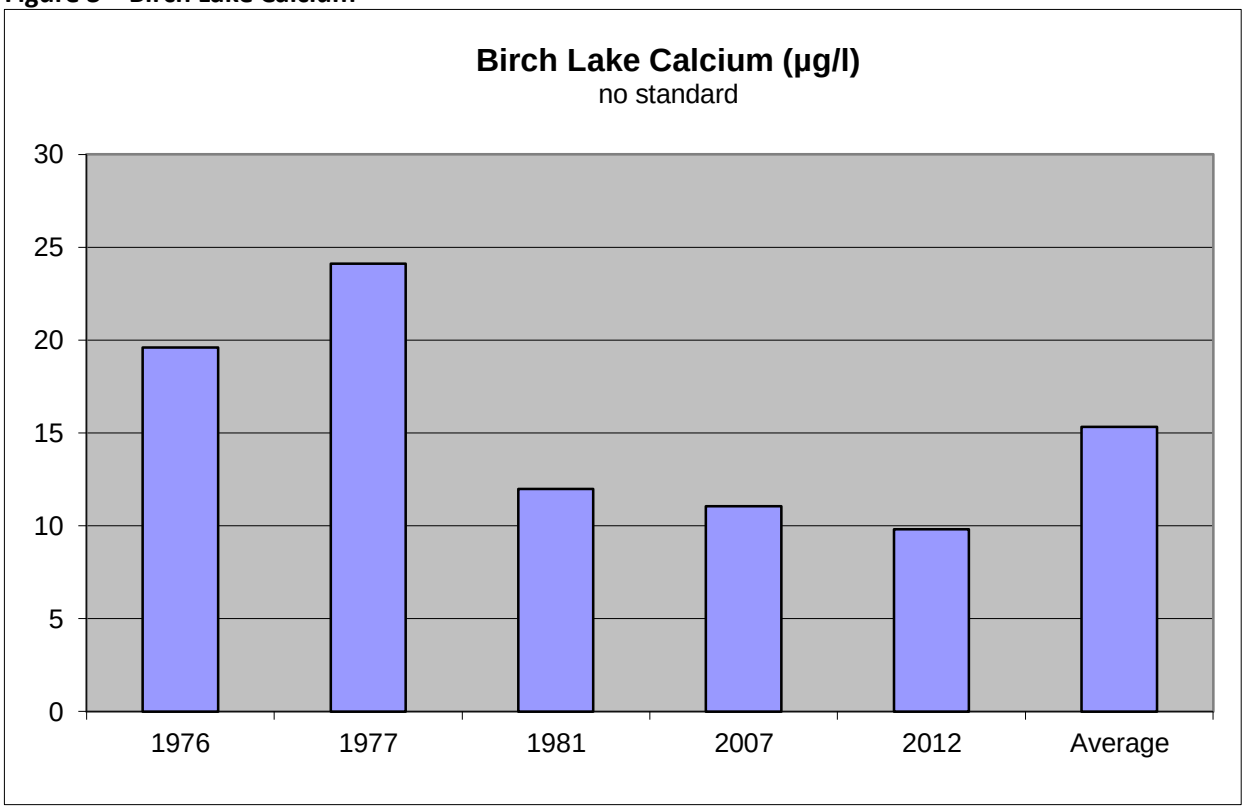


Figure 4 - Birch Lake Copper

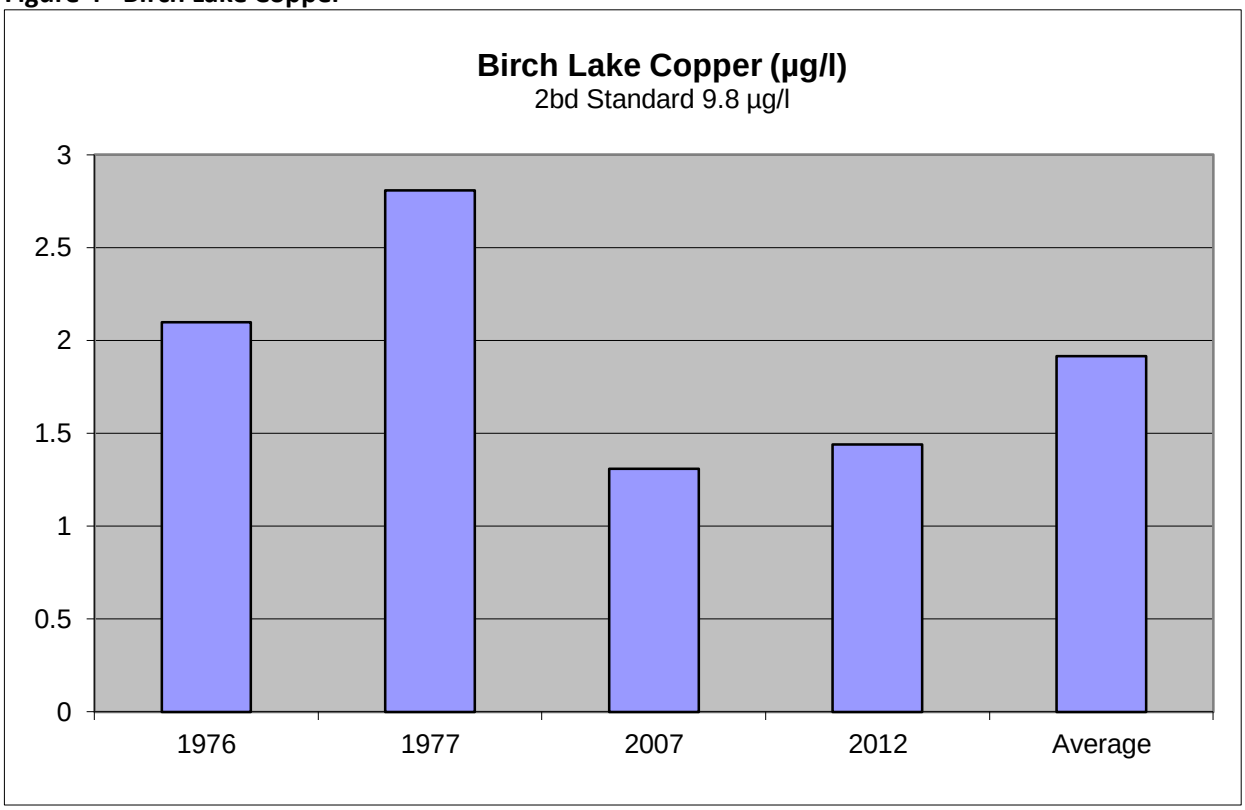


