Report on 2015-2016 water sampling in the Lake Superior Ojibwe Treaty-ceded Territories:

Iron River, Michigan

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Administrative Report 17-08
October 2017

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Dober Mine pit flow to ponds, August 2016.

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SUMMARY

Extensive mining occurred near the Iron River, in Iron County, Michigan, from the late 1800's until the 1970's. This mining, centered near the towns of Iron River, Mineral Hills, Stambaugh, Caspian, and Gaastra, severely contaminated the Iron River. Although certain measures of water quality in the river have apparently improved since the 1970's, several mine sources of contamination continue to discharge into the river. As part of a study of cumulative water quality effects of mining in the Lake Superior Ojibwe Treaty-ceded Territories, we identified potentially mine-related sources of contamination and concentrations of contaminants entering the Iron River in the summers of 2015 and 2016.

We determined that potentially mine-related contaminants were entering the Iron River primarily from the old Buck mine site wetland discharge, the old Dober mine site wetland discharge, and from pipes between 7th and 4th Avenues in the town of Iron River. Those latter pipes probably discharged mine-influenced groundwater. The Caspian mine pit and adjacent Baker Creek also discharged some contaminants into the river. Certain characteristics of the water appeared to exceed applicable or recommended criteria in the discharges. Those exceedances and other high concentrations occurred at the following discharges:

- **7th-4th Ave pipes** (western two pipes): **Total Dissolved Solids (TDS)[1], dissolved oxygen (DO), and pH** (June) did not meet Groundwater Surface Water Interface (GSI) criteria; **sulfate** and **manganese** exceeded MI and EPA residential/drinking water criteria; **selenium** (SC124) exceeded Canadian surface water criterion; **uranium** and **cadmium** occurred at concentrations greater than in the Iron River and reference sites in other Upper Peninsula zones.

- **Dober Mine**: **temperature** exceeded the MI criterion; **TDS, turbidity**, and **iron** exceeded MI or EPA surface water criteria; **manganese** exceeded MI and EPA residential/drinking criteria; **sulfate, nickel, cobalt,** and **thallium** occurred at relatively high concentrations and **DO** at a relatively low concentration.

- **Caspian Pit**: **temperature** exceeded the MI criterion; **selenium** exceeded Canadian surface water criterion and approached the EPA lake criterion; **pH** was relatively high and **uranium** was present at concentrations greater than in the river;

- **Buck Mine**: **TDS** and **iron** exceeded MI or EPA surface water criteria; **uranium** exceeded EPA drinking water criteria; **sulfate** and **manganese** exceeded MI and EPA residential/drinking criteria; **fluoride** exceeded Canadian surface water criteria; **cobalt**, **nickel, zinc, cadmium**, and **thallium** occurred at relatively high concentrations.

Comparison of upstream and downstream water quality in the Iron River indicated that mine-related discharges were associated in certain reaches with measured increases in specific conductance, alkalinity, TDS, TSS, turbidity, total hardness, sulfate, Li, B, Na, Mg, K, Ca, Mn, Fe, Co, Ni, Zn, Se, Rb, Sr, Cd, Tl, and U. Although some measurements in 2015-2016 were of less concern than those published in reports from previous decades, specific conductance and sulfate have remained high downstream of the US-2 bridge zone on the east side of the town of Iron River. In addition, the Dober and Buck outfalls have continued to demonstrate pH dips in recent years and have remained relatively high in specific conductance, sulfate, Mn, Fe, Ni, and Zn (Buck).

Cluster analyses and Kruskal-Wallis tests comparing sites downstream of mines with reference sites suggested that the mine influence extended at least from the 7th-4th Ave. pipes to the Brule River at Damitz Road, or a distance of 16.5 river-kilometers in the Iron and Brule Rivers.

Mine-related contamination in the Iron River system appears to remain extensive and incompletely remediated to this day.

[1] Throughout this document, bold highlights indicate water quality characteristics that exceed criteria or recommendations or that are at concentrations greater than reference concentrations and of potential concern.

1.INTRODUCTION

The Iron River in Iron County, Michigan, is a coldwater river that has received extensive contamination from past mining and municipal waste discharge. The River and its tributaries Sunset Creek, Stanley Creek, Holmes Creek are state-designated trout streams (MIDNR 2016). Downstream of the towns of Iron River, Stambaugh, Gaastra, and Caspian, the Iron River joins the Brule River, which is also a designated trout stream for most of its length, including the reach where the Iron River joins the Brule (MIDNR 2016).

Mining began in the Iron River region in the 1880's and continued into the 1970's (Fetterolf and Carr 1963, Willson 1973, Johnson & Frantti 1978). More than 50 mining operations occurred in the area and consisted of underground vertical shafts and stopes (Johnson & Frantti 1978). Significant pyrite occurred in and adjacent to the mined Riverton Iron Formation, as well as manganese minerals and other minerals of potential concern for water quality such as sphalerite, chalcopyrite, galena, and uraninite (James *et al*. 1968, Johnson & Frantti 1978).

Some of those mines and their discharges to Sunset Creek and the Iron River caused severe impacts on water quality and aquatic life during and after mine operations (Fetterolf and Carr 1963, Johnson & Frantti 1978). As late as 1948, a dozen mines still operated around the Iron River and disposed of mine water directly to surface waterways, resulting in a bright red color in the Iron River (Fetterolf and Carr 1963). By 1951, contamination from the mines had nearly eliminated aquatic invertebrates at the mouth of the Iron River and for several miles downstream in the Brule River (Fetterolf 1963a).

After 1951, several mines installed settling ponds and downstream macroinvertebrate populations improved, but only temporarily (Fetterolf 1963a). The Iron River was yellow-brown in color because of discharges from the Homer, Hiawatha #1, Hiawatha #2, and Sherwood Mines (Fetterolf and Carr 1963). Macroinvertebrates were less diverse again in 1960 and 1961, and were further impacted by discharge of mine water from the M. A. Hanna Mining Co.'s Homer-Wauseca Mine to Sunset Creek in 1961-1962 (Fetterolf 1963a). Water discharged to Sunset Creek from that mine became acidic and high in ferrous iron in the spring of 1962 (Fetterolf and Carr 1963). Other mine waters also entered the river downstream (Wagner 1963). In 1962, a survey found no fish below Sunset Creek and three species of fish held in a cage in the river five miles below Sunset Creek died within 16 hours (Fetterolf 1963a, Wagner 1963). The turbid, yellow-brown mine waters and sediment deposits extended to the confluence with the Paint River, or approximately 51 km (32 miles) downstream, including at least 35 km (22 miles) on the Brule River (Fetterolf 1963a, Fetterolf 1963b, Fetterolf and Carr 1963, Willson 1969).

The M. A. Hanna Company built ponds in Sunset Creek to attempt to neutralize the acidic waters before discharge and in 1963 switched to pumping water from the overlaying glacial till for de-watering (Willson 1969, Johnson & Frantti 1978). This appeared to lead to some recovery of macroinvertebrate and fish communities by September 1963 (Fetterolf 1963a, Fetterolf and Carr 1963).

By 1968, the Homer-Wauseca and Sherwood Mines were the only mines still openly discharging mine water to the Iron River system (Willson 1969). The Sherwood discharge greatly discolored the river from the point of discharge in the general zone of 4th Ave. all the way to the Brule River (Willson 1969). Macroinvertebrates had recovered relative to 1963, but fish populations in 1968 had apparently declined relative to the recovery of 1963, and algae, though abundant below the municipal wastewater discharges, were less diverse in the reaches below Sunset Creek (Willson 1969). Macroinvertebrates were apparently still impacted by the Homer-Wauseca Mine discharge, the turbid Sherwood Mine discharge, and Iron River and Caspian wastewater treatment plant (WWTP) discharges (Willson 1969).

Contamination continued in the 1970's. Although the M. A. Hanna Company's Homer-Wauseca Mine became inactive ca. 1969-1971, Inland Steel's Sherwood Mine switched its discharge to Sunset Creek and continued to discharge until 1978 (Willson 1973, Sylvester 1974, Johnson & Frantti 1978, Woods & Buda 1980). The Sherwood Mine discharge to Sunset Creek was likely contaminating that creek and the Iron River with sulfate, manganese, iron, copper, zinc, nickel, and oil (Sylvester 1974, Johnson & Frantti 1978, Woods & Buda 1980). Probably because of groundwater rebound and the connected Hiawatha underground mines, the former Dober Mine of M. A. Hanna Co. began in the fall of 1972 to release large volumes of acidic waters through drainage trenches, the Stambaugh WWTP, and possible subsurface seepages (Willson 1973, Sylvester 1974, Johnson & Frantti 1978, Woods & Buda 1980). The Dober site continued to discharge water high in sulfate, manganese, iron, nickel, copper, zinc, lead, and cadmium and coat the Iron River bottom with iron precipitates (Sylvester 1974, Johnson & Frantti 1978, Woods & Buda 1980). By 1976, the former Buck mine group of Picklands Mather and Company was also discharging waters high in sulfate, iron, and manganese to the Iron River (Johnson & Frantti 1978). Discoloration and turbidity from the mine waters continued downstream to the Brule River (Johnson & Frantti 1978). Johnson & Frantti (1978) even hypothesized that mining had led to transport of so much manganese downstream that it may have been an important contributor to the formation of manganese nodules in Green Bay.

The Dober Mine discharge to the Iron River continued from the 1980's on, and appeared to continue to impact water quality and aquatic life in the Iron River (White 1983, Sayles 1989). The Dober Mine discharge and the Buck Mine water remained toxic to test organisms at least into the early 2000's (Butler 2001e, 2002).

A variety of other sources contributed and may still contribute contamination to the Iron River. Municipal wastewater discharges in Iron River, Stambaugh, Caspian, and Gaastra contributed algae-promoting nutrients, oil, iron, PCBs, and coliform bacteria to the Iron and Brule Rivers and reduced macroinvertebrate diversity (Fetterolf 1963a, Willson 1969, Willson 1973, Sylvester 1974, Woods & Buda 1980). Mine water entered the Stambaugh treatment plant and may have infiltrated as groundwater at the Iron River municipal plant as well (Woods & Buda 1980). Effluent from all four municipal wastewater discharges contained relatively high (58-250 mg/l) sulfate in 1978, though sulfate can also result from certain modern de-chlorination processes (Woods & Buda 1980). A slaughterhouse also discharged to Stanley Creek (Wagner 1963). A commercial laundry company discharged effluent to the Caspian municipal discharge as well, contributing oil and grease and toxic chemicals to the system (Woods & Buda 1980, White 1983, Hull 1986a, b). The effluent of a newer West Iron County WWTP was initially reported to be less toxic than the four treatment systems that it replaced, but still discharged water with relatively high conductivity and concentrations of fluoride, chloride, sulfate, nickel copper, zinc, and oil and grease (Walker 1987, Quinn 1992). The WWTP effluent remained chronically toxic in 1992 at least, and continued to impact macroinvertebrates (Sayles 1989, Quinn 1992). Faulty septic systems may also leak to the Iron River, and urban runoff, gravel mining operations, livestock, and dam sediment have also impacted the Iron River (Bond 2001).

Several management efforts in the last 20 years have endeavored to improve habitat and reduce contaminated discharges to the Iron River. This includes upstream dam removal (Premo *et al*. 2009), and stream habitat restoration at the confluence with the Brule River (Taft 2012a). It has also included diverting Iron River water into the Dober site, and constructing, dredging out, and maintaining treatment/settling ponds at the Buck Mine site in 1997 and 2007-2008 (Weston Solutions 2009, Taft 2012b).

In spite of those efforts, concern has remained about contamination entering the river and little recent sampling has occurred. Mine wastes at the Dober, Buck, and other sites have remained exposed or incompletely reclaimed. Sampling for several constituents in recent decades has also lacked a thorough set of analytes and adequate spatial distribution. For example, although reports since at least the 1950's indicated that uraninite was present in the Buck Mine (James *et al*. 1968), limited sampling, with high detection limits (Johnson & Frantti 1978), had apparently not documented uranium in the discharge until DEQ sampling in 2013 (MIDEQ 2014). Similarly, data from NPDES applications for the Dober mine were sparse, and Discharge Monitoring Report data from PolyOne Corp. for the Dober mine now appear to only provide information on flow, pH, TSS, and total and dissolved iron.

As part of a study of cumulative water quality effects of mining in the Lake Superior Ojibwe Treaty-ceded Territories, we sought to fill an information gap on recent water quality measurements related to mining impacts in the Iron River watershed. In particular, we collected data to identify contaminants and their sources and concentrations, and determine the downstream spatial extent of contamination from mining in the Iron River.

2. METHODS

Field methods—field measurements

At all sites, we used standard surface water monitoring protocols (USGS variously dated; USEPA 2012) and recorded temperature, specific conductance, and chloride concentration with a YSI Pro Plus multimeter in the field. In addition, at sites sampled for anions, we measured dissolved oxygen (DO), pH, and oxidation-reduction potential (ORP). We calibrated specific conductance, chloride, pH, and DO sensors daily, and verified ORP calibration daily (re-calibrating as necessary). At sites sampled for metals and trace elements, we also measured turbidity with a Hanna Instruments 93703 turbidimeter (calibrated once per sampling trip), and velocity and depth profiles for Equal Width Increment discharge calculations with a Swofford 3000 velocity meter (USGS, variously dated).

Field methods – sample collection

We collected samples for major anions, alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), and metals and trace elements (Table 1). Where possible, we collected samples at well-mixed sites below a riffle zone. We used a hand dip sampling technique at the centroid of flow with the Clean Hands – Dirty Hands technique (USGS variously dated, USEPA 1996). We rinsed bottles three times with sample water and kept bottles capped when submerging into or removing from the water. At some sites where we only sampled for major anions, we used a one-person modification of Clean Hands-Dirty Hands technique. This involved using one hand as the "clean hand" and one as "dirty hand." In August 2015, we only collected four anions samples in the Iron River region. In June 2016, we collected 13 anion samples and 1 field sequential replicates and 1 blank. In August 2016, we collected 28 anion samples and 2 field sequential replicates and 2 blanks. In that month, we also collected 17 trace element and alkalinity samples and 1 field sequential replicate and 1 blank of each. We also collected 10 TDS/TSS samples. We filtered anion samples using syringes and 25 mm diameter, 0.45 µm polysulfone cartridge filters (Pall Acrodisc 4585) within 14 hours of sample collection. We analyzed those samples by ion chromatography within 10 days after sample collection. We did not filter the metal and trace element samples.

We recorded field measurements and collected four anion samples on the 26th August 2015. We also measured field characteristics and collected anion samples (n=12) on the 18th and 19th June 2016. In a more detailed study, we recorded field measurements and collected anion (n=25), alkalinity/TDS/TSS (n=15 alkalinity, 10 TDS/TSS), and metal and trace element (n=15) samples the 16th – 22nd August 2016.

Table 1. Types of water quality samples and associated sampling, preservation, and analysis methods.

Analysis category	**Analytes**	**Analysis type**	**Laboratory method**	**Field sampling bottle type**	**Field filtration and/or preservation**	**Analysis location**
General	Alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS)	Titration (alkalinity), gravimetry (TDS and TSS)	SM2320B (alkalinity), SM2540C (TDS), SM2540D (TSS)	High Density Polyethylene (HDPE) 950 ml	< 4 C	WI Lab of Hygiene
Major anions	Bromide, chloride, fluoride, nitrate, sulfate	Anion ion chromatography	EPA 300.1	HDPE 60 ml or 125 ml	Syringe filtration (0.45µm Pall polysulfone Acrodisc), < 4 C	UW-Madison WSEL
Metals & trace elements	50 metal(loid)s (totals)	Inductively-coupled plasma mass spectrometry	Magnetic Sector ICP-MS	Polytetra-fluoroethylene (PTFE) 250 ml	< 4 C	WI State Lab of Hygiene

Laboratory methods

We conducted ion chromatography following EPA method 300.1, with a Dionex ICS-2100 and autosampler. We configured the instrument with a 4 mm x250 mm Dionex IonPac AS11 column, AG-11 guard, and ASRS-4mm suppressor. We used a 100µL injection loop, flow rate of 0.6 ml/min (2016, 1.0 ml/min in 2015), suppressor current of 45 mA (2016, 65 mA in 2015), column temperature of 30 C, and 30 mM NaOH eluent. We measured Method Detection Limits (MDLs) by running seven standard-fortified samples through an analysis sequence in two different batches on two (2015) or three (2016) separate days (Table 2).

Table 2. Ion chromatography Method Detection Limits (MDL) for major anions analyzed.

	Year	**F^-**	**Cl^-**	**SO_4^{2-}**	**Br^-**	**NO_3^-**
MDL concentration (mg/l)	2016	0.00835[1]	0.00919	0.0268[2]	0.00528[1]	0.00548
	2015	0.01676[2]	0.01127[3]	0.0302[3]	0.00162	0.00449

[1] MDL from 6 samples only (other failed QAQC)
[2] MDL from 5 samples (2 others failed QAQC)
[3] MDL was lower than Minimum Reporting Limit.

The Wisconsin State Laboratory of Hygiene analyzed metal and trace element samples for 50 elements using a Thermo-Finnigan Element 2 Sector-Field (Magnetic Sector) ICP-MS. Nitric acid digestion at 85 C for 12 hrs preceded ICP-MS analysis. Laboratory Quality Control samples for each batch included sample duplicates, sample spikes for at least 14% of samples, and additional calibration blank and verification samples. Measurement uncertainty estimates included standard deviation of triplicate analysis of each sample and the standard deviation of 4-5 method blanks for each batch. We used total concentrations of Ca and Mg to calculate an estimate of total hardness for each sample.

Additional Quality Assurance and Quality Control (QAQC)

In addition to field and laboratory blanks and replicates, we verified that field and sample laboratory measurements for pH and specific conductance differed by less than 10% for those sampling events with both field and laboratory measurements. We also verified that a minimum estimate of TDS, as the sum of element concentrations from ICP-MS (which did not include all constituents) and anion concentrations minus TSS, was less than the TDS measured in the laboratory.

Spatial, statistical, and related analyses

We sought to establish the extent of contamination and the contaminants associated with the mining through (1) analysis of downstream trends, (2) comparisons with reference sites, and (3) assessment of temporal trends.

(1) For analysis of downstream trends, we assessed the relation of water quality characteristics with river distance upstream of the confluence of the Little Fork River and the Willow River. We digitized study site distance upstream of major confluences using heads-up digitizing and a DigitalGlobe 2011 image (~0.3 m resolution) at a spatial resolution of 1:5000 or finer. We conducted a non-parametric local regression (LOESS) analysis for characteristics with adequate sample size (specific conductance, fluoride, chloride, sulfate, and the ratios of chloride and sulfate to specific conductance) to identify trends in the relationship with river distance. As part of the downstream trend assessment, we also graphically assessed patterns of Rare Earth Element (REE) to identify similarities in patterns of concentrations that might be indicative of similar sources.