Figure 5 – Birch Lake Magnesium

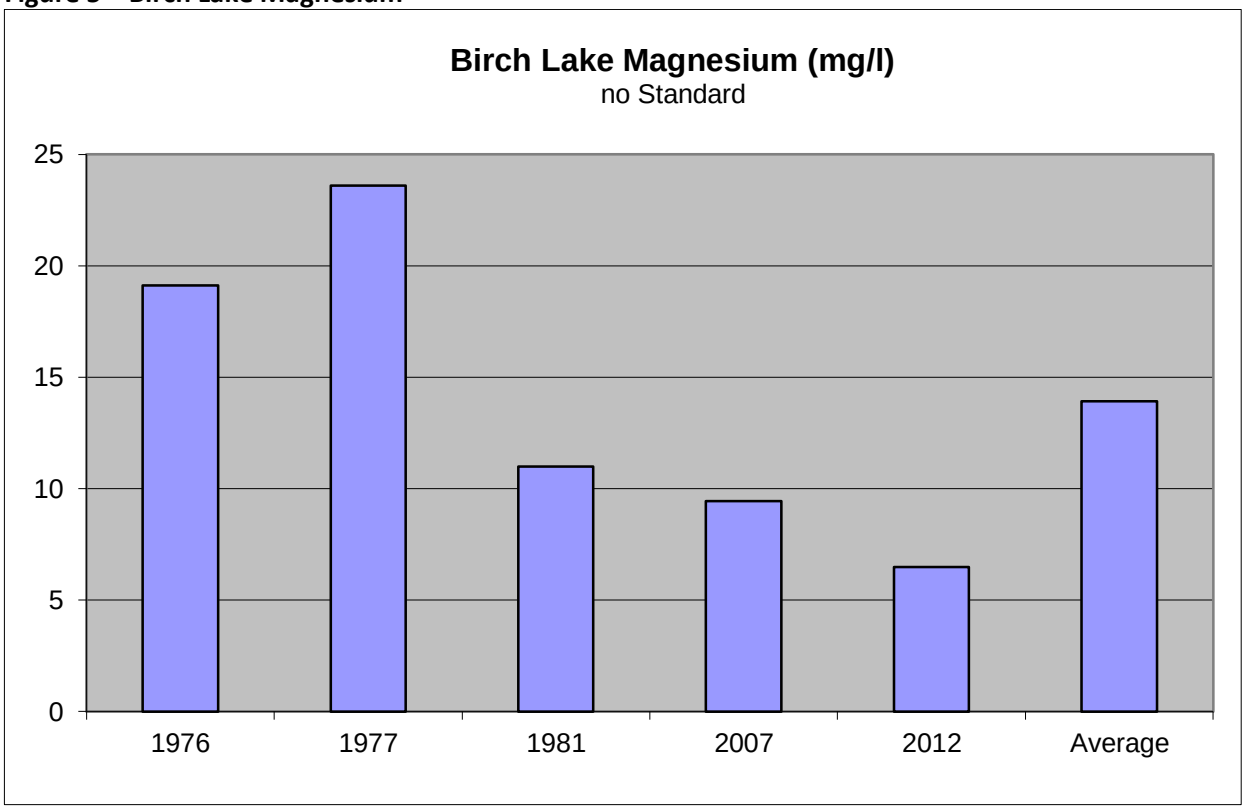


Figure 6 – Birch Lake Manganese

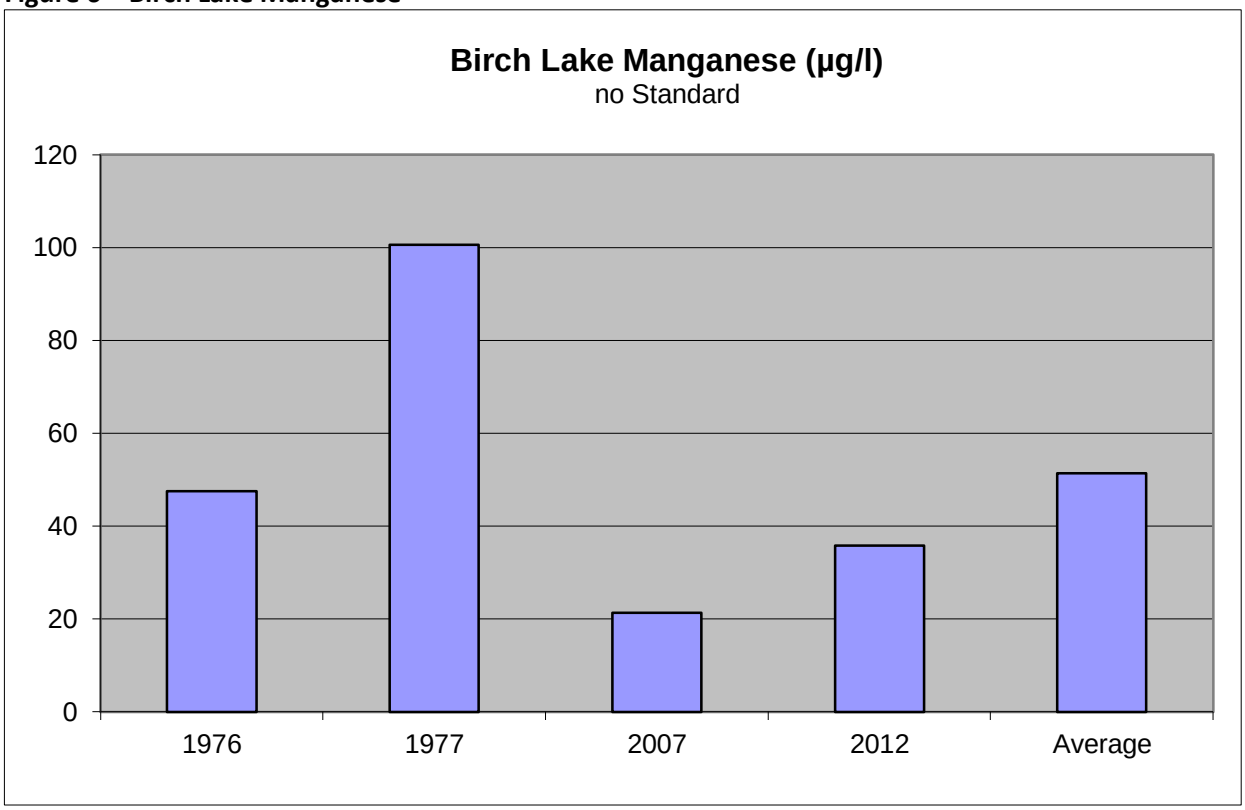


Figure 7 - Birch Lake Mercury

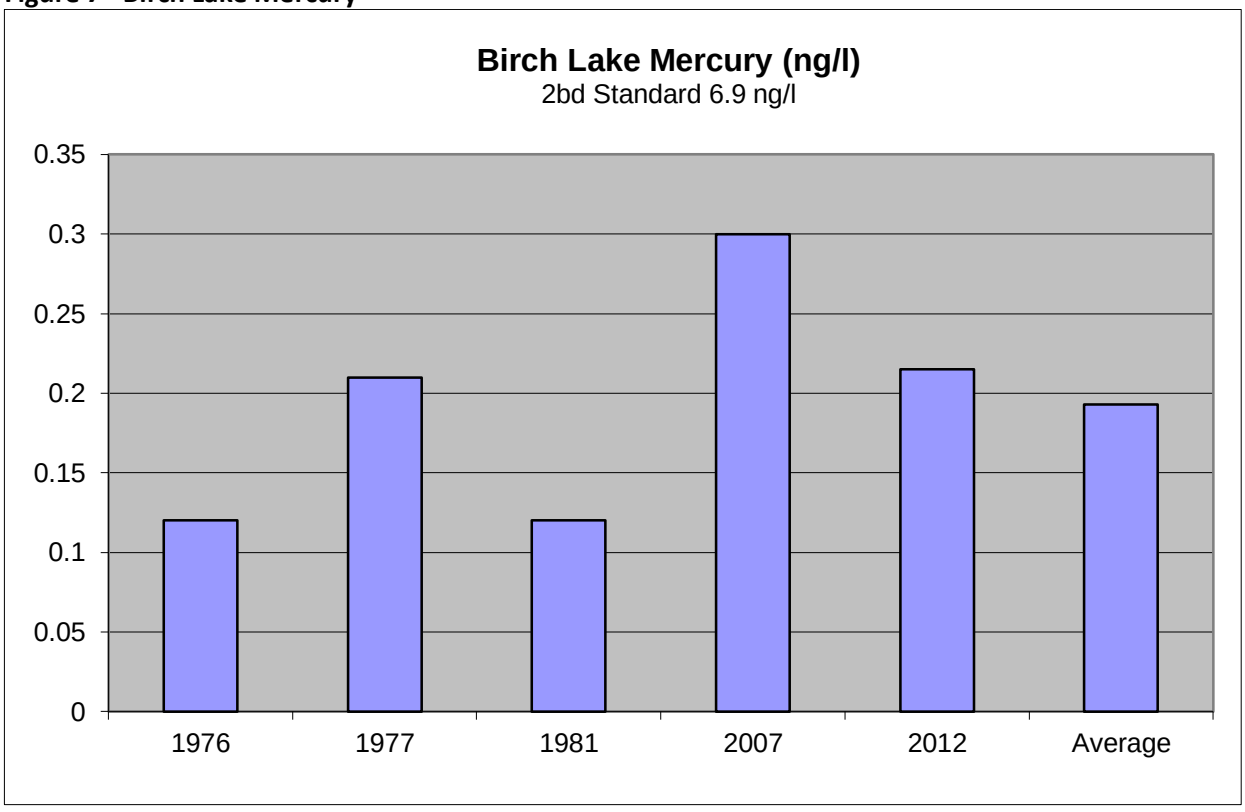
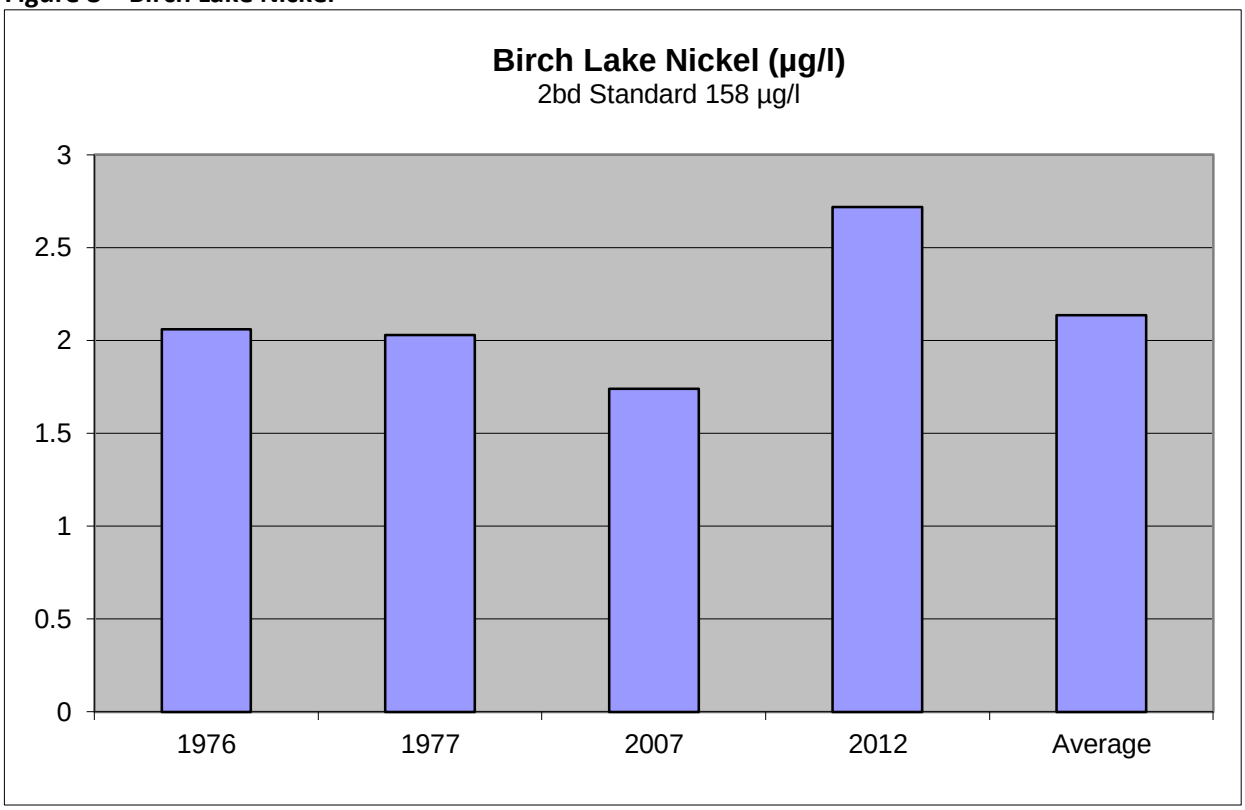