(2) To compare sites downstream of the mines with reference sites, we assessed the range of values at different sites and conducted analyses to statistically compare sites. We used a cluster analysis, using Ward's hierarchical accumulative method with squared Euclidian distances and z-score standardization, in order to identify sites that are more closely related based on specific conductance, anion concentrations, and ratios of anion concentrations to specific conductance. We log-transformed data for the cluster analyses. Finally, we tested for differences between downstream and reference sites using a non-parametric Kruskal Wallis test on un-transformed data.

(3) We also sought to determine any changes in characteristics over time that might indicate a change related to mining activity. We used data from the Water Quality Portal (2017), which combines data from STORET (EPA) and NWIS (USGS), state databases (MiSWIMS), and also data from regulatory documents and agency or other reports.

We conducted all statistical analyses using SAS software (SAS Institute 2010). In reporting and analyzing anion concentrations from ion chromatography, we used ½ of the Minimum Reporting Limit (MRL) for major ion results that were below calibration MRLs.

Study zones

The Iron River, in Michigan just north of the Wisconsin border, flows through urban zones and zones with a large number of old iron mines (Fig. 1). The landscape surrounding the river included forest, agriculture, and urban land cover (Figs. 1-5). We sampled upstream and downstream of the mine zones and at the confluence of the Iron River with the Brule River (Figs. 1-5). We also sampled semi-synoptically along the length of the potentially mine-influenced reaches and in August 2016 focused sampling on zones that preliminary sampling had indicated were sources of measurable discharges into the river. Those included the pipes discharging into the river between 7th Avenue and 4th Avenue in the town of Iron River (Figs. 2, 6); the Dober mine zone in the town of Caspian (Fig. 3, 7), the Caspian Pit discharge (Figs. 4, 8), and the Buck mine zone to the south-east of the town of Caspian (Figs. 4, 9). We also measured field characteristics and sampled at upstream and tributary reference sites (Fig. 1).

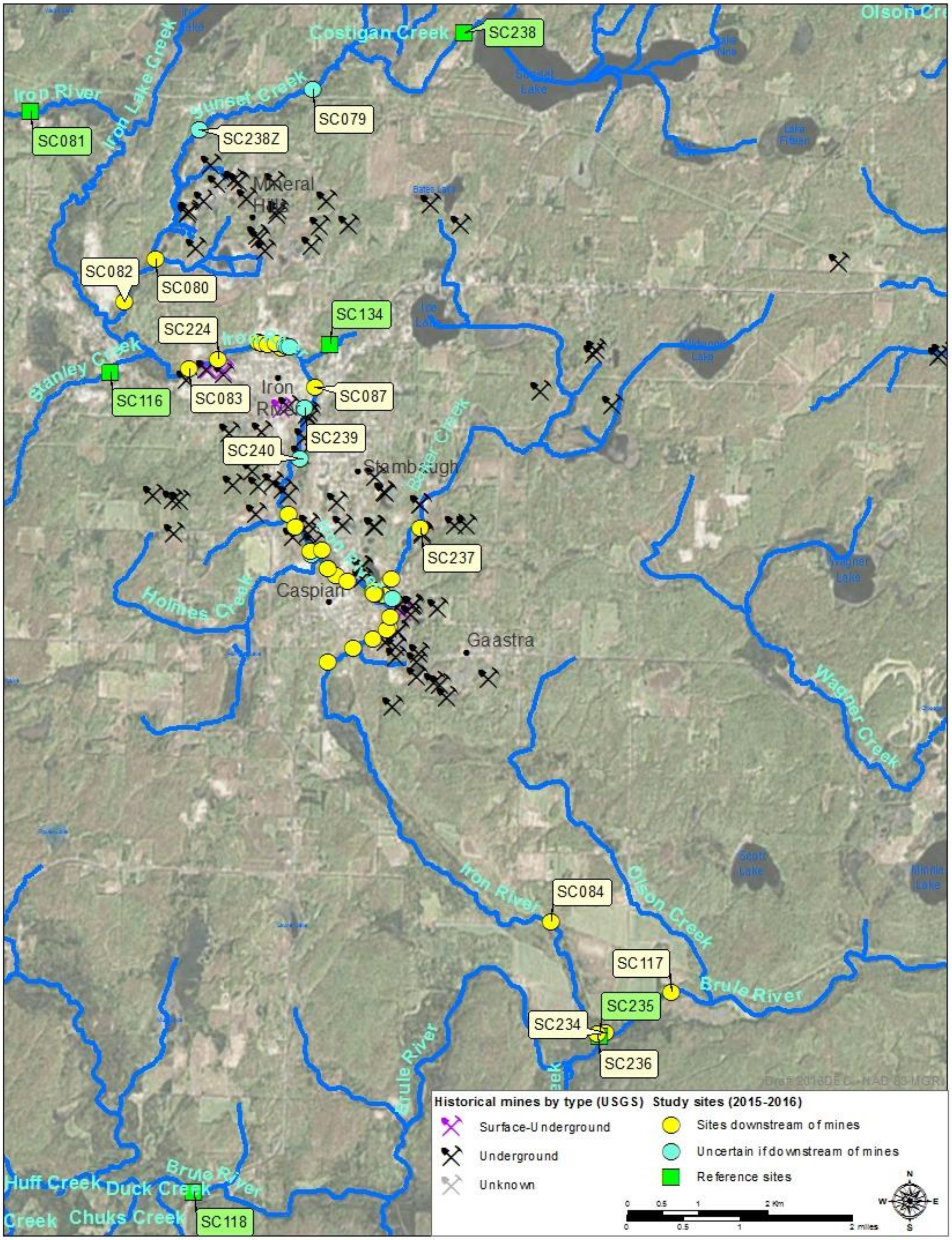

Fig. 1. Overview map of sampling sites in the Iron River watershed. The Iron River flows to the southeast. Sampling sites without labels have labels in Figs. 2-5.

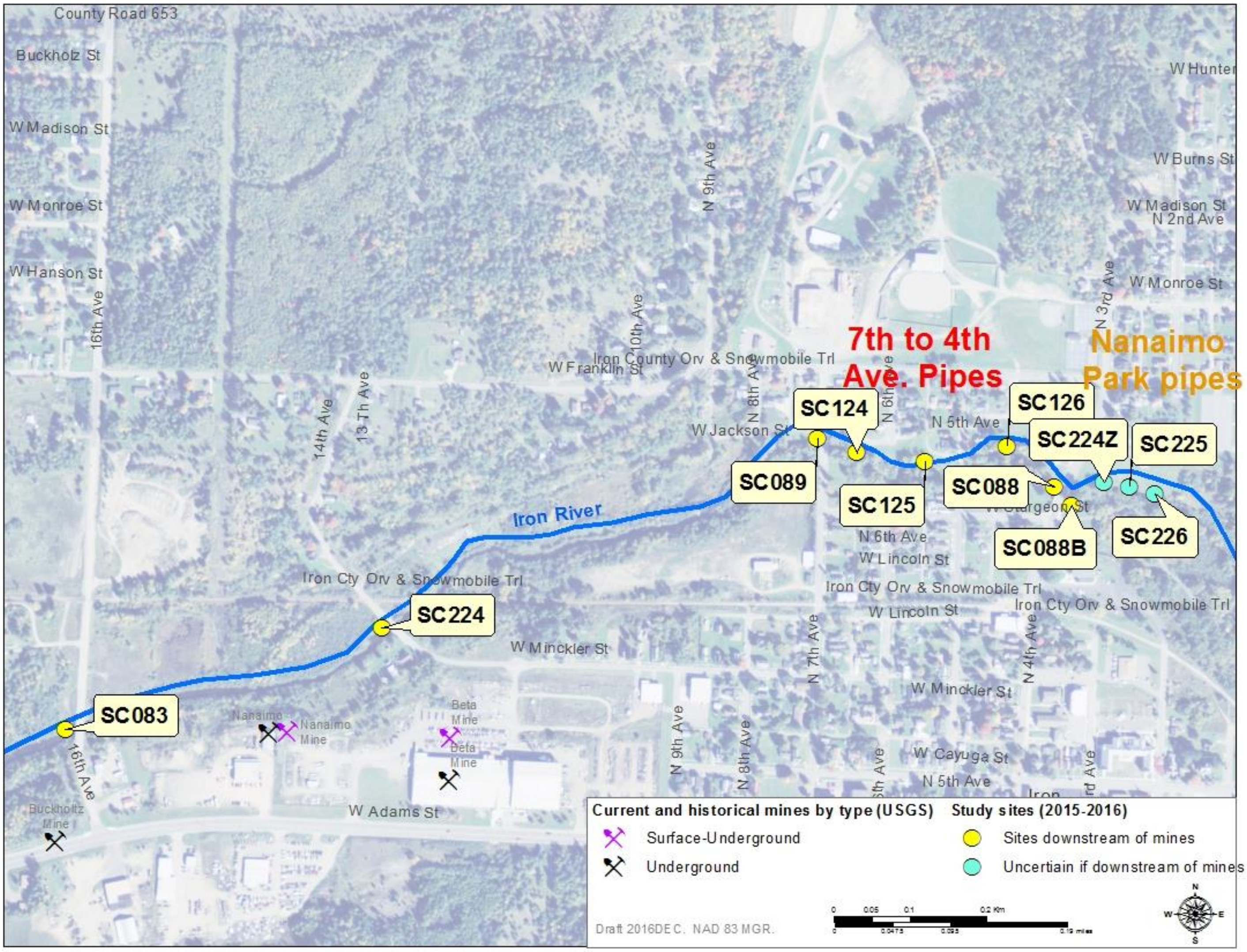

Fig. 2. Map of sampling locations at the mine drainage pipes between 7th Avenue and 4th Avenue in the town of Iron River (SC124-SC126) and upstream (SC089) and downstream (SC088/SC088B) in the Iron River.

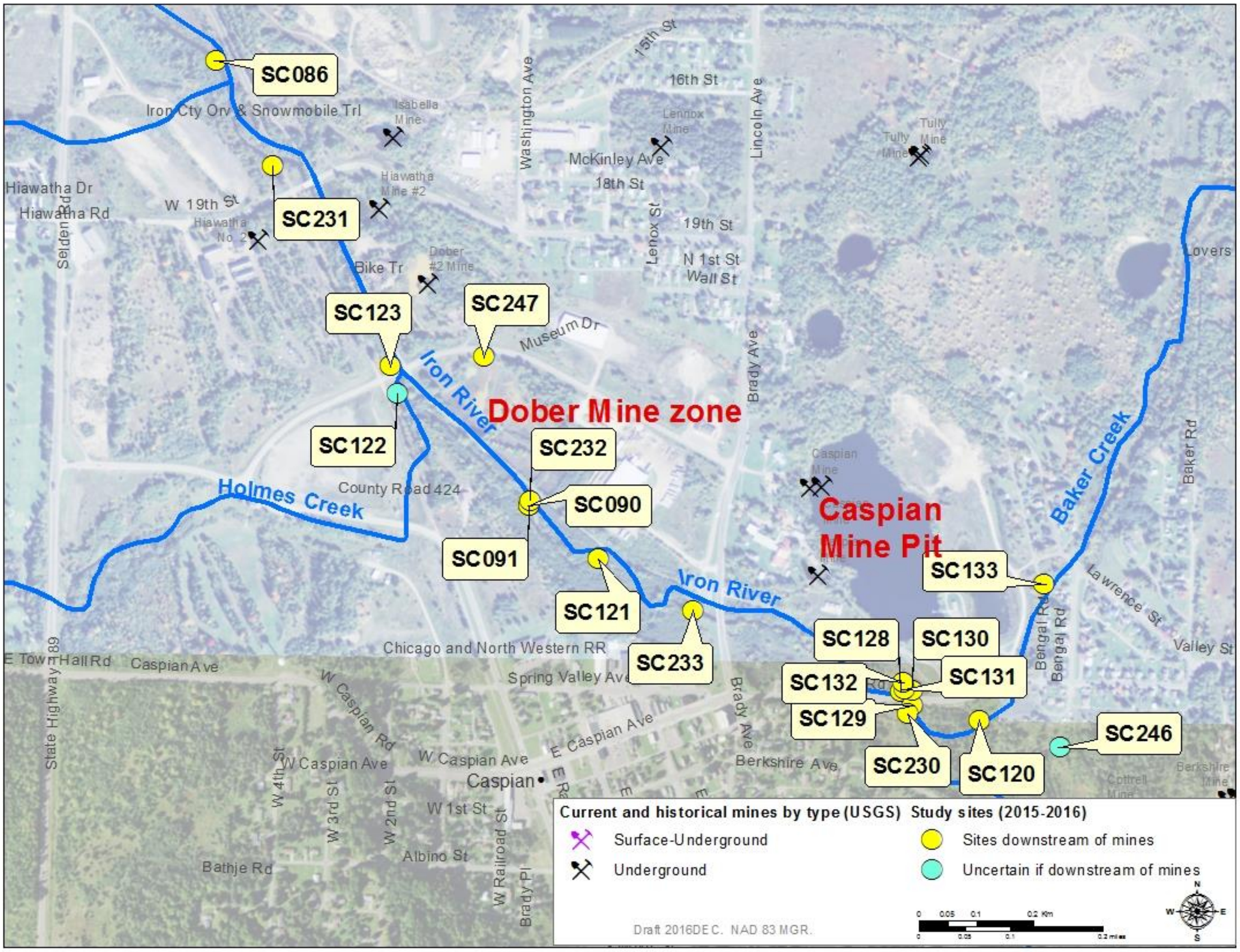

Fig. 3. Map of sampling sites near the Dober Mine and Caspian Mine cave-in pit zones.

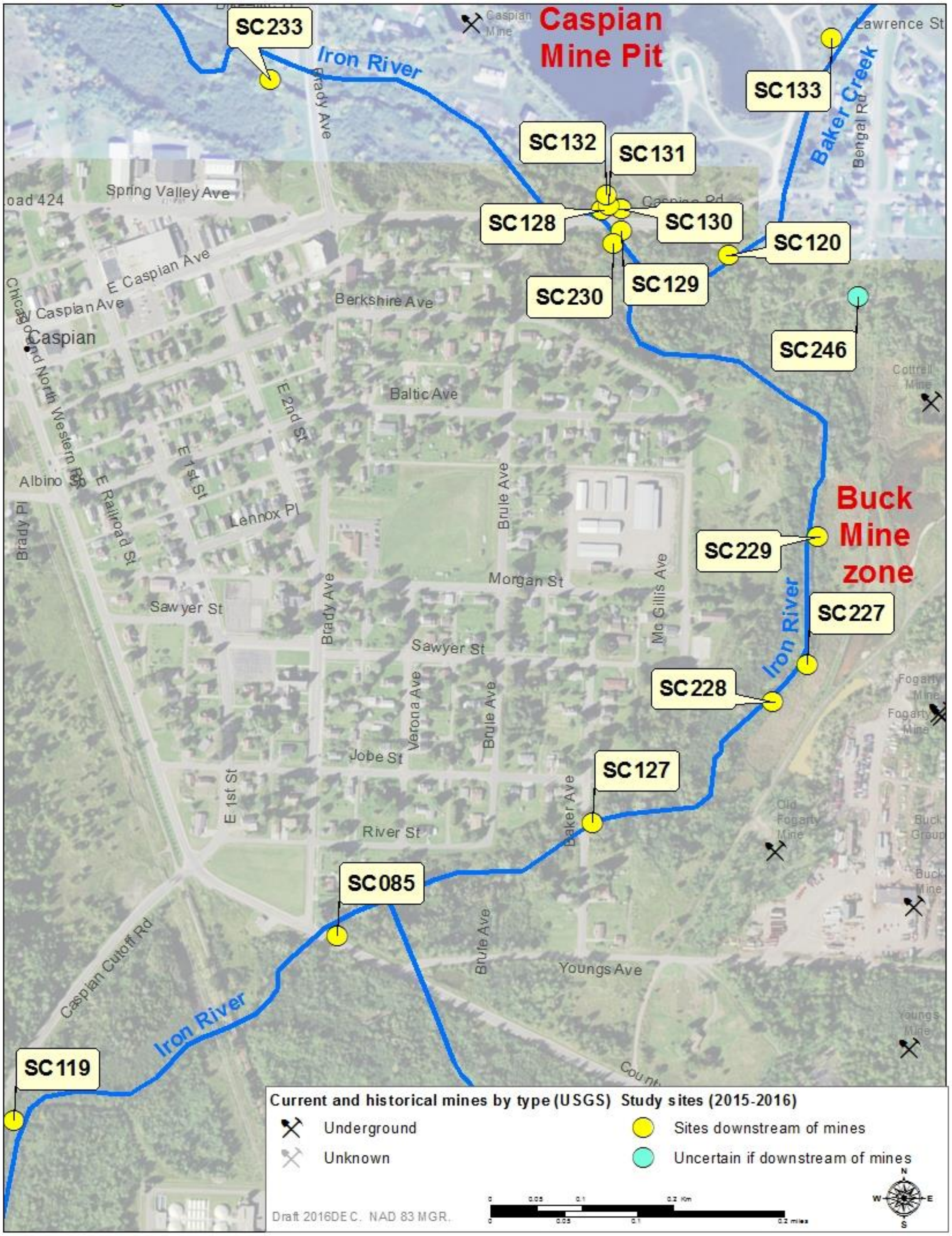

Fig. 4. Map of sampling sites near the Buck Mine and Caspian Mine cave-in pit zones.

Fig. 5. Map of sampling locations at the confluence of the Iron River with the Brule River. The rivers flow to the east.

	
Fig. 6. Discharge pipe flowing into Iron River at site SC126 (photo from 18 June 2016).	Fig. 7. Discharge channel from the Dober Mine ponds to the Iron River at SC232 (photo from 18 August 2016).

	
Fig. 8. Discharge from Caspian Mine Pit into Iron River at SC132 from below wooden beam opening (photo from 17 August 2016).	Fig. 9. Discharges from Buck Mine zone wetlands into Iron River at SC 227 (photo from 17 August 2016). Photo credit: Emma Cassidy

3. RESULTS

A) Outfalls, downstream trends, and exceedances

Outfall discharge overview

We measured water quality characteristics in four principle outfall zones: the 7^{th}-4^{th} Ave pipes, the Dober Mine, the Caspian Pit, and the Buck Mine (Figs. 1-4).