Figure 8 – Birch Lake Nickel



White Iron Lake

1. <QL indicates a non-detect (the analyte may be present, but it is below the resolution of the analysis method used)
2. There were no exceedances to Minnesota State Standards, please see Table 2 – White Iron Lake Water Column Metals Temporal Comparison.

Table 2 – White Iron Lake Water Column Metals Temporal Comparison

Parameter	1977-81	2007	2012	Units	Class 2bd Standard
Aluminum	115.38	53.6	87.7	µg/l	125.0 µg/l
Antimony	*not sampled*	0.6	< 1	µg/l	5.5 µg/l
Arsenic	0.68	<QL	< 1	µg/l	2.0 µg/l
Barium	*not sampled*	6.1	6.56	µg/l	*none*
Beryllium	*not sampled*	0.4	< 0.4	µg/l	*none*
Boron	*not sampled*	<QL	< 20	µg/l	*none*
Cadmium	0.65	0.1	< 0.10	µg/l	1.1 µg/l
Calcium	12.37	19	7.15	mg/l	*none*
Chromium	*not sampled*	0.74	0.66	µg/l	207.0 µg/l
Copper	1.94	1.7	1.95	µg/l	9.8 µg/l
Lead	<QL	<QL	< 1	µg/l	3.2 µg/l
Magnesium	10.99	21	3.77	mg/l	*none*
Manganese	81.94	86	33.7	µg/l	*none*
Mercury	2.3	2.3	3.21	ng/l	6.9 ng/l
Molybdenum	*not sampled*	<QL	< 1	µg/l	*none*
Nickel	1.01	2.1	2.02	µg/l	158.0 µg/l
Phosphorus as P	0.026	0.024	0.016	mg/l	*none*
Selenium	*not sampled*	<QL	< 1	µg/l	5.0 µg/l
Silver	*not sampled*	<QL	< 0.2	µg/l	1.0 µg/l
Thallium	*not sampled*	1	< 1	µg/l	0.028 µg/l
Titanium	*not sampled*	*not sampled*	< 5	µg/l	*none*
Zinc	<QL	<QL	< 10.0	µg/l	106.0 µg/l

3. Some water column metals have a slight increase in concentration for the 2012 sampling event; however all metals with adequate 2012 resolution - except for copper, mercury and nickel - indicate a decrease since the 1977-81 sampling. See Figures 8 - 14 below.

Figure 9 - White Iron Aluminum

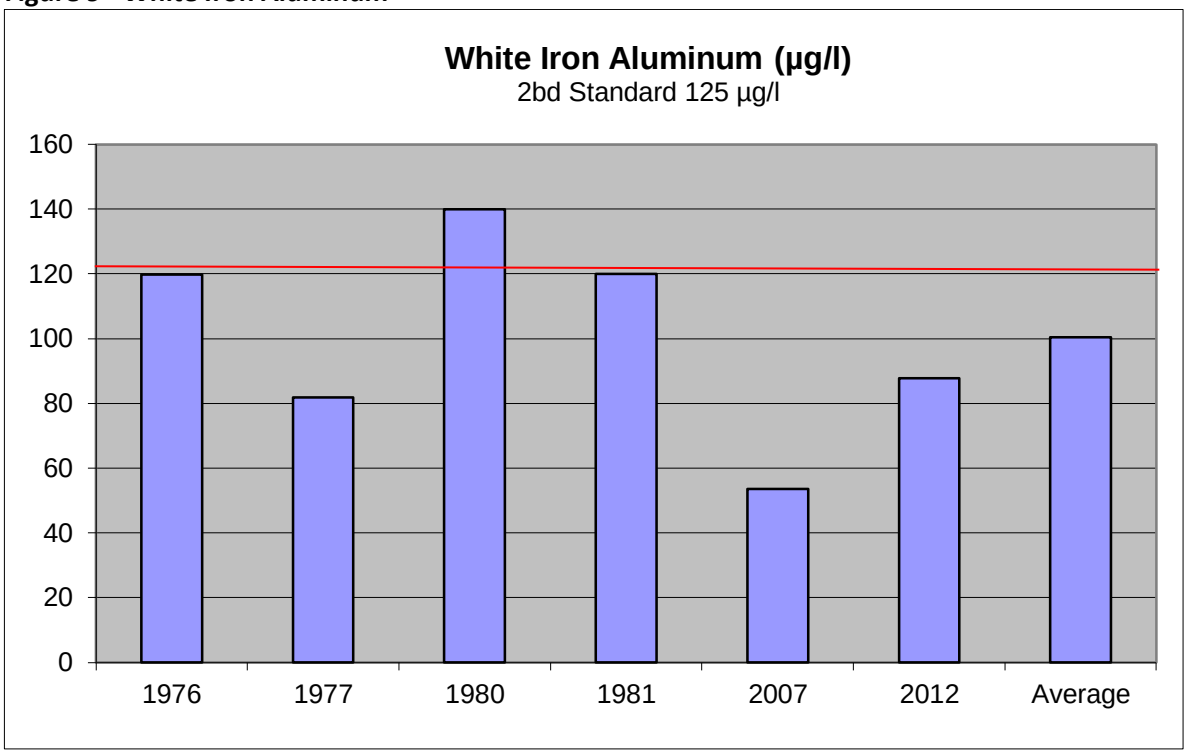


Figure 10 – White Iron Calcium

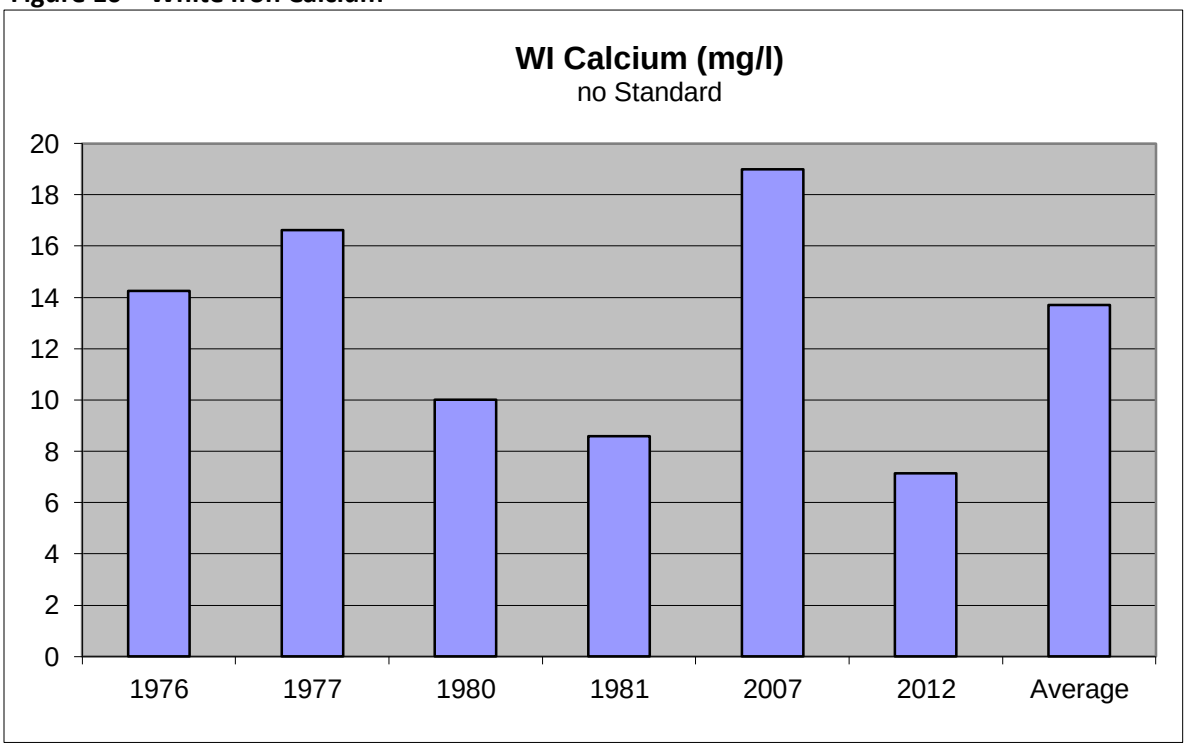