On the north side of the town of Iron River, a series of six pipes discharged water to the Iron River. This included three pipes with limited flow in Nanaimo Park and moderately high specific conductance and chloride (SC224Z, SC225, SC226), and three pipes with greater flow between 7^{th} Ave and 4th Ave (SC124-126; Fig. 2). The 7^{th}-4^{th} Ave. pipes (SC124-126) demonstrated the following characteristics: low DO and pH in the western two pipes; high specific conductance, TDS, total alkalinity, total hardness, chloride, sulfate, Mg, Ca, Mn, and **U**[2]; and moderately high **nitrate** (holding time exceeded), Li, B, Na, K, Cr, Ni, Se, Sr, **Cd**, Ba, and Tl (Tables 3, 6; Figs. 10, 12-15, 18, 20-23, 25, 28, 30-33; Appendix C). Of those measurements, the **TDS, DO,** and **pH** measurements in the western two pipes appeared to not meet state groundwater-surface water interface (GSI) criteria (Tables 3, 6). The **manganese** and **sulfate** concentrations exceeded the state of MI residential and EPA human health/drinking water criteria and, in the western-most pipe, the state Mn drinking water criterion and the USGS Mn non-cancer health-based screening level of 300 µg/l (Toccalino *et al*. 2014; Tables 3, 6). The **selenium** concentration in the discharge also exceeded the EPA lake criterion of 1.5 µg/l, was within 25% of the value of the EPA stream aquatic life chronic criterion of 3.1 µg/l, and exceeded the Canadian criterion (Table 6). Measurements upstream (SC089) and downstream (SC088) of the set of three principle pipes indicated an increase in the Iron River between those two points for specific conductance, alkalinity, TDS, total hardness, sulfate (19 and 43 mg/l), nitrate (holding time exceeded), B, Na, Mg, K, Ca, Sc, Mn (83 and 157 µg/l), Fe, Sr, Cd, U, and other elements (Figs. 10, 15, 18, 20-23, 25, 26, 31, 33, Appendix C). The westernmost pipe (SC124) represented the single greatest measured sulfate and manganese load into the Iron River (Figs. 34, 35).

The Dober mine zone main discharge stream to the Iron River via wetlands (SC232) in August 2016 was high in temperature, specific conductance, turbidity, TDS, total hardness, **sulfate**, Ca, Mn, Fe, and **Ni**; low in DO; and moderately high in concentrations of chloride, Li, B, Mg, Al, **Co**, Zn, Sr, and **Tl** (Tables 3, 6; Figs. 10-11, 13-15, 20, 22-29, 32; Appendix C). Of these, **TDS** exceeded surface water criteria (Table 6) and potentially **turbidity** did as well (turbidity criterion is to not "become injurious to any designated use"). **DO** was also below the cold season state surface water limit of 7 mg/l (Table 3). In addition, the **iron** concentration exceeded the EPA surface water criterion of 1000 µg/l, and the **manganese** concentration exceeded the MI residential and EPA human health criteria and the USGS non-cancer health-based screening level (Toccalino *et al*. 2014; Table 6). Although we only detected a change in river temperature from 19.4°C to 19.5°C at the Iron River locations measured upstream (SC123) and ca. 180 m downstream (SC121)of the discharge, **temperature** of the discharge (23.0 C) in 2016 was 3.6°C, or 6.5°F greater than the temperature of the river (Table 3, 5). This temperature difference appeared to exceed the 2°F mixing zone edge heat load limit to coldwater streams and rivers like the Iron River. The Iron River also increased in specific conductance, turbidity, hardness,

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[2] Throughout the text of this document, bold highlights indicate water quality characteristics that exceed criteria or recommendations or that are at concentrations greater than reference concentrations and of potential concern.

sulfate, B, Na, Mg, Ca, Mn, Fe, Co, Ni, Sr, Tl, and other elements based on measurements upstream (SC123) and downstream (SC121) of the discharge (Figs. 10, 15, 22, 23, 25-27, 28, 32, Appendix C). Discharge sulfate load was greatest in the 7^{th}-4^{th} Ave pipes and the Dober Mine discharge (Fig. 34). The Dober discharge also represented the second greatest manganese loading into the Iron River (Fig. 35).

The Caspian mine pit discharge to the Iron River (SC132), just north of the Caspian Road bridge, was moderately high in specific conductance, temperature, **pH**, alkalinity, total hardness, chloride, **sulfate**, B, Mg, Ca, Mn, Se, Sr, and **U** (Tables 3, 6; Figs. 10-12, 21, 25, 30, 33; Appendix C). The **temperature** exceeded coldwater surface water criteria, and the **selenium** concentration nearly exceeded the EPA lake surface water criterion and exceeded the Canadian criterion (Tables 3, 6). Comparison of sites upstream (SC121) and downstream (SC230) of the Caspian pit outfall indicated an increase in B, Na, Mg, Ca, Se, and Sr (Figs. 23, 30, Appendix C).

Baker Creek, which flows from old mine zones and near the Caspian mine pit, joins the Iron River just downstream of the Caspian Road bridge. At SC120 on Baker Creek, we recorded moderately high specific conductance, alkalinity, total hardness, **sulfate**, bromide, Mg, P, Ca, Fe, Ni, Cu, As, Mo, Cd, and **U** (Tables 5-6; Figs. 10, 15, 21-22, 26, 28, 31, 33; Appendix C). That water exceeded health-based and drinking water criteria for **iron** (Table 6).

The Buck mine zone wetlands discharged to the Iron River through at least four small waterfall-like discharges, three of which we sampled (SC227-229). The sampled discharges from the Buck mine treatment wetlands into the Iron River were high in specific conductance, total hardness, and concentrations of TDS, sulfate, Li, B, Mg, Ca, Mn, Fe, **Co**, **Ni**, **Zn**, Sr, and U; moderately low in DO and ORP; and moderately high in TSS, turbidity, alkalinity, fluoride, chloride, Al, K, Rb, Rh, **Cd**, and Tl (Tables 3, 6; Figs. 10, 13-15, 19-29, 31-33; Appendix C). The **TDS** exceeded Michigan surface water criteria (Table 6). The **sulfate** concentrations at all three measured discharges exceeded MI residential-based and EPA health/drinking water criteria (Table 3). Total Suspended Solids (TSS) were at a concentration of 3.2 mg/l in the Buck discharge sample from site SC228, and some contaminants from that site may have been in suspended, not dissolved form. Nonetheless, the discharges exceeded the EPA surface water aquatic life criterion for **iron** (at SC228) and the drinking water Maximum Contaminant Level (MCL) for **uranium** (at SC229; Table 6). In addition, the **thallium** concentration was greater than 10% of the EPA human health criterion (at both measured sites; Appendix C). The **manganese** concentrations exceeded the MI residential health-based and drinking water criteria, EPA health-based criteria, and USGS non-cancer health-based screening level (Toccalino *et al*. 2014; Table 6). **Fluoride** concentrations were also greater than the Canadian long-term criterion (Table 3). Relative to an Iron River site upstream (SC230) of the Buck mine zone outfalls, the Iron River site downstream of that zone (SC127) was higher in specific conductance, total alkalinity, total hardness, turbidity, and concentrations of TDS, TSS (2.4 mg/l to 3.0 mg/l), fluoride, sulfate, Li, B, Mg, Al, K, Ca, Mn, Fe, Co, Ni, Zn, Rb, Sr, Tl, U, and other elements (Figs. 10, 15, 19-23, 25-27, 29, 32-33, Appendix C) . The **manganese** concentration was below the USGS screening level (300 µg/l; Toccalino *et al*. 2014) upstream (236 µg/l), but above that level downstream (328 µg/l; Fig. 25). The northern Buck Mine site (SC229) represented the greatest individual uranium measured loading to the Iron River, followed by the Caspian Pit outfall (SC132; Fig 36). The 7^{th}-4^{th} Ave. pipes, however, jointly represented a greater uranium load than the other measured individual sites (Fig. 36).

Downstream trends - general water quality characteristics

Most of the general water quality characteristics were low upstream and increased downstream, near mine zones, in the Iron River. Specific conductance, TDS, alkalinity, and hardness all increased from upstream to downstream measurements in the Iron River (Tables 4-6). Specific conductance also increased downstream in Sunset Creek (Fig. 10), and all four of those measures increased in the Iron River over the shortest river distances in the reaches receiving the waters from the 7th-4th Ave pipes (SC089-SC088) and the reach receiving the Buck Mine discharges (SC230-SC127; Figs. 10, 20-22). LOESS analysis confirmed those trends for specific conductance (Fig. 10). Specific conductance, TDS, alkalinity, and hardness were highest in the 7th-4th Ave. discharges and the Buck Mine discharges, but specific conductance, TDS, and hardness were also high in the Dober Mine discharge (SC075-SC074; Fig. 17; Table 3). Alkalinity, on the other hand, was lower in the Dober Mine discharge than at all other measured sites, and was relatively high for the Caspian Mine Pit discharge (Fig 21). Temperature demonstrated an increase in two zones in the Iron River in August 2015 and August 2016: upstream of 7th Avenue (SC224-SC089) and the mid-section reach including the Dober Mine zone (SC087 or SC231 to SC233; Fig. 11). The Dober Mine discharge, the Caspian Pit discharge, and Baker Creek were warmer than the Iron River (Fig. 11; Tables 3-5). Measurements for pH in the Iron River in August 2016 also increased in two similar zones: SC083-SC089 and SC231 to SC123 (Fig. 12; Table 3, 5). In August 2015, pH in the Iron River was relatively low in the Dober Mine zone, the discharge from which was also low in pH (Fig. 12; Table 3, 5). Dissolved oxygen in August 2015 and 2016 decreased downstream of SC224 until SC123 or SC121 (Fig. 13). The decrease between SC089 and SC088 corresponded with the inflow of 7th-4th Ave. pipes, which were low in DO (Fig. 13; Table 3, 5).

Although exceedances were more common in the discharges as noted in the section above, some exceedances of state or federal criteria or guidelines for the general water quality characteristics also occurred in the Iron River and stream sites. **Specific conductance** was greater than the EPA Appalachian guideline of 300 µS/cm for all sites in the Iron River downstream of SC089 (near 7th Ave.; Fig. 10). For temperature, the Iron River temperature was greater than the coldwater relevant monthly limit in June 2016 at SC089 (Fig. 11). Measurements of DO were also below the state minimum for warm months in Stanley Creek (SC116; Fig. 13).

Downstream trends -- major anions

Similar to most of the general water quality characteristics, concentrations of most measured major anions increased over the course of the Iron River near the mine zones. Chloride increased over the shortest distance near the 7th-4th Ave pipes (SC089 to SC088), near the unnamed Northeast tributary (SC088 to SC087), near the Caspian Pit and upstream zone (SC121 to SC230), and near the municipal wastewater treatment plant discharge (SC085 to SC119; Table 5, Fig. 14). LOESS analysis indicated that concentrations tended to increase across those zones and level off downstream of SC119 (Fig. 14). The ratio of chloride to specific conductance increased downstream but not as greatly as did the chloride concentration, and it decreased in the zone of the 7th-4th Ave pipes (Fig. 16). The ratio was highest for several sites for which the status as downstream of mining was uncertain: the urban pipe (SC239), the northeast tributary (SC134), and the Nanaimo pipes (SC224Z, SC225, SC226; Fig. 16). Sulfate also increased downstream of the reference site of SC081, with the greatest increases over the shortest distances between SC083 and SC224, SC224 and SC089, SC089 and SC088 (the reach receiving the 7th-4th Ave discharges), SC123 and SC121 (the reach receiving the Dober Mine discharge), and SC230 to SC127 (the reach receiving the Buck Mine discharges; Fig. 15). All sites downstream of SC224 exceeded the Minnesota wild rice waters sulfate limit of 10 mg/l (Fig. 15). The ratio of sulfate to specific conductance demonstrated a similar pattern as the sulfate concentration (Fig. 17). The calculated sulfate load increased downstream of the Iron River reference site (SC081) but measurements of flow and load decreased between SC123 and SC121 (Fig. 34). Fluoride and nitrate did not demonstrate distinct downstream trends, but both were greater downstream (SC119) than upstream (SC085) of the reach receiving waters from the municipal wastewater treatment plant (Figs. 18, 19), though nitrate samples exceeded holding times. The northeast tributary and Baker Creek in June had **fluoride** concentrations greater than the Canadian guideline (Table 5, Fig 19).

Downstream trends -- trace elements

The measurements for several metals and other trace elements increased in successive downstream reaches receiving additional mine discharges. These metals and trace elements included boron, manganese, and strontium, which increased in association with all three main discharge zones (Figs. 23, 25, Appendix C). Cobalt, nickel, and thallium also increased in association with the Dober and Buck Mine discharges, but not necessarily, when considering laboratory measurement standard deviations, with the 7^{th}-4^{th} Ave discharges (Figs. 27, 28, 32; Appendix C). Iron, and uranium also increased downstream but only in the 7^{th}-4^{th} Ave discharge reach and the Buck Mine discharge reach (Figs. 26, 33; Appendix C). Iron and uranium did not not necessarily increase downstream, when considering measurement standard deviations, in the Dober Mine discharge reach (Figs. 26, 33; Appendix C). A zinc increase was only associated with high zinc in the Buck Mine outfall (Fig. 29), a selenium increase only with the Caspian Pit outfall (Fig. 30), and a cadmium increase only with the 7^{th}-4^{th} Ave pipes (Fig. 31).

Several of the trace element measurements exceeded criteria or guidelines in the Iron River. **Manganese** concentrations were greater than the Michigan residential health-based level and the EPA drinking water level at the Iron River sampling sites (Table 6, Fig. 25). **Iron** concentrations exceeded Michigan and EPA drinking water, and Canadian criteria at all Iron River sites downstream of SC089 and in Baker Creek (Table 6, Fig. 26).

Certain metals increased downstream for most of the studied section of the Iron River without any clear relation to mining inputs. This was the case for aluminum (Fig. 24), and copper, though part of the copper increase was in the reach receiving higher copper from Baker Creek (Appendix C).

Table 3. Discharge (D) site measurements of anion concentrations and other general regulated water quality characteristics relative to state and other criteria. Measurements in **bold and underlined** exceeded apparently applicable Michigan criteria, and measurements that are only **bold** exceeded other listed criteria or guidelines.

		Temperature (°C)	Specific conductance (uS/cm)	Dissolved Oxygen (mg/l)	pH	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
MI surface water, not cold		Diff. of 5°F (2.8°C); < 80°F (< 26.7°C)		5 (or 4 in warm season)	6.5-9.0	2.4-3.8		
MI surface water, coldwater		Diff. of 2°F (1.1°C); < 68°F (< 20°C)		7 (or 6 in warm season)	6.5-9.0	2.4-3.8		
MI GSI				7 (to coldwater)	6.5-9.0		125 if public water supply	
MI residential health-based					6.5-8.5	2.0	250	250
MI human drinking water							50	
EPA aquatic life CCC					6.5-9.0		230	
EPA drinking water (1° & 2°)					6.5-8.5	2 or 4	250	250
EPA Appalachia sp. cond			300					
Canada aquatic life, longterm				6.5-9.5 (cold)	6.5-9.0	0.12	120	
Date	SiteCode							
2015-Aug-26	SC091 (D)	**17.7**	**715**	8.8	6.9	**0.128**	22	**250.3**
2016-Jun-18	SC124 (D)	10.3	**2586**	**1.8**	**6.3**	0.091	39	**1342.7**
2016-Jun-18	SC125 (D)	9.1	**1280**	**4.8**	**6.4**	0.102	30	**431.3**
2016-Jun-18	SC126 (D)	8.0	**624**	**6.8**	7.0	0.075	11	109.9
2016-Aug-16	SC124 (D)	10.8	**2642**	**0.8**	6.6	0.077	42	**1301.0**
2016-Aug-16	SC125 (D)	9.7	**1332**	**4.3**	6.9	0.038	37	**438.1**
2016-Aug-16	SC126 (D)	9.0	**636**	9.0	7.3	0.053	12	109.7
2016-Aug-17	SC229 (D)	21.0	**1655**	6.6	7.3	**0.289**	27	**754.4**
2016-Aug-17	SC227 (D)	17.9	**1744**	6.7	6.7	**0.296**	27	**840.7**
2016-Aug-17	SC228 (D)	18.9	**1759**	7.0	7.2	**0.296**	27	**859.0**
2016-Jun-19	SC132 (D)	**22.1**	**540**	9.2	8.0	0.118	26	44.3
2016-Jun-19	SC131 (D)	**22.0**	**540**	9.5	8.0		30	
2016-Aug-17	SC132 (D)	**23.6**	**543**	9.2	8.3	0.079	26	43.1
2016-Jun-18	SC091 (D)	**24.3**	**735**	7.8	**6.3**		22	
2016-Aug-22	SC247 (D)	17.1	**683**	**4.1**	**5.8**	**0.175**	28	223.8
2016-Aug-18	SC232 (D)	**23.0**	**696**	6.8	6.7	0.080	25	229.4
2016-Aug-16	SC224Z (D)	13.0	**450**				34	
2016-Aug-16	SC225 (D)	12.9	**483**				41	
2016-Aug-16	SC226 (D)	13.3	**608**				**63**	
2016-Aug-20	SC239 (D)	10.4	**916**				**165**	

Table 4. 2015 measurements of anion concentrations and other general regulated water quality characteristics relative to state and other criteria at stream and river sites. Measurements in bold and underlined exceeded apparently applicable Michigan criteria, and measurements that are only bold exceeded other listed criteria or guidelines. (R) are reference sites.

		Temperature (°C)	Specific conductance (uS/cm)	Dissolved Oxygen (mg/l)	pH	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
MI surface water, not cold		Diff. of 5°F (2.8°C); < 80°F (< 26.7°C)		5 (or 4 in warm season)	6.5-9.0	2.4-3.8		
MI surface water, coldwater		Diff. of 2°F (1.1°C); < 68°F (< 20°C)		7 (or 6 in warm season)	6.5-9.0	2.4-3.8		
MI GSI				7 (to coldwater)	6.5-9.0		125 if public water supply	
MI residential health-based					6.5-8.5	2.0	250	250
MI human drinking water							50	
EPA aquatic life CCC					6.5-9.0		230	
EPA drinking water (1° & 2°)					6.5-8.5	2 or 4	250	250
EPA Appalachia sp. cond			300					
Canada aquatic life, longterm				6.5-9.5 (cold)	6.5-9.0	0.12	120	
Date	SiteCode							
2015-Aug-26	SC081 (R)	14.1	256	12.6	8.5		4	
2015-Aug-26	SC083	14.4	281	11.0	8.3		7	
2015-Aug-26	SC089	15.6	**332**	10.5	8.1	0.062	8	25.1
2015-Aug-26	SC088	14.9	**421**				7	
2015-Aug-26	SC087	14.6	**422**				8	
2015-Aug-26	SC086	14.3	**425**	10.3	7.8		10	
2015-Aug-26	SC090	16.2	**567**	9.4	7.4	**0.137**	18	187.7
2015-Aug-26	SC085	14.3	**490**	10.3	7.8		11	
2015-Aug-26	SC084	14.7	**484**	10.8	8.1	**0.151**	16	82.0
2015-Aug-26	SC080	15.0	272	8.2	7.8		2	
2015-Aug-26	SC082	18.2	266	7.2	7.6		2	
2015-Aug-26	SC079	13.3	271	6.2	7.3		2	

Table 5. 2016 measurements of anion concentrations and other general regulated water quality characteristics relative to state and other criteria at stream and river sites. Measurements in bold and underlined exceeded apparently applicable Michigan criteria, and measurements that are only bold exceeded other listed criteria or guidelines. (R) are reference sites.