Figure 11 – White Iron Copper

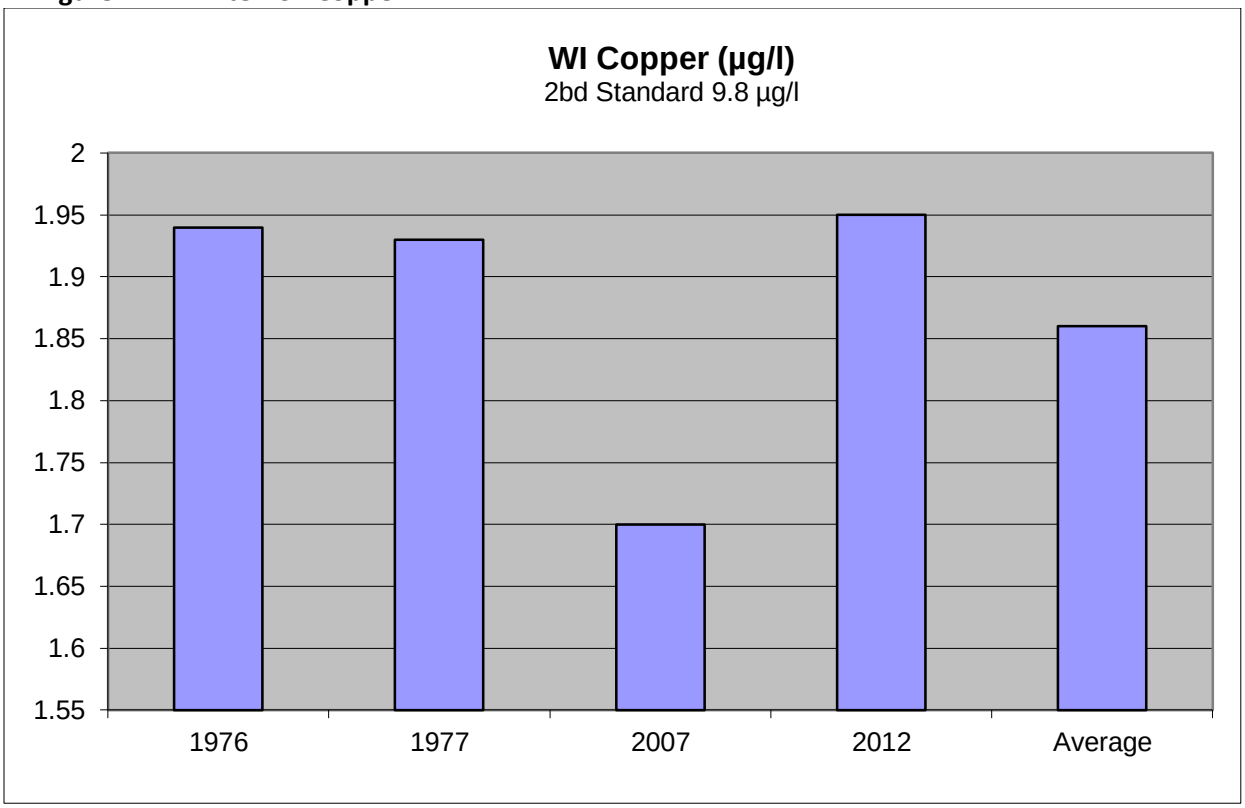


Figure 12 – White Iron Magnesium

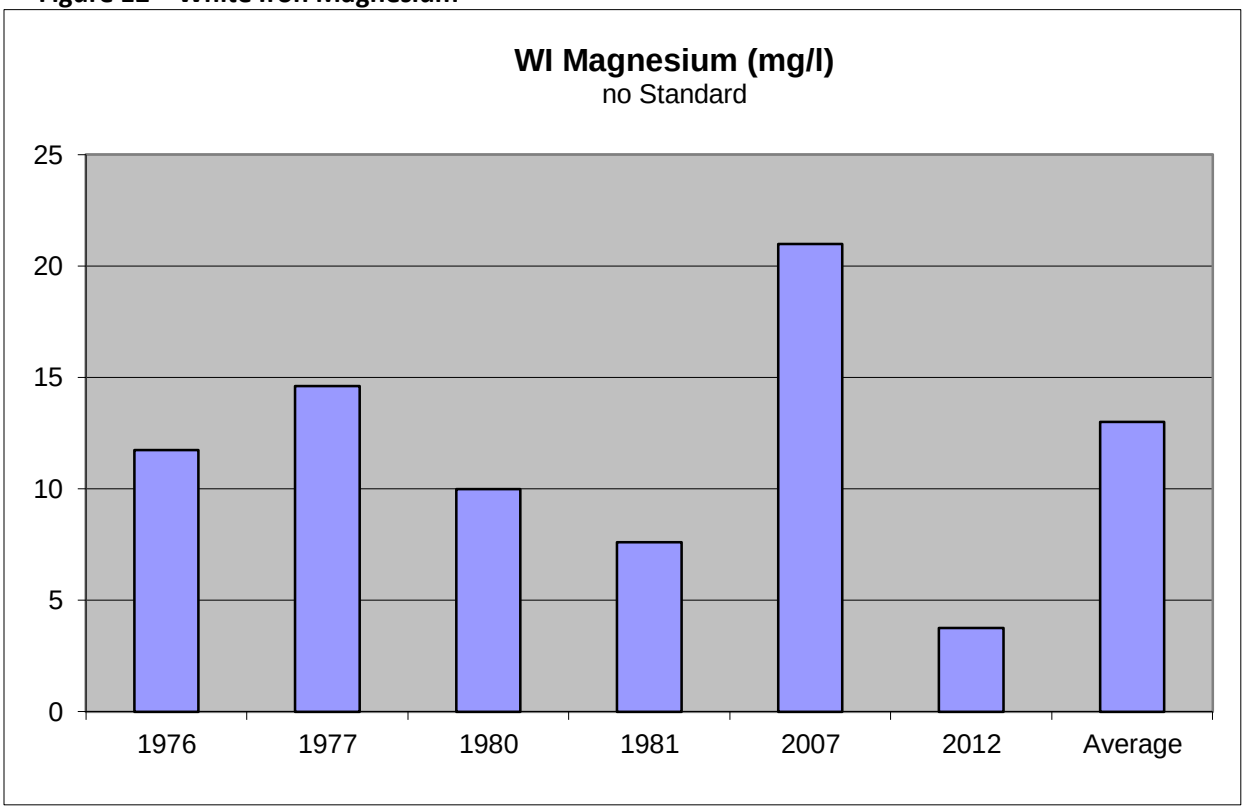


Figure 13 - White Iron Manganese

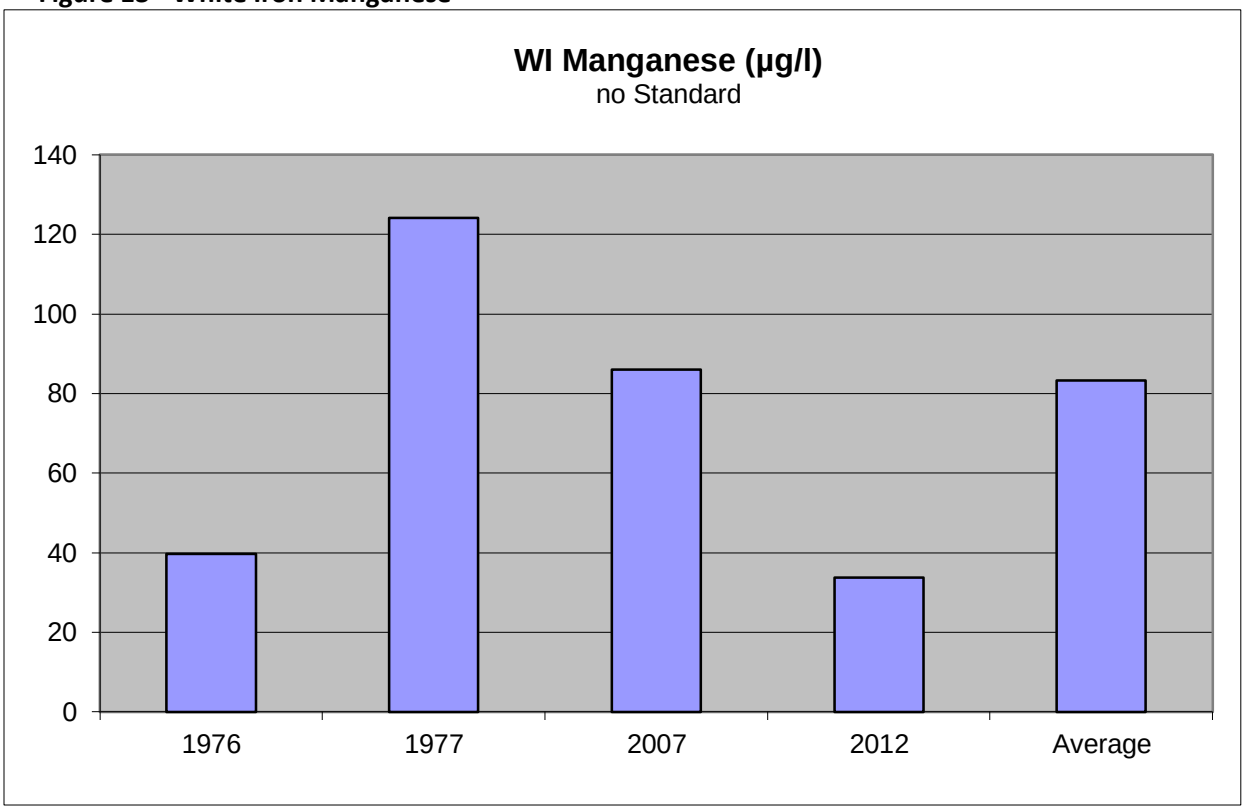


Figure 14 – White Iron Mercury

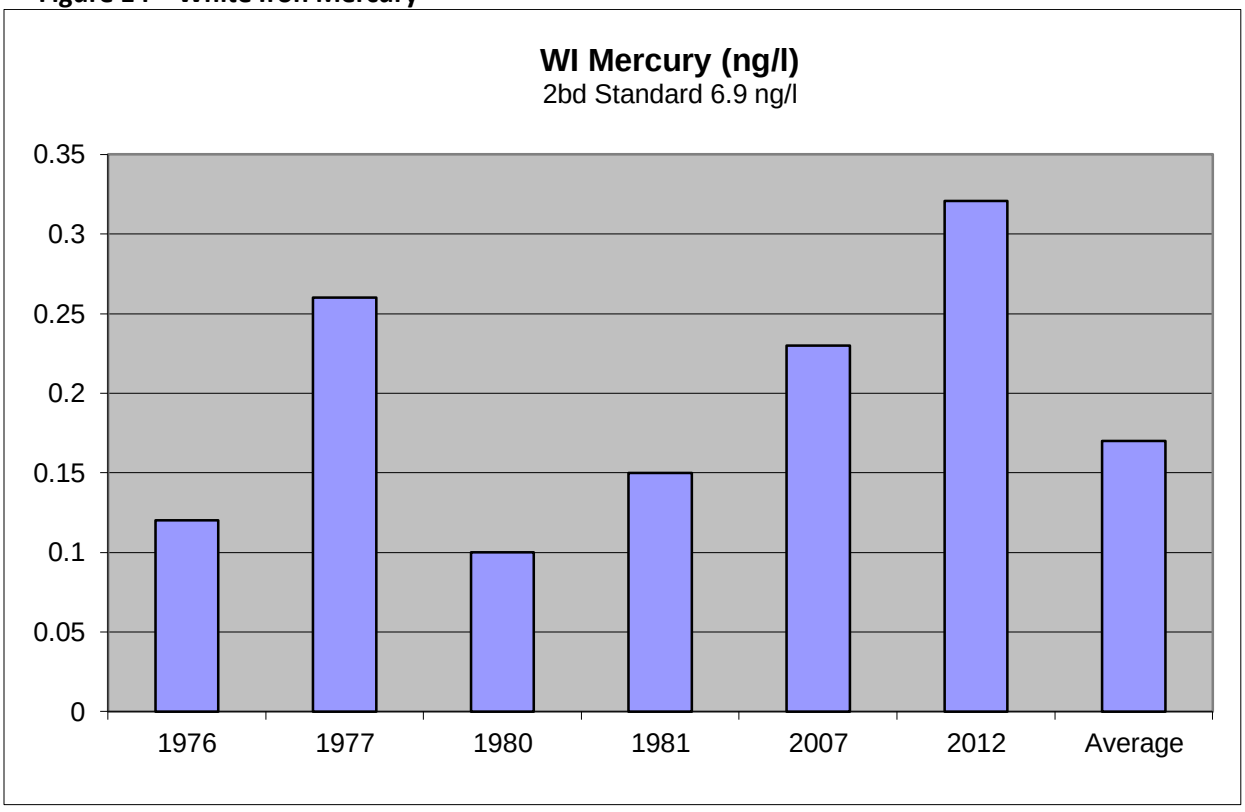
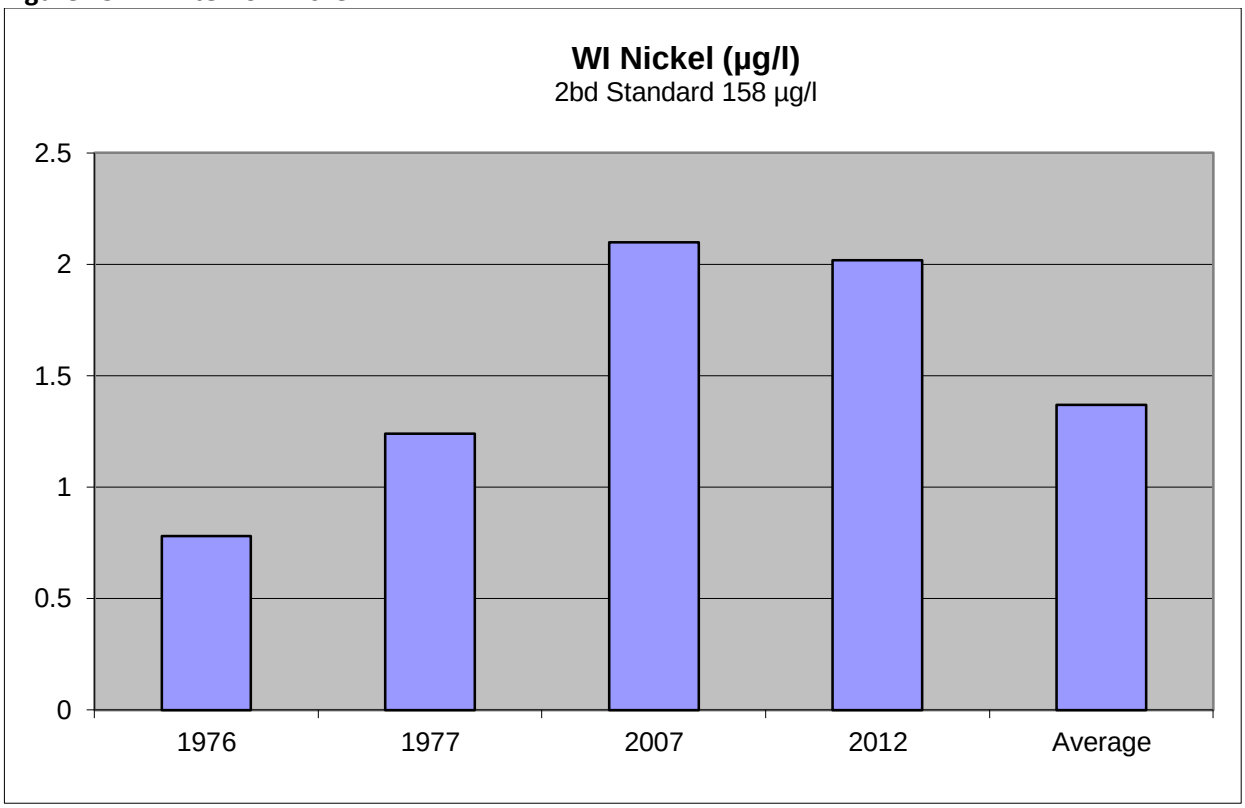