		Temperature (°C)	Specific conductance (uS/cm)	Dissolved Oxygen (mg/l)	pH	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)			Temperature (°C)	Specific conductance (uS/cm)	Dissolved Oxygen (mg/l)	pH	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
MI surface water, not cold		Diff. of 5°F (2.8°C); < 80°F (< 26.7°C)		5 (or 4 in warm season)	6.5-9.0	2.4-3.8			MI surface water, not cold		Diff. of 5°F (2.8°C); < 80°F (< 26.7°C)		5 (or 4 in warm season)	6.5-9.0	2.4-3.8		
MI surface water, coldwater		Diff. of 2°F (1.1°C); < 68°F (< 20°C)		7 (or 6 in warm season)	6.5-9.0	2.4-3.8			MI surface water, coldwater		Diff. of 2°F (1.1°C); < 68°F (< 20°C)		7 (or 6 in warm season)	6.5-9.0	2.4-3.8		
MI GSI				7 (to coldwater)	6.5-9.0		125 if public water supply		MI GSI				7 (to coldwater)	6.5-9.0		125 if public water supply	
MI residential health-based					6.5-8.5	2.0	250	250	MI residential health-based					6.5-8.5	2.0	250	250
MI human drinking water							50		MI human drinking water							50	
EPA aquatic life CCC					6.5-9.0		230		EPA aquatic life CCC					6.5-9.0		230	
EPA drinking water (1° & 2°)					6.5-8.5	2 or 4	250	250	EPA drinking water (1° & 2°)					6.5-8.5	2 or 4	250	250
EPA Appalachia sp. cond			300						EPA Appalachia sp. cond			300					
Canada aquatic life, longterm				6.5-9.5 (cold)	6.5-9.0	0.12	120		Canada aquatic life, longterm				6.5-9.5 (cold)	6.5-9.0	0.12	120	
Date	SiteCode								Date	SiteCode							
2016-Jun-19	SC133	22.5	**453**				7		2016-Aug-16	SC087	17.3	**378**	9.2	7.3	0.049	9	42.6
2016-Jun-18	SC120	22.8	**533**	7.1	7.3	**0.143**	5	80.9	2016-Aug-18	SC087	19.0	**380**				10	
2016-Aug-19	SC237	21.1	**501**				8		2016-Aug-19	SC087	17.7	**400**				11	
2016-Aug-17	SC120	20.4	**460**	7.3	8.0	0.089	7	47.5	2016-Aug-18	SC231	19.2	**384**	8.7	7.1	0.050	11	44.2
2016-Jun-18	SC117	**20.9**	238	10.2	7.7	0.073	6	15.7	2016-Aug-18	SC123	19.4	**386**	8.4	7.6	0.053	11	45.3
2016-Aug-19	SC234	18.0	**449**	8.9	7.3	0.086	14	63.6	2016-Aug-18	SC121	19.5	**397**	8.5	7.6	0.053	11	50.8
2016-Jun-18	SC118 (R)	**21.3**	180	9.9	7.6	0.065	5	5.2	2016-Aug-18	SC233	19.6	**398**				15	
2016-Aug-19	SC235 (R)	**20.2**	195	9.3	7.9	0.039	5	5.0	2016-Aug-18	SC128	19.3	**393**				15	
2016-Jun-18	SC122	**22.2**	194				7		2016-Aug-17	SC230	19.0	**408**	9.1	7.7	0.045	11	52.4
2016-Jun-18	SC081 (R)	17.6	232	8.7	7.2	**0.132**	5	5.2	2016-Aug-18	SC230	19.3	**394**				13	
2016-Jun-18	SC089	**21.1**	281				7		2016-Aug-19	SC230	17.9	**416**				16	
2016-Jun-18	SC088B	**20.1**	**360**	8.1	7.4	0.072	8	46.6	2016-Aug-17	SC127	18.0	**448**	9.1	7.6	0.052	12	69.7
2016-Jun-18	SC123	20.0	**373**	9.2	7.1	0.076	10	48.9	2016-Aug-17	SC085	17.7	**448**	8.7	7.5	0.052	12	70.0
2016-Jun-18	SC121	20.0	**385**	9.4	7.1	0.078	10	53.7	2016-Aug-17	SC119	17.6	**459**	9.0	7.4	0.071	15	70.3
2016-Jun-19	SC121	19.3	**388**				11		2016-Aug-19	SC236	17.9	**455**	8.9	7.8	0.071	15	65.4
2016-Jun-19	SC128	19.3	**390**				12		2016-Jun-19	SC130	26.3	**567**				46	
2016-Jun-19	SC129	19.8	**416**				14		2016-Jun-19	SC134 (R)	20.6	**660**				**66**	
2016-Jun-19	SC127	19.1	**434**				12		2016-Aug-22	SC134 (R)	12.2	**616**			**0.149**	**58**	5.5
2016-Jun-18	SC085	19.5	**425**	9.3	7.2	0.086	12	70.2	2016-Aug-20	SC240	16.5	**328**				32	
2016-Jun-18	SC119	19.4	**428**	9.4	7.1	0.087	13	70.2	2016-Jun-18	SC116 (R)	21.9	256	**<u>4.7</u>**	6.7		11	
2016-Aug-16	SC081 (R)	18.3	253	8.9	7.6	0.048	4	3.9	2016-Aug-20	SC238 (R)	16.8	65				2	
2016-Aug-16	SC083	18.0	272	9.8	7.3	0.051	7	5.9	2016-Aug-20	SC079	15.4	209				3	
2016-Aug-16	SC224	18.1	277	9.9	7.7	0.052	7	7.0	2016-Aug-20	SC238Z	17.9	261				4	
2016-Aug-16	SC089	18.6	**310**	9.6	7.8	0.049	7	18.8	2016-Aug-20	SC080	18.6	243				3	
2016-Aug-16	SC088	18.5	**369**	9.5	7.6	0.053	8	43.1	2016-Aug-22	SC246	15.1	**437**			**0.342**	17	46.2

Table 6. Measurements of TDS, manganese, iron, selenium, cadmium, and uranium relative to state and other criteria at sites in the Iron River watershed. Measurements in **bold and underlined** exceeded apparently applicable Michigan criteria, and measurements that are only **bold** exceeded other listed criteria or guidelines. Criteria with a (d) represented dissolved concentrations. Our measurements represented total concentrations. We calculated the criteria that show ranges using our site hardness measurements. (D) are discharge sites and (R) are reference sites.

		TDS (mg/l)	Mn-55 (µg/l)	Fe-56 (µg/l)	Se-82 (µg/l)	Cd-111 (µg/l)	U-238 (µg/l)
MI surface water, not cold		500 (month avg.) or 750	2492-25081		5	2.7-18.9 (d)	
MI surface water, coldwater		500 (month avg.) or 750	2492-25081		5	2.7-18.9 (d)	
MI GSI		500	2492-6643		5	2.7-6.2 (d)	
MI residential health-based			50	300	50	5	
MI human drinking water			1300		120	2.5	
EPA aquatic life CCC				1000	3.1 or 1.5	0.88-6.3 (d)	
EPA drinking water (1° & 2°)		500	50	300	50	5	30
Canada aquatic life, longterm				300	1	0.20-0.37	15
Date	SiteCode						
2016-Aug-16	SC124 (D)	**<u>2340</u>**	**3283**	21.3	**2.4**	0.089	6.7
2016-Aug-16	SC125 (D)	**<u>1000</u>**	**279**	14.9	0.97	0.019	4.4
2016-Aug-16	SC126 (D)	390	16	0.7	0.86	0.009	3.1
2016-Aug-17	SC229 (D)	**1350**	**833**	**964**	0.76	0.030	**35.6**
2016-Aug-17	SC228 (D)	**1460**	**1835**	**7142**	0.73	0.058	**22.6**
2016-Aug-17	SC132 (D)		**54**	9.7	**1.3**	0.008	2.0
2016-Aug-18	SC232 (D)	**518**	**855**	**1214**	0.36	0.013	0.54
2016-Aug-17	SC120		15	**422**	0.70	0.021	3.1
2016-Aug-16	SC081 (R)		**169**	201	0.28	0.004	0.19
2016-Aug-16	SC089	198	**83**	298	0.32	0.007	0.39
2016-Aug-16	SC088	222	**157**	**323**	0.33	0.010	0.56
2016-Aug-18	SC123		**231**	**393**	0.38	0.013	0.72
2016-Aug-18	SC121		**241**	**419**	0.36	0.013	0.75
2016-Aug-17	SC230	252	**236**	**389**	0.45	0.012	0.79
2016-Aug-17	SC127	268	**328**	**591**	0.41	0.013	1.3

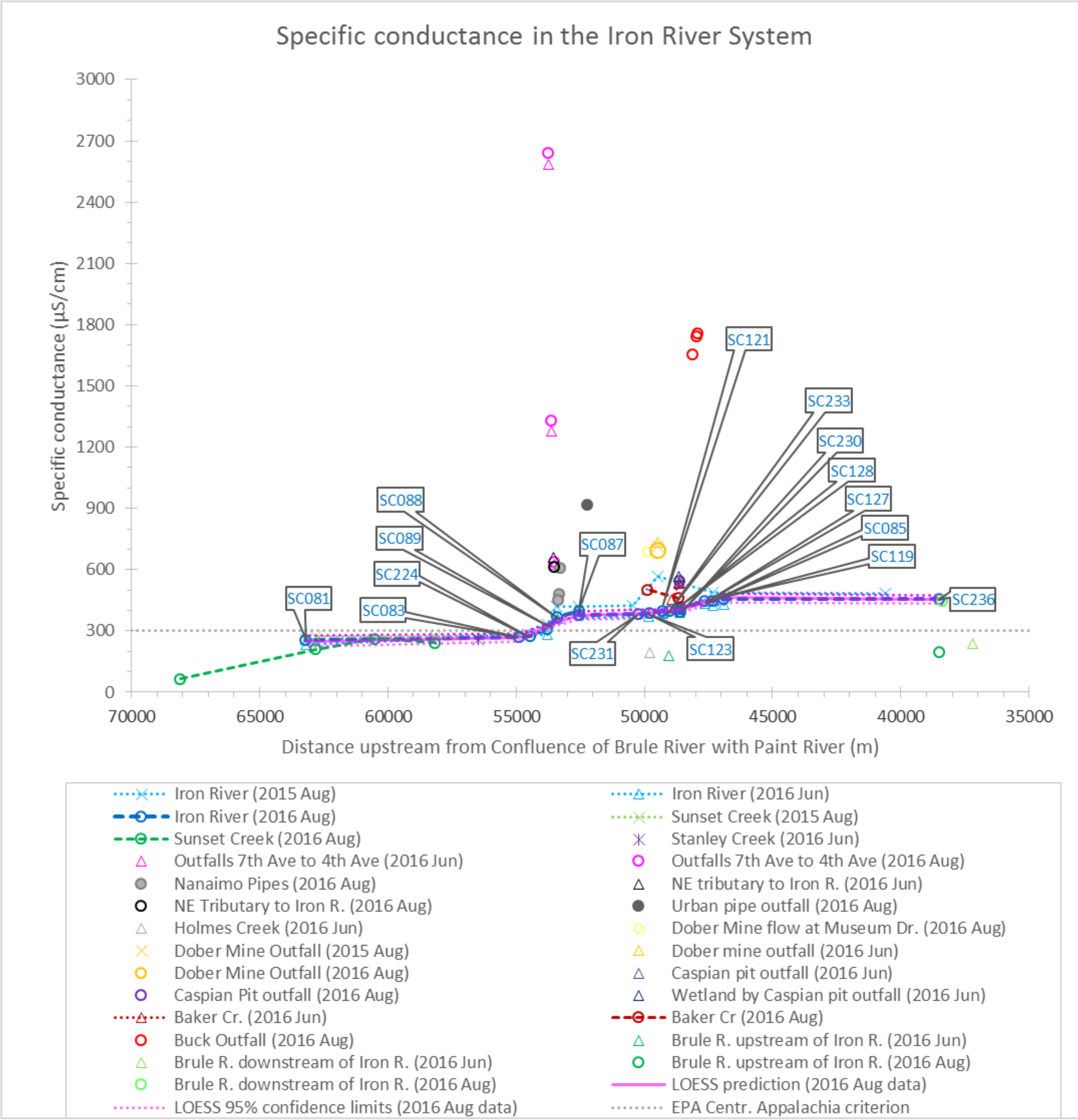


Fig. 10. Specific conductance in the Iron River in August 2016 increased in the reaches receiving waters from the outfalls of the 7th to 4th Avenue mine drainage and the Buck mine outfalls. Specific conductance also increased upstream of 7th Avenue (between SC224 and SC089) and in Sunset Creek. The 7th-4th Avenue pipes and the Buck mine drainage were the outfalls with the highest conductivity. Iron River sites downstream of SC089 all had specific conductance greater than 300 µS/cm. Specific conductance remained higher than at the SC081 upstream reference site at all downstream sites into the Brule River. SC240 (328 µS/cm) and SC246 (437 µS/cm) are not displayed, as their flow connection to the Iron River was uncertain.

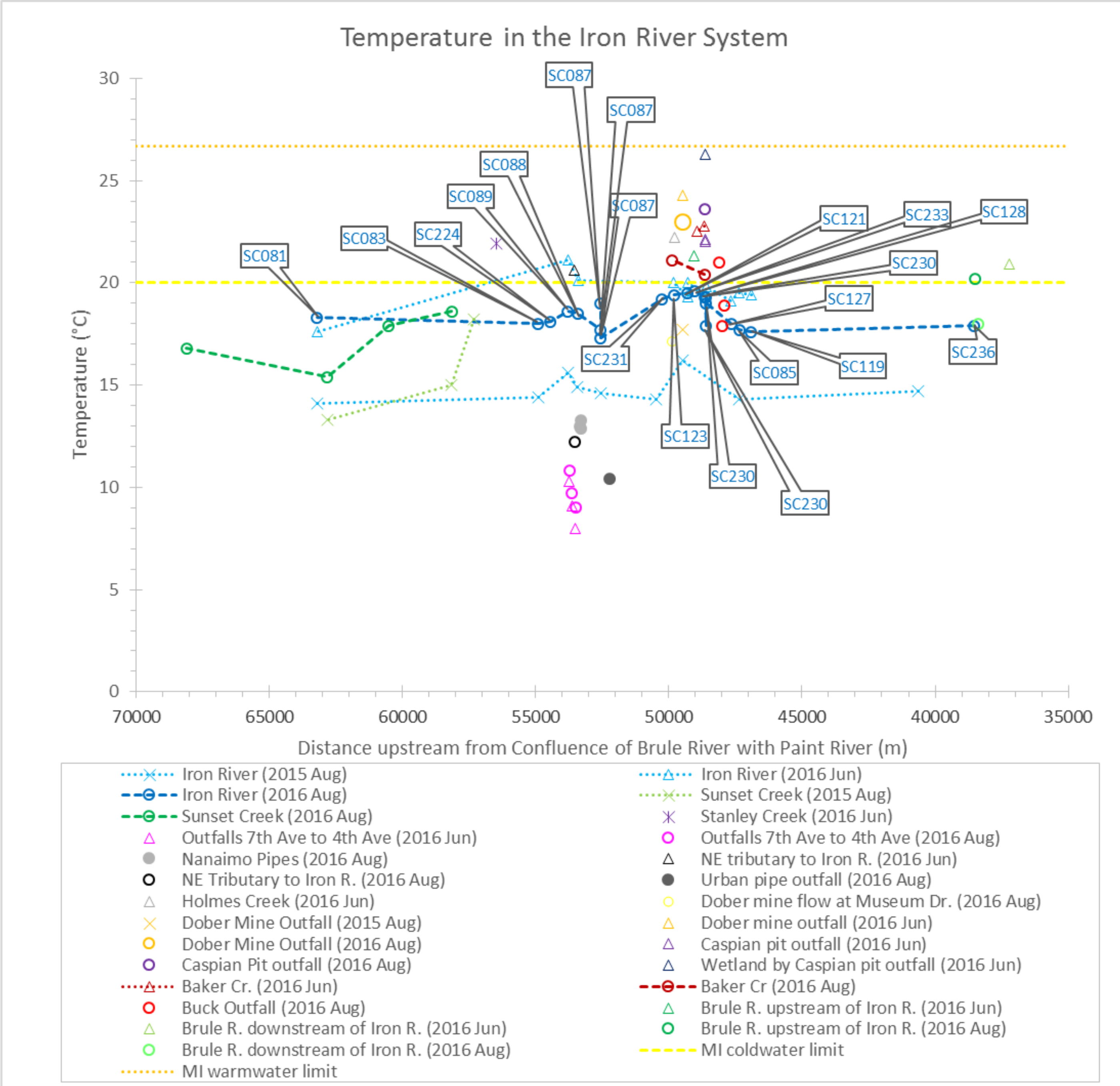


Fig. 11. Temperature in the Iron River in August 2016 increased between SC224 and SC089, SC087 and SC231, and SC231 to SC233. The latter of those reaches received the warmer waters of the Dober Mine wetland outfall. The 2016 August temperatures for the Dober Mine outfall, Caspian Pit outfall, Baker Creek, and one of the Buck Mine outfalls exceeded the Michigan coldwater fisheries limit. Temperature increased further downstream in the Iron River in August 2015 and August 2016 upstream of 7th Avenue (SC224-SC089) and in the mid-section reach including the Dober Mine zone (SC087 or SC231 to SC233). SC240 and SC246 are not displayed, as their flow connections to the Iron River was uncertain.

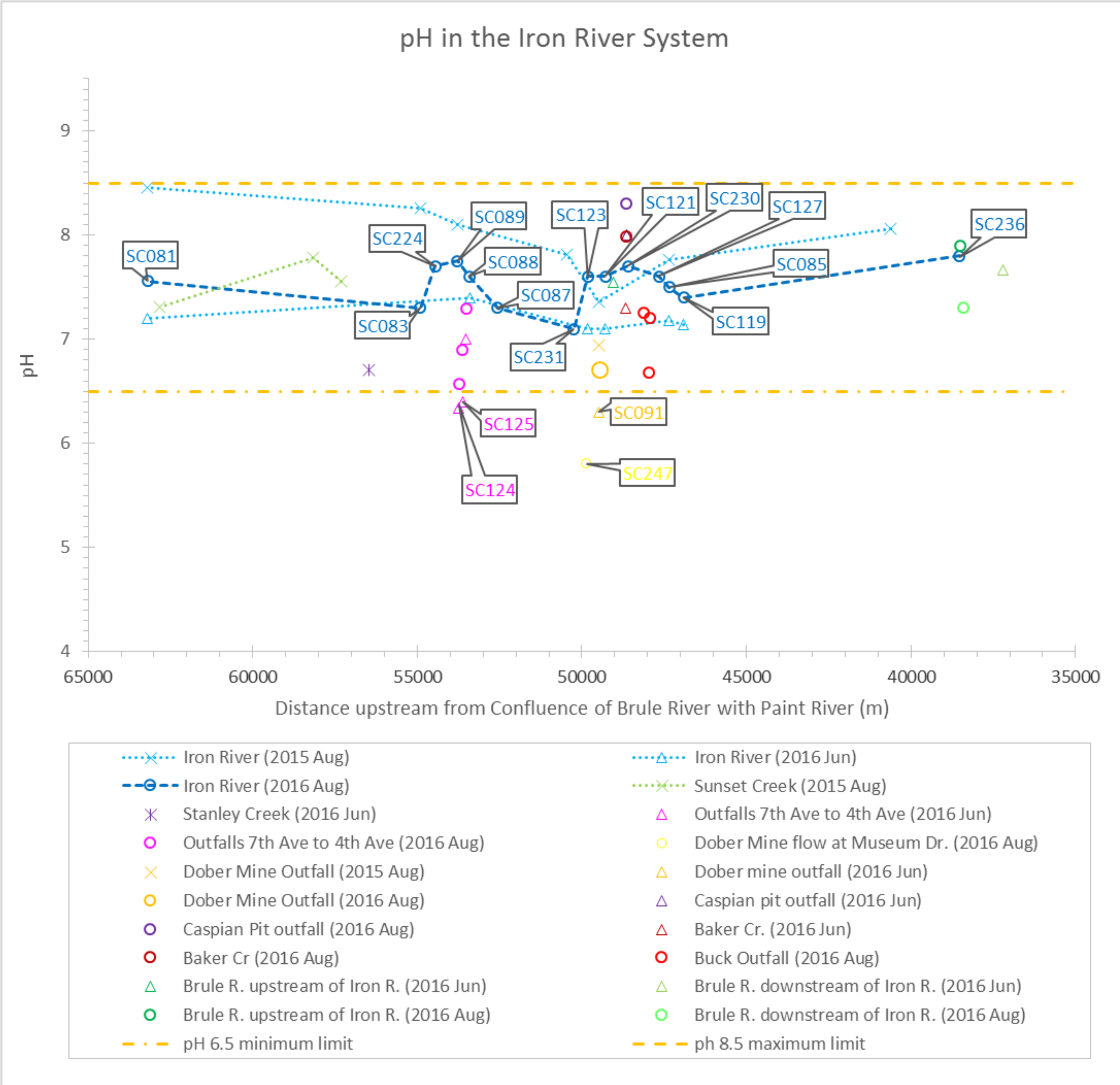


Fig. 12. The pH in the Iron River in August 2016 increased between SC083 and SC224, and SC231 and SC123. The pH decreased between SC089 and SC088 (the reach receiving the waters from the 7th to 4th Avenue outfalls), SC088 to SC231, SC230 to SC127 (the reach receiving the Buck Mine outfalls), and SC127 to SC119. The Dober Mine outfall in June 2016, the Dober mine flow at Museum Dr. in August 2016, and the 7th to 4th Ave outfalls of SC124 and SC125 in June 2016 had pH measurements less than 6.5.

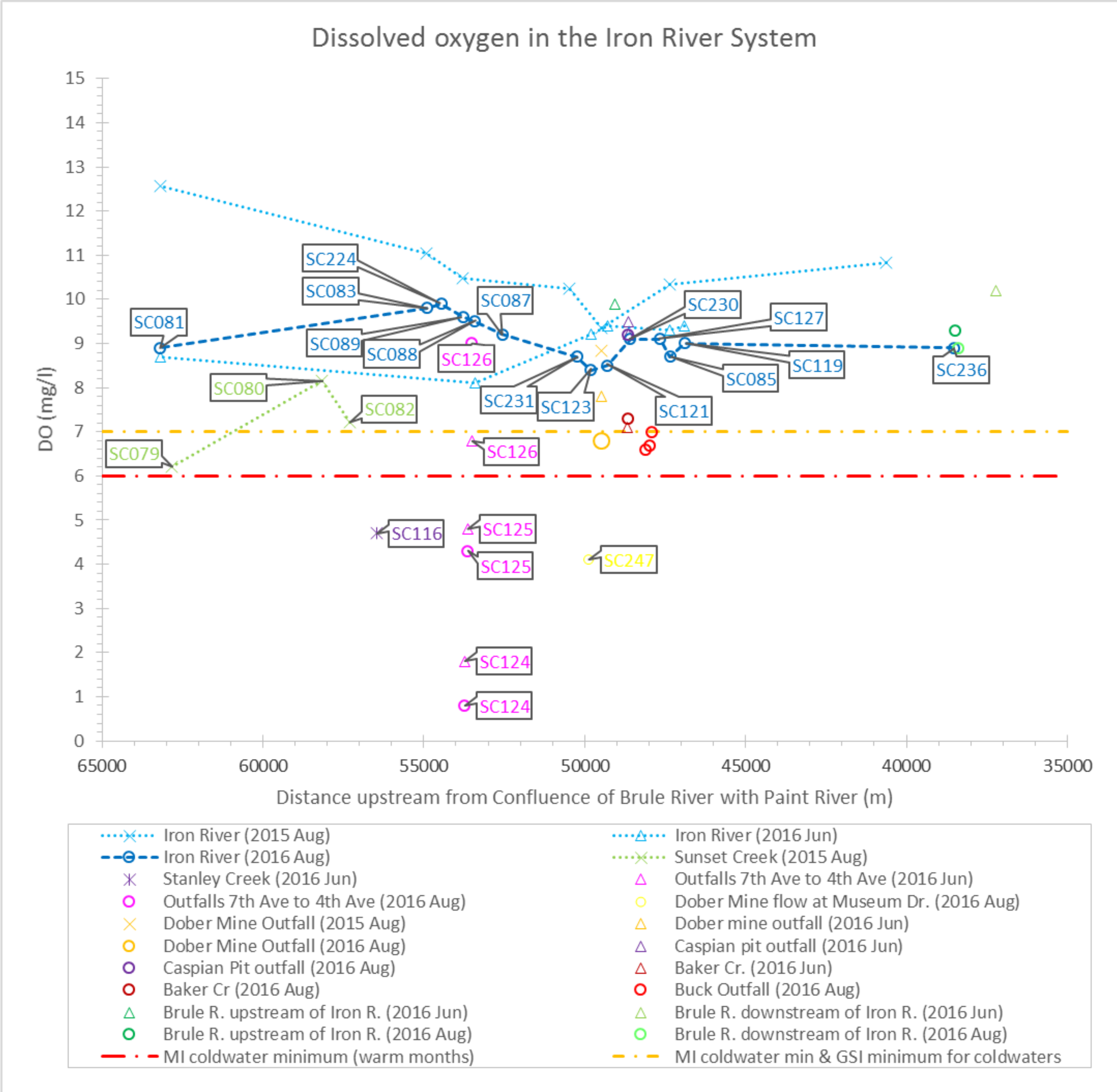


Fig. 13. Dissolved oxygen (DO) in August 2016 decreased in the Iron River between SC224 and SC123 (including the reach receiving the 7th to 4th Ave outfalls), and between SC127 and SC085. Measurements of DO were below the Michigan minimum for warm months in most of the 7th to 4th Ave outfalls, in the Dober Mine flow at Museum Dr., and in Stanley Creek. All but one of the 7th to 4th Ave outfalls also had DO measurements below the Groundwater-Surface water Interface criterion for discharge to coldwater streams.

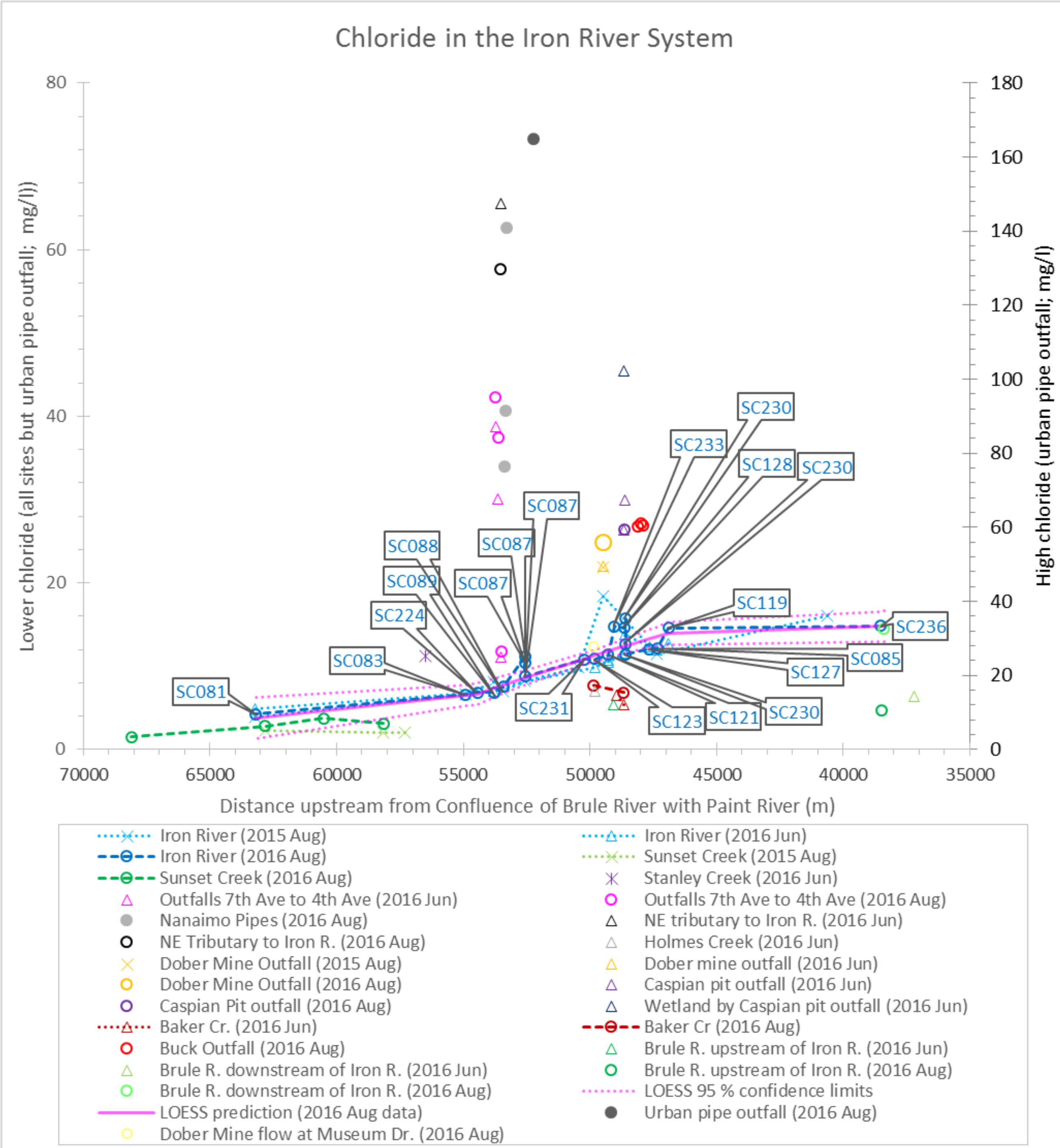


Fig. 14. Chloride in the Iron River in August 2016 increased between SC089 and SC088 (the reach receiving the 7th to 4th Ave outfall waters), SC088 and SC087 (the reach receiving the NE tributary waters), SC087 and SC231 (the reach adjacent to the urban pipe outfall), SC121 and SC230, and SC085 to SC119 (the reach receiving waters from the municipal wastewater treatment plan). Chloride remained higher than at SC081 downstream into the Brule River. The measurement for the urban pipe outfall, the highest chloride concentration we measured, is plotted on the secondary vertical axis. The other highest measurements were in the NE tributary, the Nanaimo pipes, the 7th to 4th Ave pipes, and the Dober, Caspian Pit, and Buck discharges. SC240 (31.5 mg/l) and SC246 (17.0 mg/l) are not displayed, as their flow connections to the Iron River was uncertain.

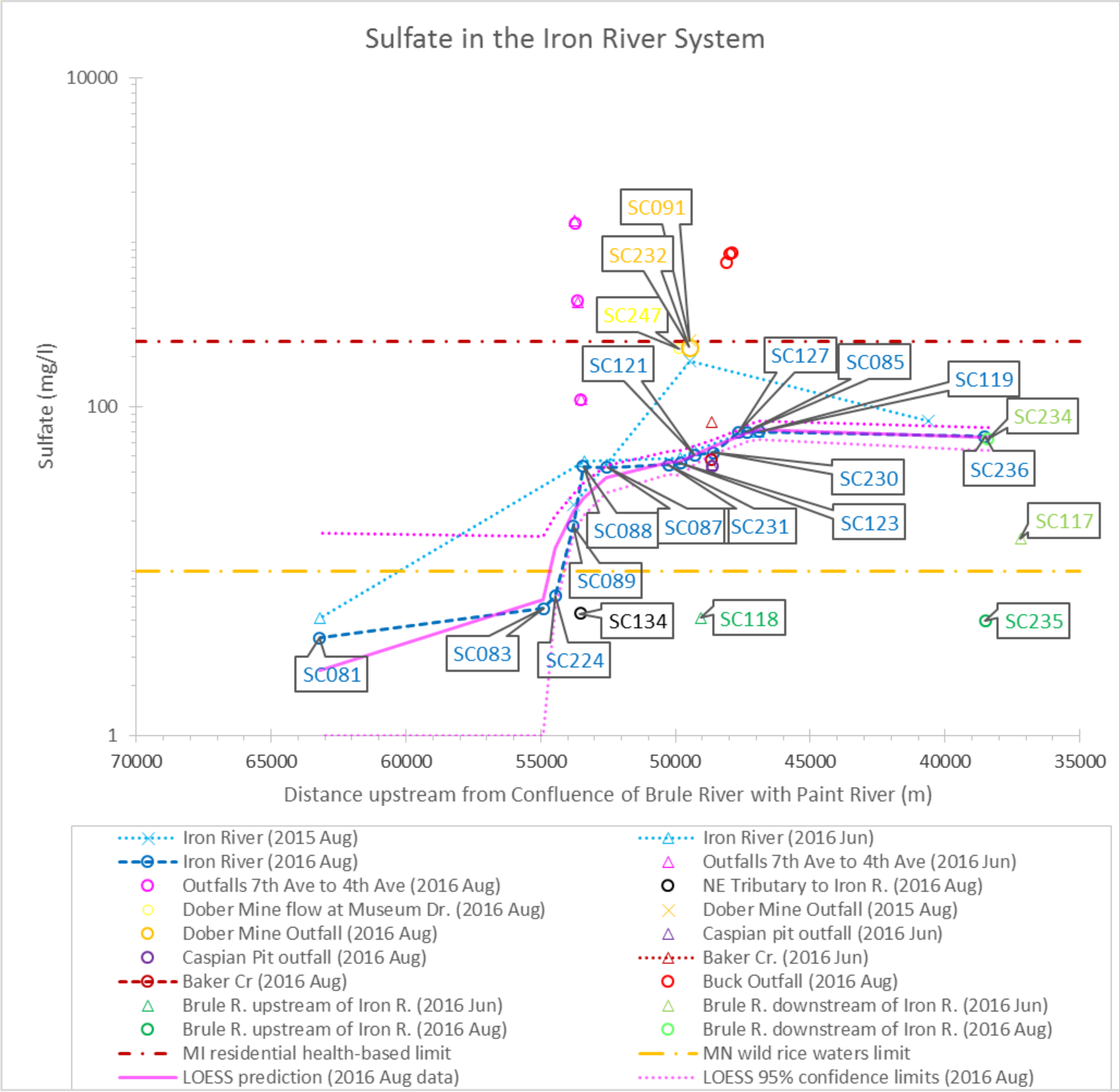


Fig. 15. Increases in sulfate concentration (plotted on $\log_{10}$-scale) in the Iron River in August 2016 occurred in the reach upstream of 7th Ave. (between SC224 and SC089), the reach receiving water from the 7th to 4th Avenue mine drainage outfalls (between SC089 and SC088), the reach receiving the Dober mine outfall water (between SC123 and SC121), and the reach receiving the Buck mine outfalls (between SC230 and SC127). Sulfate concentrations were greatest in the 7th-4th Ave outfalls, the Buck mine outfalls, and the Dober mine outfalls. Concentrations in the 7th-4th Ave outfalls and the Buck mine outfalls were greater than the Michigan residential health-based limit of 250 mg/l, and all sites downstream of SC224 exceeded the Minnesota wild rice waters limit of 10 mg/l. SC246 (46.2 mg/l) is not displayed, as its flow connection to the Iron River was uncertain.