Figure 15 – White Iron Nickel



Sediment

Birch Lake and White Iron Lakes

1. Few Conclusions can be drawn with only two data points for each metal. A search was conducted for background sediment metals concentrations in the Kawishiwi Watershed without success. The data allows us to begin development of a metals background characteristics database.
2. There are some relatively large changes in the concentrations of a few metals from 2007 to 2012, for example the Birch Aluminum decreases by 33% while the White Iron Aluminum increases by 23%. These and the other relatively large changes in concentration are somewhat puzzling, but they could be caused by sediment resuspension and mixing during storm events, mixing by burrowing benthic organisms, sample collection errors or it may be that the 2012 samples were collected a few feet away from the 2007 samples and the differences just represent differing depositional and/or flux rates.

Table 3 – Birch Lake Metals in Sediment

Parameter	1977-81	2007	2012	Units
Aluminum	*not sampled*	29,000	19,900	mg/kg
Antimony	*not sampled*	1	ND	mg/kg
Arsenic	*not sampled*	70	33.1	mg/kg
Barium	*not sampled*	190	172	mg/kg
Beryllium	*not sampled*	<QL	ND	mg/kg
Boron	*not sampled*	<QL	5.25	mg/kg
Cadmium	*not sampled*	<QL	1	mg/kg
Calcium	*not sampled*	8,700	6,730	mg/kg
Chromium	*not sampled*	96	31.1	mg/kg
Copper	*not sampled*	30	38.2	mg/kg
Lead	*not sampled*	28	41.2	mg/kg
Magnesium	*not sampled*	5,700	4,520	mg/kg
Manganese	*not sampled*	2,500	1,960	mg/kg
Mercury	*not sampled*	0.52	0.34	mg/kg
Molybdenum	*not sampled*	<QL	ND	mg/kg
Nickel	*not sampled*	78	50.6	mg/kg
Selenium	*not sampled*	<QL	10.3	mg/kg
Silver	*not sampled*	<QL	ND	mg/kg
Thallium	*not sampled*	<QL	*3.1J*	mg/kg
Titanium	*not sampled*	6.3	5.3	mg/kg
Zinc	*not sampled*	160	160	mg/kg

Table 4 – White Iron Lake Metals in Sediment

Parameter	1977-81	2007	2012	Units
Aluminum	*not sampled*	31,400	41,000	mg/kg
Antimony	*not sampled*	0.6	ND	mg/kg
Arsenic	*not sampled*	43	47.7	mg/kg
Barium	*not sampled*	187	291	mg/kg
Beryllium	*not sampled*	<QL	*1.0J*	mg/kg
Boron	*not sampled*	18	7.8J	mg/kg
Cadmium	*not sampled*	7.9	1.9	mg/kg
Calcium	*not sampled*	*not sampled*	9,640	mg/kg
Chromium	*not sampled*	57.9	66.7	mg/kg
Copper	*not sampled*	27.2	44.8	mg/kg
Lead	*not sampled*	26.6	94.4	mg/kg
Magnesium	*not sampled*	*not sampled*	6,950	mg/kg
Manganese	*not sampled*	2330	2,220	mg/kg
Mercury	*not sampled*	*not sampled*	0.53	mg/kg
Molybdenum	*not sampled*	<QL	ND	mg/kg
Nickel	*not sampled*	67	74.3	mg/kg
Selenium	*not sampled*	<QL	19.2	mg/kg
Silver	*not sampled*	0.66	ND	mg/kg
Thallium	*not sampled*	<QL	*5.1J*	mg/kg
Titanium	*not sampled*	*not sampled*	837	mg/kg
Zinc	*not sampled*	151	310	mg/kg

Recommendations

- Resample every five years to identify changes and possible trends
    - Evaluate and amend the Iron Range Metals suite as appropriate
    - Evaluate and determine appropriate level of analysis for each parameter
- If future statistical trends in metal concentrations are increasing consider detailed metals speciation to determine bioavailability
- Consider modifying metals sampling methodology. A 6" Ekman dredge was used for the 2007 and 2012 sampling. The small size makes it difficult to avoid vertical mixing. Sampling could be done with a larger dredge which would allow for samples to be taken from the dredge with Plexiglas tubes, which could then be sectioned to the desired depth (for 07 and 12 the target depth was 7.5 cm) lessening the possibility of vertical mixing. Another option would be to take all samples with a gravity core
- Conduct a detailed search for data relevant metals in Birch and White Iron Lakes sediments, develop bibliography
- Analyze how the Kawishiwi Metals data compare to data collected for the Minnesota Fish Consumption Advisory
- A paleolimnological analysis of historical metals sediment concentrations that extends to pre-European settlement would provide useful information regarding background conditions

Attachment A

Iron Range Metals Suite 2012

Sites:

- Birch Lake 69-0003 – 00-101
- White Iron Lake 69-0004-00-103

- Metals identified in the geologic deposits:
  - Copper (LL) - Total
  - Mercury - Total
  - Zinc - Total

- Other metals to consider:
  - Aluminum - Total
  - Antimony - Total
  - Arsenic - Total
  - Barium - Total
  - Beryllium - Total
  - Boron - Total
  - Cadmium - Total
  - Calcium - Total
  - Chromium - Total
  - Lead - Total
  - Magnesium - Total
  - Manganese - Total
  - Molybdenum Total
  - Nickel - Total
  - Selenium - Total
  - Silver - Total
  - Thallium - Total
  - Titanium - Total

    Three Samples per site (Water Column, Sediment & Sample Blank)

- Additional Parameters:
  - Hardness
  - Sulfate
  - Chloride
  - Nitrate/Nitrite
  - Phosphorus
  - TDS

    One Sample per site (Water Column)

Attachment B

Data Spreadsheet