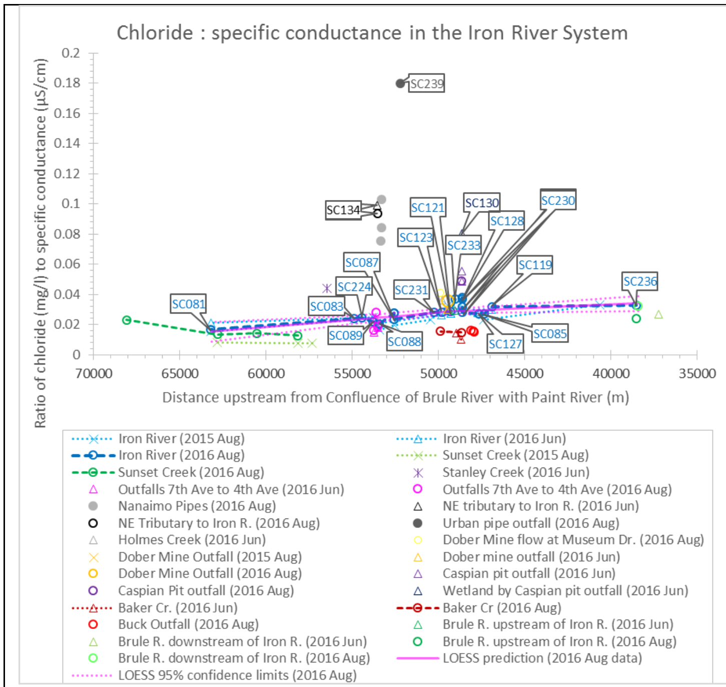
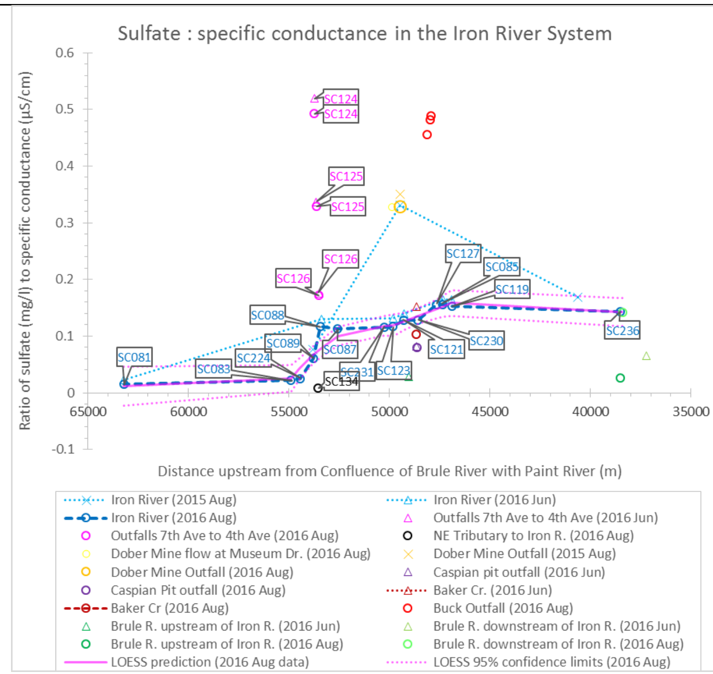
	

Fig. 16. The ratio of chloride to specific conductance was greatest for the urban pipe outfall, the NE tributary, and the Caspian Pit outfall. The ratio was lowest for the Buck Mine discharges, Baker Creek, and the lower reach in Sunset Creek.	Fig. 17. The ratio of sulfate to specific conductance was greatest in the 7th-4th Ave pipes, the Dober Mine outfall, and the Buck Mine outfalls. The ratio was lowest in the NE tributary, in the Iron River upstream of SC224 in August 2016, and in the Brule River upstream of the confluence with the Iron River.

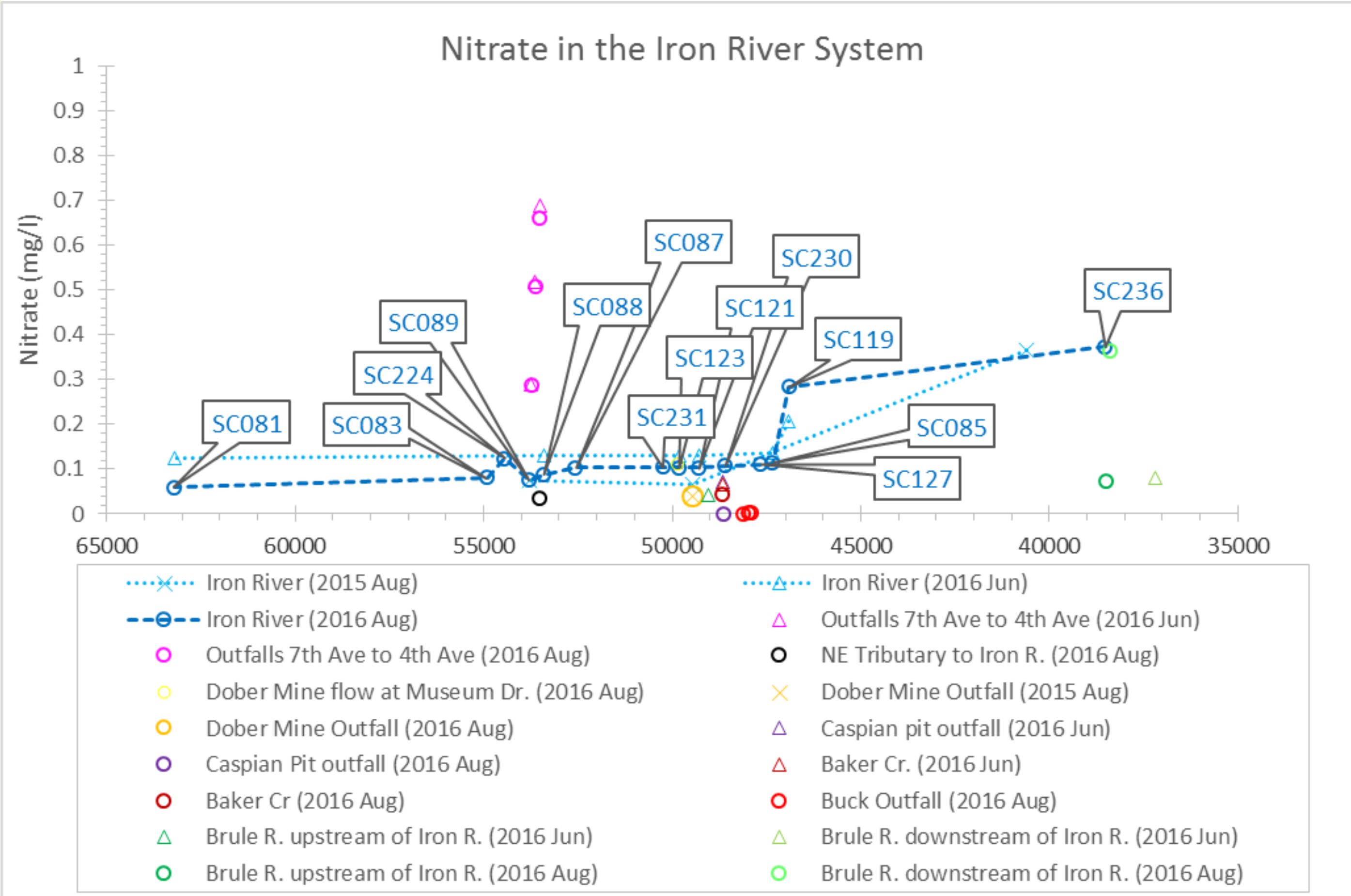


Fig. 18. Nitrate (as N), for which samples exceeded method holding time, in the Iron River in August 2016, increased between SC083 and SC224, between SC089 and SC088/SC087 (the reach receiving the 7th-4th Ave discharges), and between SC085 and SC119 (the reach receiving waters from the municipal wastewater treatment plant). Nitrate measurements were greatest in the 7th-4th Ave pipe outfalls, and lowest in the Caspian Pit and Buck Mine discharges. SC246 nitrate (< 0.002 mg/l) is not displayed, as its flow connection to the Iron River was uncertain.

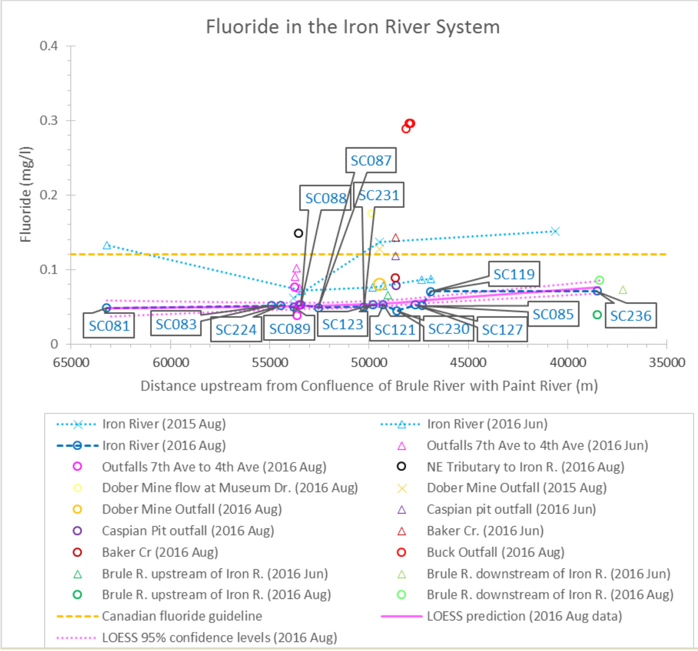


Fig. 19. Fluoride in the Iron River in August 2016 increased between SC230 and SC127 (the reach receiving the Buck Mine outfall waters), and between SC085 and SC119 (the reach receiving the waters from the municipal wastewater treatment plant). Fluoride concentrations were greater than the Canadian guideline of 0.12 mg/l in the NE tributary, in the Buck Mine outfalls, for some sampling events in the Iron River, in Baker Creek, and in the Dober Mine waters. SC246 fluoride (0.34 mg/l) is not displayed, as its flow connections to the Iron River was uncertain.

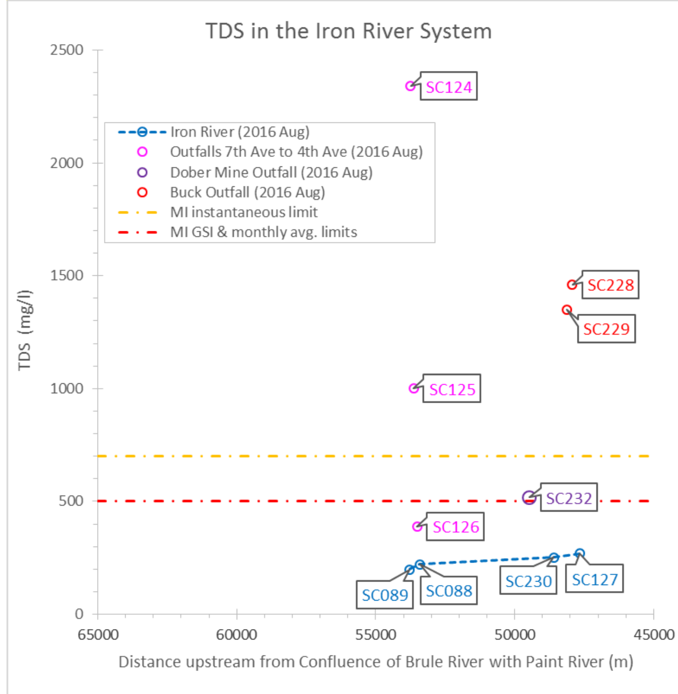
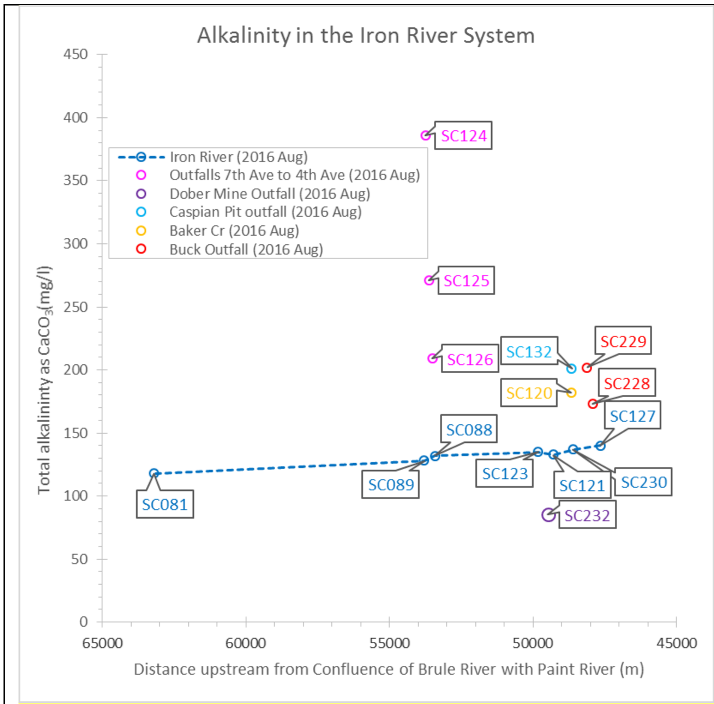


Fig. 20. Total Dissolved Solids (TDS) increased in the Iron River in the reach receiving the waters from the 7th-4th Ave outfalls and the reach receiving the waters from the Buck Mine outfalls. TDS was greatest in those outfalls, and greater than state criteria in the Buck outfalls and some of the 7th-4th Ave outfalls.



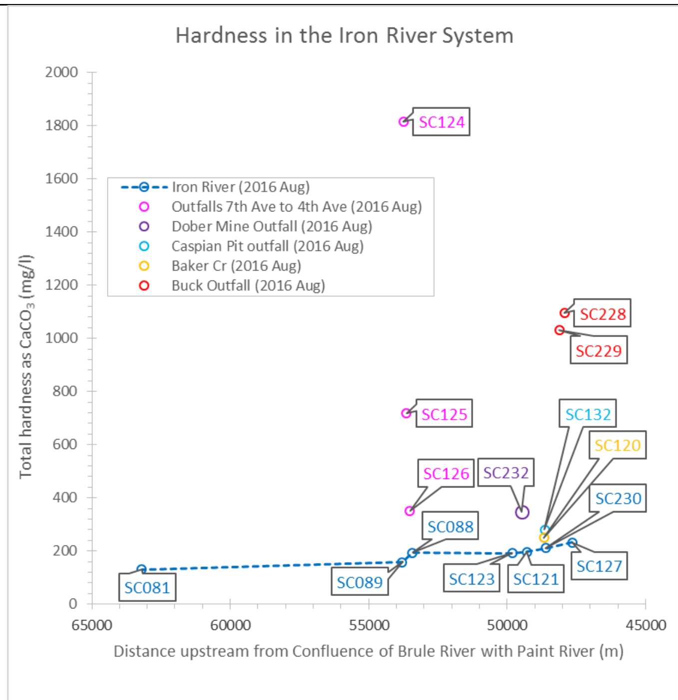


Fig. 21. Total alkalinity increased over the measured course of the Iron River and increased over the shortest distance in the reach receiving the waters from the 7th-4th Ave outfalls waters. Alkalinity was greatest in those outfalls and in the Caspian Pit outfall, Baker Creek, and the Buck Mine outfalls. Alkalinity was lowest in the Dober mine outfall.

Fig. 22. Total hardness increased over the measured course of the Iron River and increased over the shortest distance in the reach receiving the waters from the 7th-4th Ave outfalls waters. Hardness was greatest in those outfalls and in the Dober Mine outfall, and the Buck Mine outfalls.

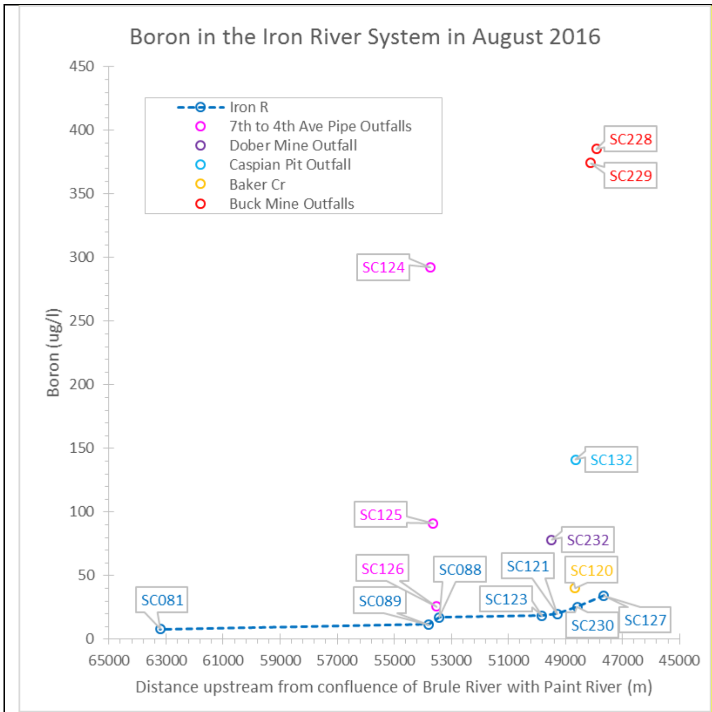


Fig. 23. Boron increased over the measured course of the Iron River and increased over the shortest distance in the reaches receiving the waters from the 7th-4th Ave outfalls waters (between SC089 and SC088) and the reach receiving the Buck Mine outfall waters (between SC230 and SC127). Boron was greatest in those outfalls and in the Dober Mine and Caspian Pit outfalls.

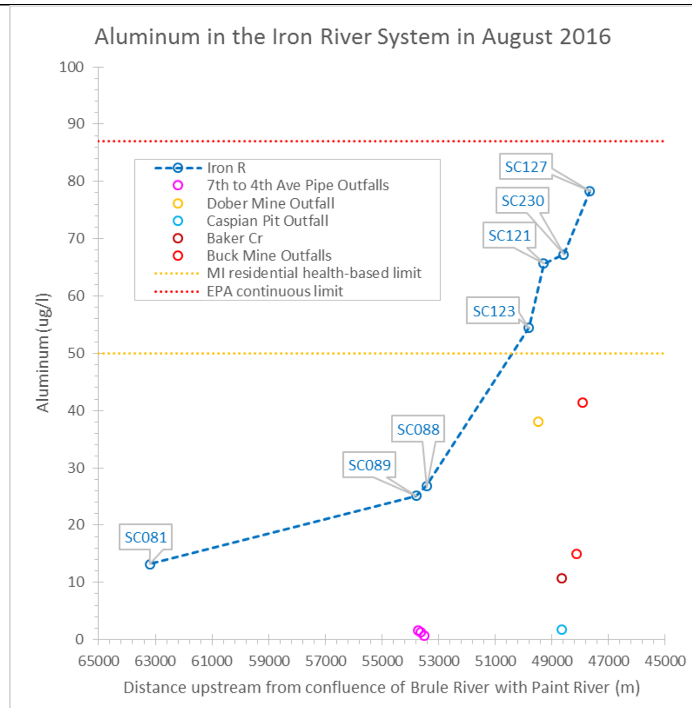


Fig. 24. Aluminum increased over the measured course of the Iron River even though measured discharges were lower in aluminum than the Iron River.

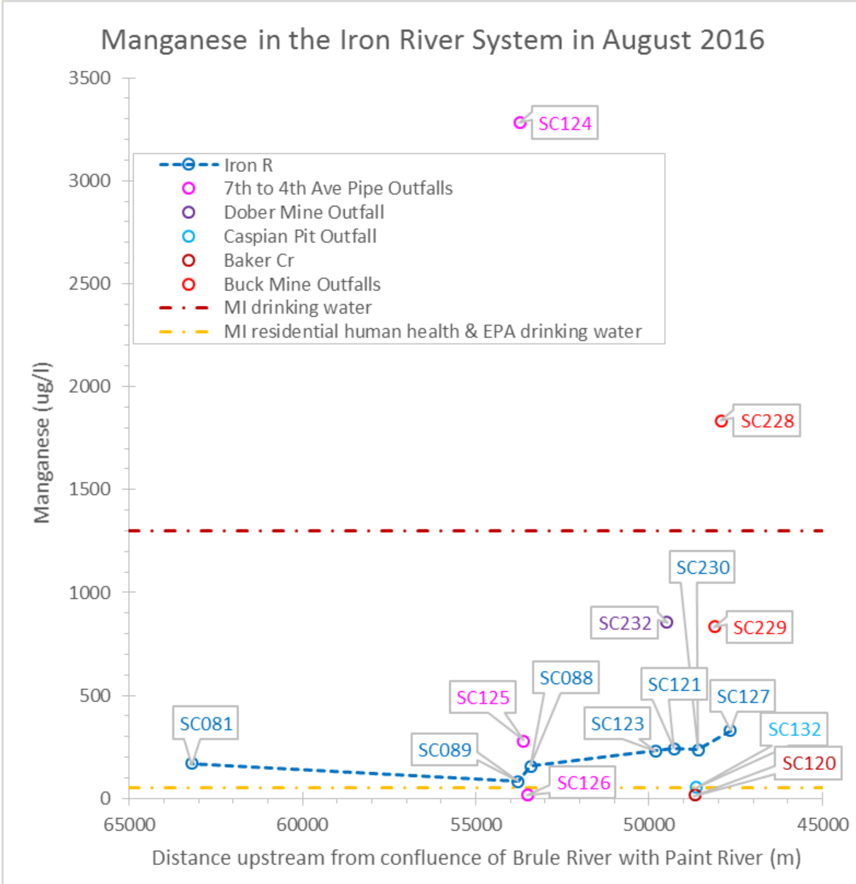


Fig. 25. Increases in manganese concentrations in the Iron River occurred in the reaches receiving water from the 7th to 4th Avenue mine drainage outfalls and the Buck mine outfalls. Manganese also increased in the middle reach of the river between SC088 and SC123. The drainage pipe near 7th Avenue (SC124) demonstrated the greatest manganese concentration, followed by the southern Buck mine outfall. Manganese at those sites was greater than the Michigan drinking water limit, and most measurements were greater than Michigan residential human health and EPA drinking water limits.

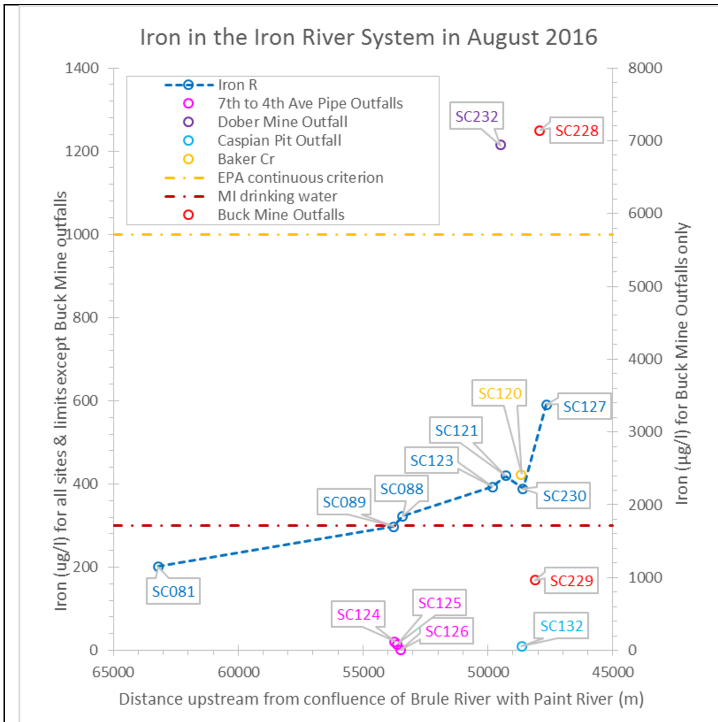


Fig. 26. Iron increased over the measured course of the Iron River but decreased between SC121 and SC230, the reach receiving the low-iron Caspian Pit waters. Iron increased over the shortest distance in the reaches receiving the waters from the 7th-4th Ave outfalls (between SC089 and SC088), the Dober Mine outfall (between SC123 and SC121), and one of the Buck Mine outfalls (between SC230 and SC127). Iron was greatest in that Buck Mine outfall and in the Dober Mine outfall, and those sites and all Iron River sites downstream of SC089 demonstrated iron concentrations greater than the Michigan drinking water limit. The concentrations in those outfalls was also greater than the EPA continuous criterion concentration. Iron was lowest in the 7th-4th Ave outfalls and the Caspian Pit outfall.

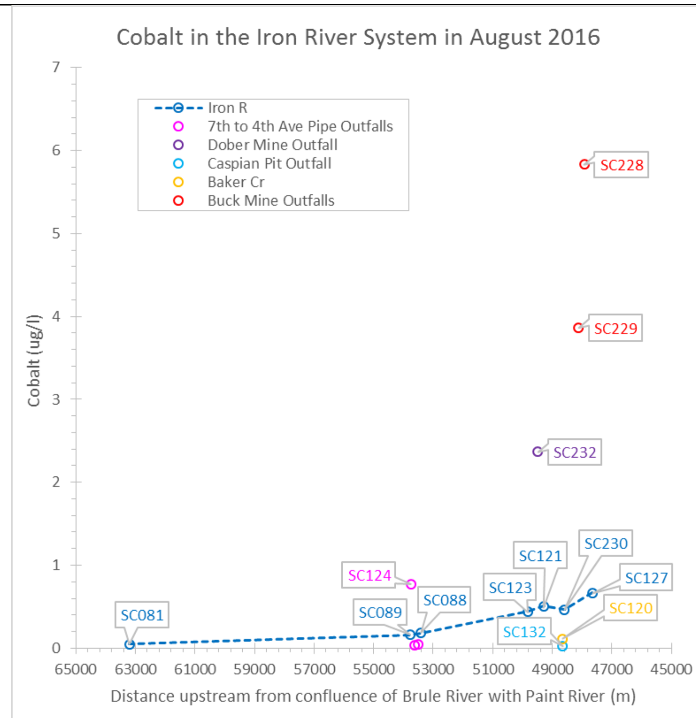


Fig. 27. Cobalt increased over the measured course of the Iron River, but decreased between SC121 and SC230, the reach receiving the low-cobalt Caspian Pit waters. Cobalt increased over the shortest distance in the reaches receiving the waters from the Dober Mine outfall (between SC123 and SC121) and from the Buck Mine outfalls (between SC230 and SC127). Cobalt was greatest in those outfalls and in the Dober Mine outfall, and lowest in two of the 7th-4th Ave outfalls, the Caspian Pit outfall, Baker Creek, and the upstream Iron River site (SC081).

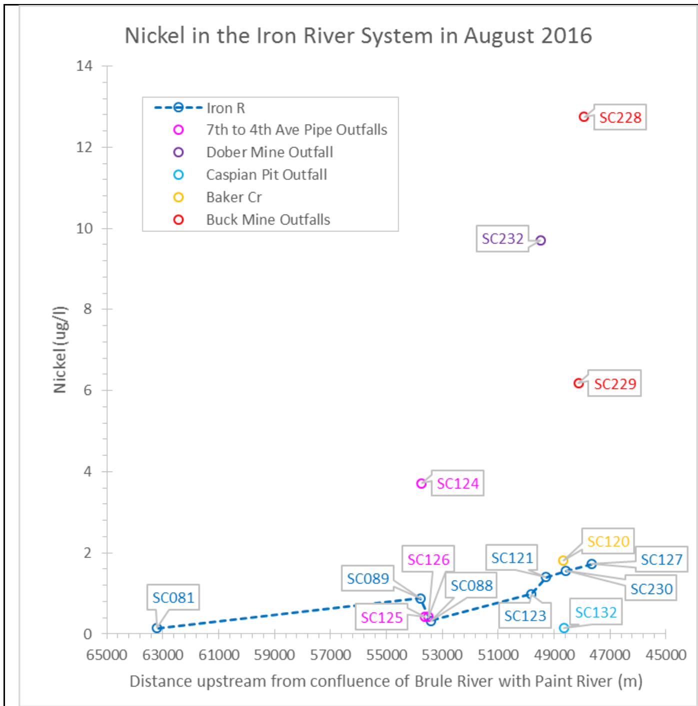
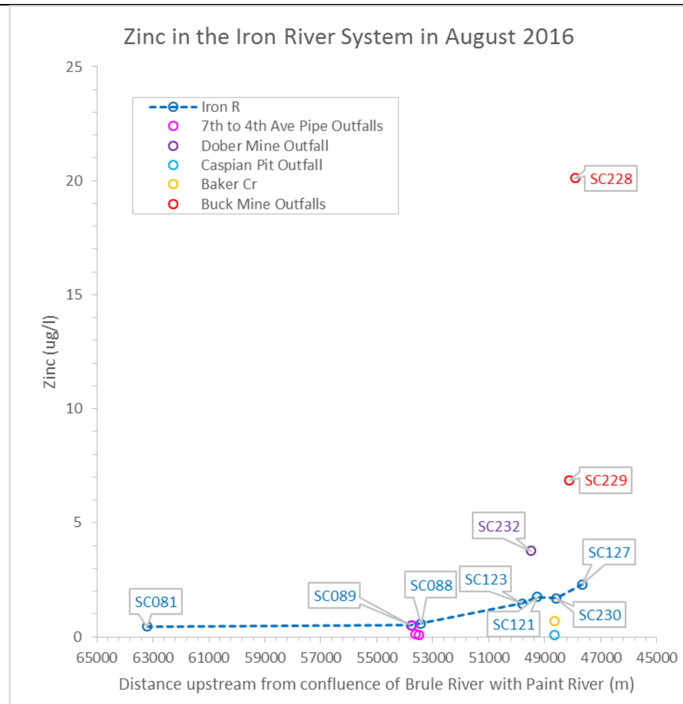
	

Fig. 28. Nickel increased over the measured course of the Iron River but decreased between SC089 and SC088, the reach receiving the 7th-4th Ave outfall waters. Nickel increased over the shortest distance in the reaches receiving the waters from the Dober Mine outfall (between SC123 and SC121). Nickel was greatest in the Dober Mine outfall and in the Buck Mine outfalls, and lowest in the Caspian Pit outfall and the Iron River upstream site at SC081.	Fig. 29. Zinc increased over the measured course of the Iron River, but decreased between SC121 and SC230, the reach receiving the Caspian Pit waters. Zinc increased over the shortest distance in the reach receiving the waters from the Buck Mine outfalls (between SC230 and SC127). Zinc was greatest in the Dober Mine outfall and in the Buck Mine outfalls, and lowest in the Caspian Pit outfall and the eastern two of the 7th-4th Ave pipes.

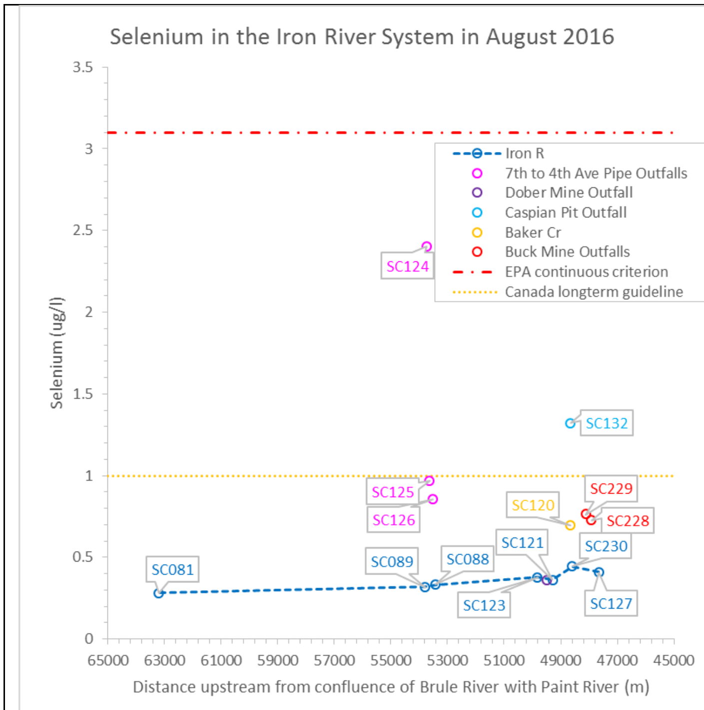


Fig. 30. Selenium in the Iron River increased in the reaches receiving waters from the 7th-4th Ave pipes (between SC089 and SC088) and the Caspian Pit (between SC121 and SC230). Concentrations of selenium in the westernmost of the 7th-4th Ave pipes and in the Caspian pit outfall exceeded the Canadian 1 µg/l long-term guideline.

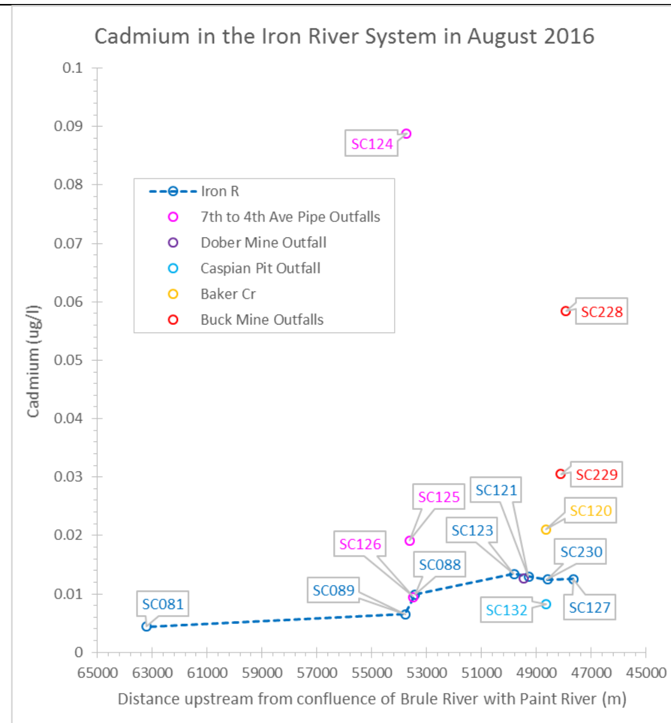


Fig. 31. Cadmium in the Iron River increased between SC089 and SC088 (the reach receiving the 7th-4th Ave outfall waters) and between SC088 and SC123. The cadmium concentrations were greatest in the 7th-4th Ave outfalls and the Buck Mine outfalls. Cadmium concentrations were lowest in the Iron River upstream site, SC081.

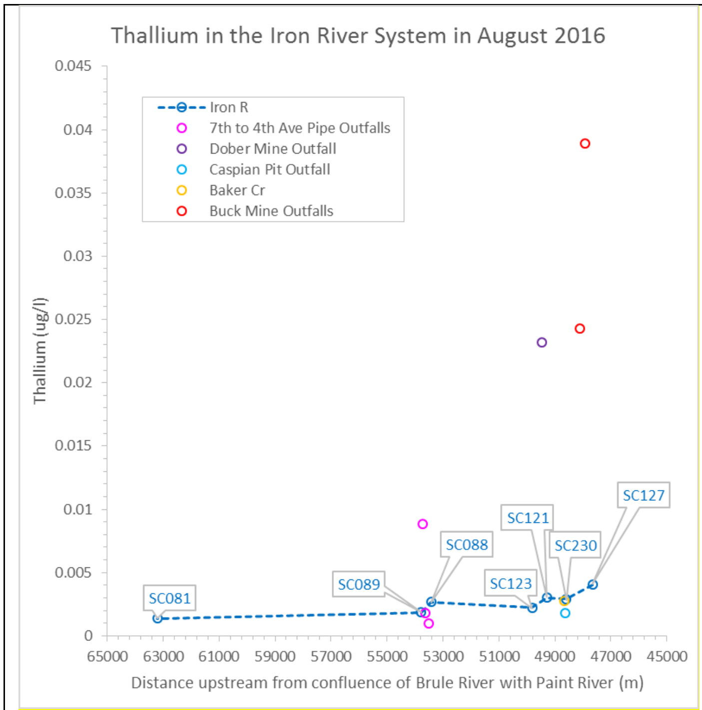
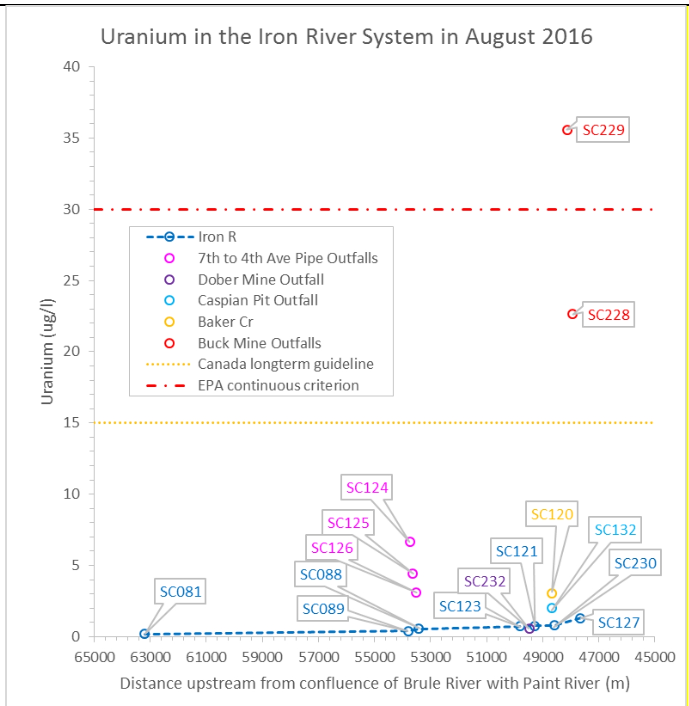
 	

Fig. 32. Thallium increased in the reaches receiving waters from the 7th-4th Ave outfalls (between SC089 and SC088), the Dober Mine outfall (between SC123 and SC121), and the Buck Mine outfalls (between SC230 and SC127). Thallium concentrations were greatest in those outfall waters.	Fig. 33. Increases in uranium concentrations in the Iron River occurred in the reaches receiving water from the 7th to 4th Avenue mine drainage outfalls (between SC089 and SC088) and the Buck mine outfalls (between SC230 and SC127). The Buck mine outfalls demonstrated the greatest uranium concentrations. Those outfall concentrations exceeded Canadian long-term guideline and EPA continuous criterion concentrations.

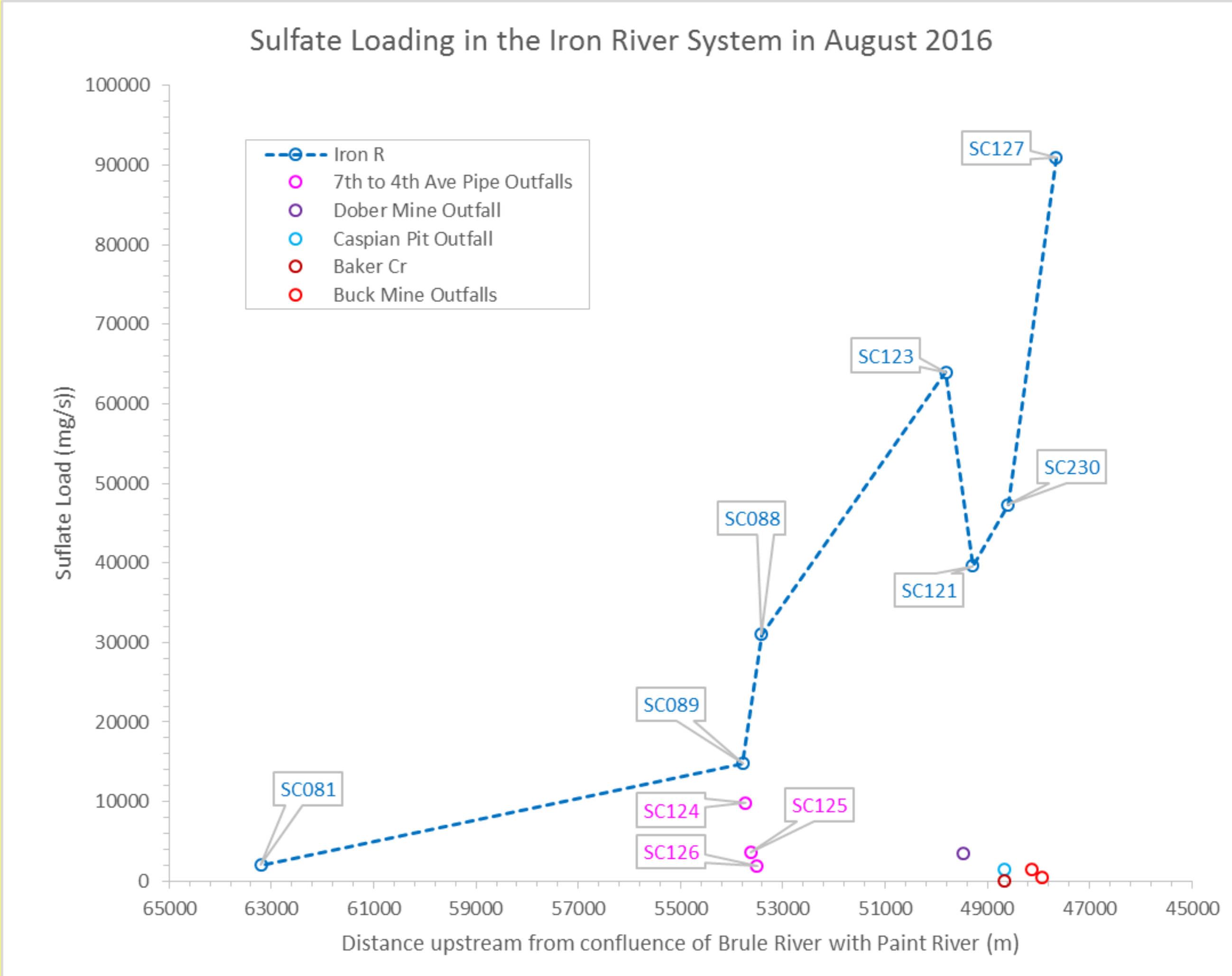


Fig. 34. Increases in sulfate loading in the Iron River occurred in the reaches receiving water from the 7th to 4th Avenue mine drainage outfalls and the Buck mine outfalls. Sulfate loading also increased upstream of 7th Avenue (between SC081 and SC089) and in the middle reach of the river (between SC088 and SC123). The drainage pipe near 7th Avenue (SC124) represented the greatest individual source of sulfate loading, followed by the middle pipe upstream of 5th Avenue (SC125) and the Dober mine outfall (SC232).

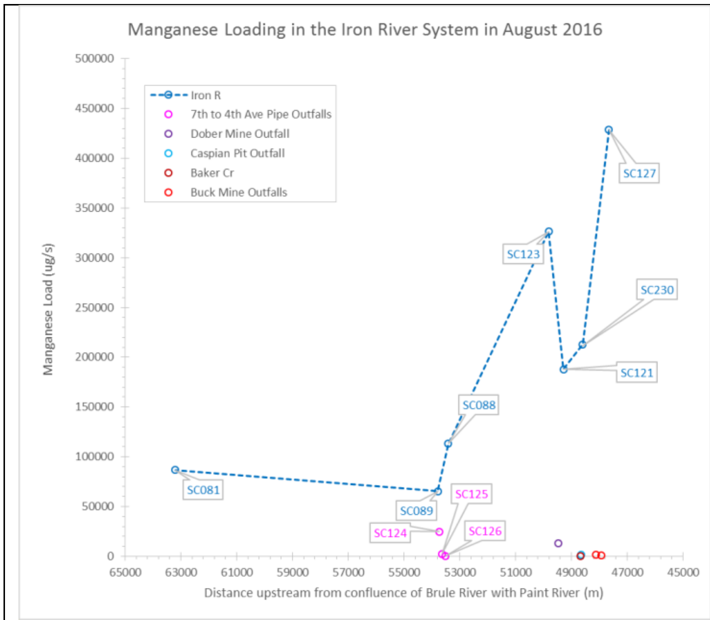


Fig. 35. Increases in the manganese loading in the Iron River occurred in the reaches receiving water from the 7th to 4th Avenue mine drainage outfalls and the Buck mine outfalls. Loading also increased in the middle reach of the river between SC088 and SC123. The drainage pipe near 7th Avenue (SC124) represented the greatest individual measured source of manganese loading, followed by the Dober mine outfall (SC232).

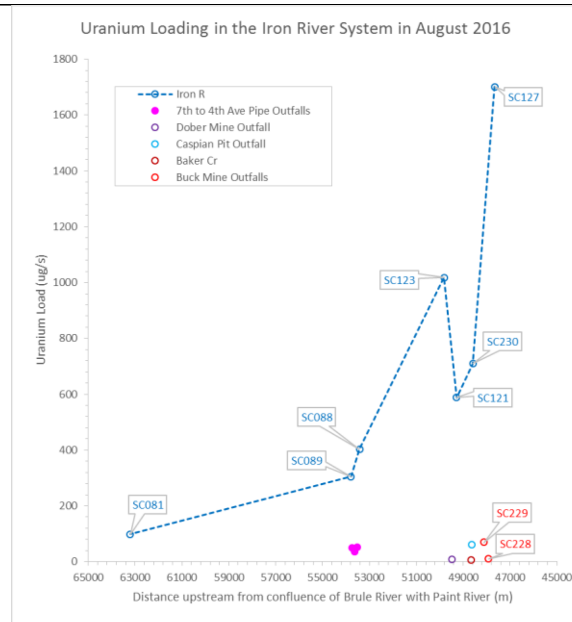


Fig. 36. Increases in the uranium loading in the Iron River occurred in the reaches receiving water from the 7th to 4th Avenue mine drainage outfalls and the Buck mine outfalls. Loading also increased upstream of 7th Avenue (between SC081 and SC089) and in the middle reach of the river between SC088 and SC123. The northern Buck outfall (SC229) represented the greatest individual source and the Caspian Pit was the 2nd greatest individual source, but the 7th-4th Avenue pipes collectively were the greatest measured source of uranium loading into the Iron River.

Comparison of REE concentrations between sites in the Iron River watershed indicated that most sites exhibited similar patterns of relative REE concentrations, but that the northern pipe outfalls were relatively low in cerium compared to all the other Iron River area sites (Fig. 37). The Iron River was also lower in cerium, relative to other REE's, at 4th Avenue, downstream of the outfalls, than the Iron River upstream at 7th Avenue (Fig. 37). The Dober outfall also exhibited a unique pattern of higher yttrium and/or lower lanthanum, relative to other REE's, and the Caspian Pit was higher in europium, relative to other REE's, than most other sites (Fig. 37).

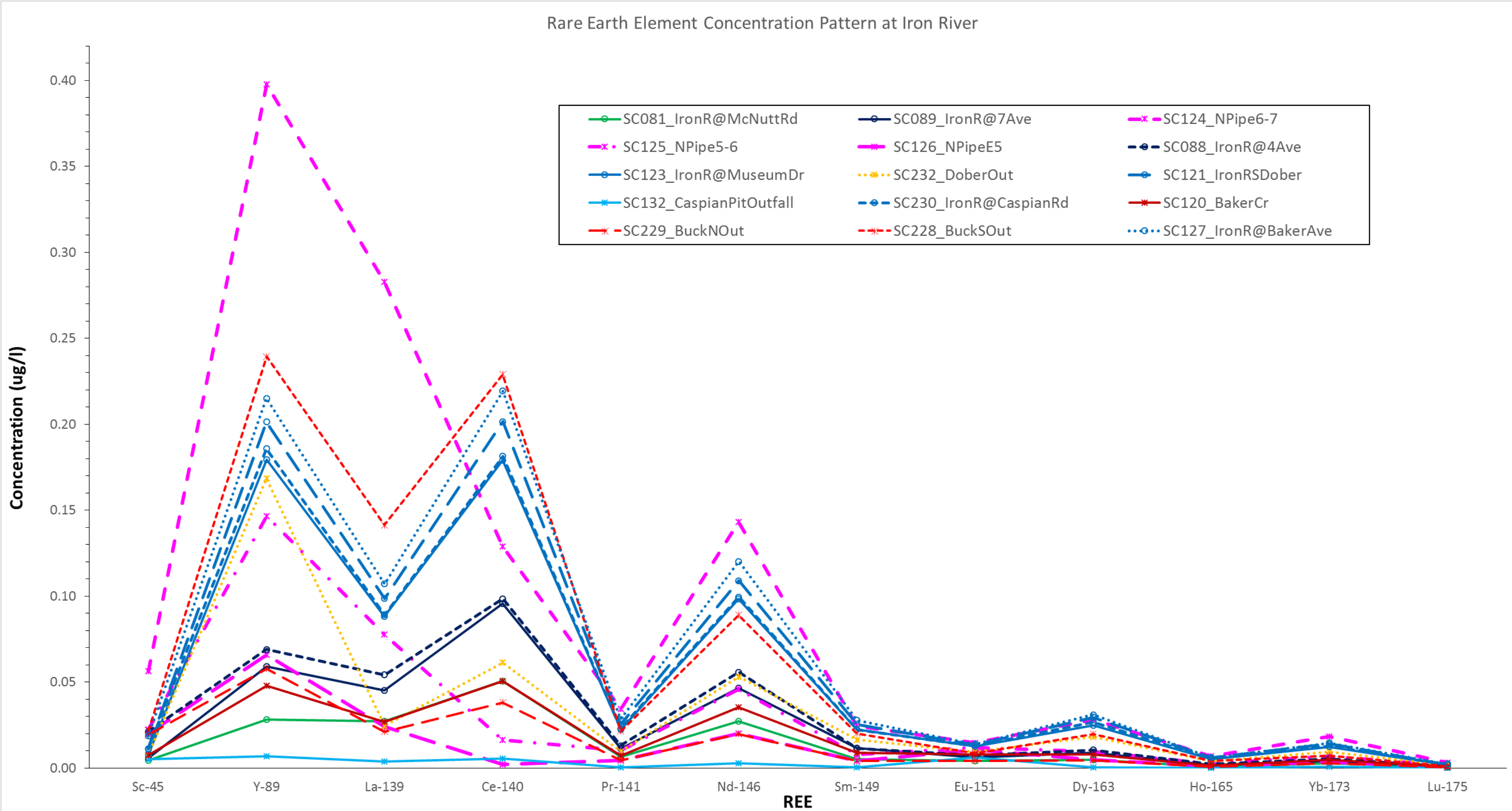


Fig. 37. Comparison of Rare Earth Element (REE) concentrations at sampled sites in the Iron River watershed indicated that the Iron River at the upstream site (SC081) was relatively low in yttrium (Y-89), and the waters in the northern outfall pipes between 4^{th} and 7^{th} Avenues (SC124, SC125, SC126) were low in cerium (Ce-140) relative to the other sites. The Iron River reflected the 7^{th}-4^{th} Ave pipe water downstream of those pipes with relatively lower cerium downstream than upstream of the pipes. A relative increase in yttrium occurred in the Iron River between there (SC088) and SC123. The Dober Mine outfall (SC232) was also high in yttrium (Y-89) and/or low in lanthanum (La-139) relative to the other sites. In addition, the southern Buck Mine site (SC228) resembled the Iron River REE pattern in that zone, but the northern Buck Mine site (SC229) had lower REE concentrations and was relatively lower in cerium (Ce-140). The Caspian Pit waters were also low in REEs, and had relatively high concentrations of europium (Eu-151).

B) Comparison of downstream sites with reference sites

Range of measurements of characteristics

Comparison of the range of measurements at reference sites (SC081, SC238, SC116, SC134, SC118, and SC235) with the range of measurements at sites downstream of mine zones indicated that sulfate (Table 5, Fig. 15), and the ratio of sulfate to specific conductance (Fig. 17) were distinct between the two groups. We did not measure metals and trace elements at reference sites other than SC081, which was lower in hardness, Li, B, Na, Mg, K, Ca, Ni, Se, Sr, Cd, and U than the non-reference sites measured (Figs. 22-23, 28, 30, 31, 33, Appendix C).

Kruskal-Wallis tests

Comparison of all sites downstream of mine zones or all downstream Iron/Brule River sites with reference sites for 2015 and 2016 data using the Kruskal-Wallis test indicated that those groups of sites differed in specific conductance, sulfate, and the ratio of sulfate to specific conductance (Table 7). The downstream sites had greater measurements for those variables (Figs. 38-45). When limiting the analysis to only the four most downstream sites (SC236, SC234, SC117, SC084) in the flow path from the mine zones and four or six reference sites, only sulfate and the ratio of sulfate to specific conductance differed (Table 7).

Table 7. Results of Kruskal-Wallis tests indicated that specific conductance, sulfate concentration, and the ratio of sulfate to specific conductance differed between reference sites and sites downstream of mines, but only sulfate and the ratio of sulfate to specific conductance were significant when comparing reference sites to the most downstream four or six sites. Chloride was also significant for the comparison of main channel sites with reference sites. These comparisons did not include sites for which the status as downstream of mining was unclear (SC246, SC079, SC238Z, SC239, SC240, SC224Z, SC225, SC226, SC122).

	Comparison of all downstream and reference sites for 2015 and 2016 (no site duplicates)					Comparison of Iron R./Brule R. main channel downstream sites with reference sites for 2015 and 2016 (no site duplicates)					Comparison of far downstream Iron R. / Brule R. sites with reference sites for 2015 and 2016 (no site duplicates)				
	n (down-stream sites)	*n* (ref. sites)	Kruskal-Wallis score	*df*	*P* -value	*n* (down-stream sites)	*n* (ref. sites)	Kruskal-Wallis score	*df*	*P* -value	*n* (down-stream sites)	*n* (ref. sites)	Kruskal-Wallis score	*df*	*P* -value
Specific conductance	38	6	7.67	1	**0.0056**	22	6	5.53	1	**0.019**	4	6	1.64	1	0.20
Chloride	38	6	3.67	1	0.055	22	6	3.84	1	**0.050**	4	6	2.23	1	0.14
Chloride : spec. cond.	38	6	0.42	1	0.52	22	6	0.03	1	0.87	4	6	0.41	1	0.52
Sulfate	27	4	10.13	1	**0.0015**	17	4	9.27	1	**0.0023**	4	4	5.33	1	**0.021**
Sulfate : spec. cond.	27	4	8.68	1	**0.0032**	17	4	7.22	1	**0.0072**	4	4	5.33	1	**0.021**

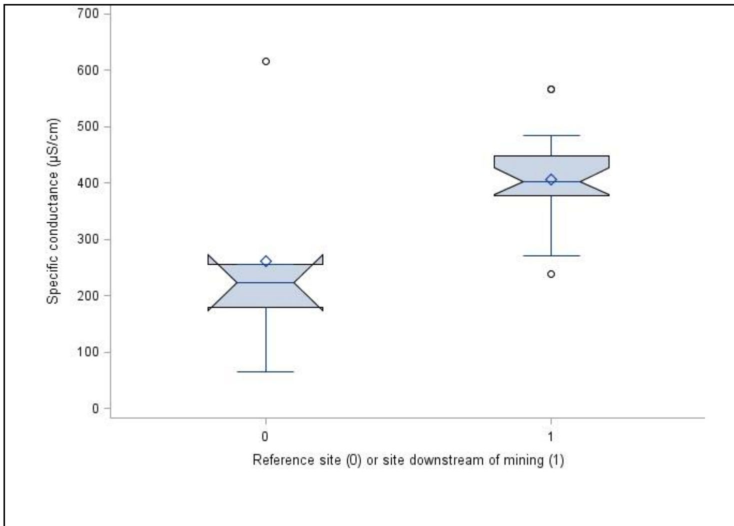


Fig. 38. Specific conductance measurements were significantly greater ($P < 0.05$) at sites downstream of mines (n = 22) than at reference sites (n = 6) according to the Kruskal-Wallis test using combined 2015-2016 Iron R./Brule R. site and reference site data, with no site duplicates. The upper and lower edges of the box represent the upper quartile (75th percentile) and lower quartile (25th percentile), respectively. A rhombus represents the mean, and a horizontal bar in the box represents the median. Whiskers extend to values that are within 1.5 times the length of the InterQuartile Range (IQR, i.e. the box height). Measurements beyond 1.5xIQR are circular points. Notches represent the median ± (1.58*IQR/$\sqrt{n}$) and may extend beyond the upper and lower quartiles or whiskers. Non-overlapping notches are indicative of significant differences.

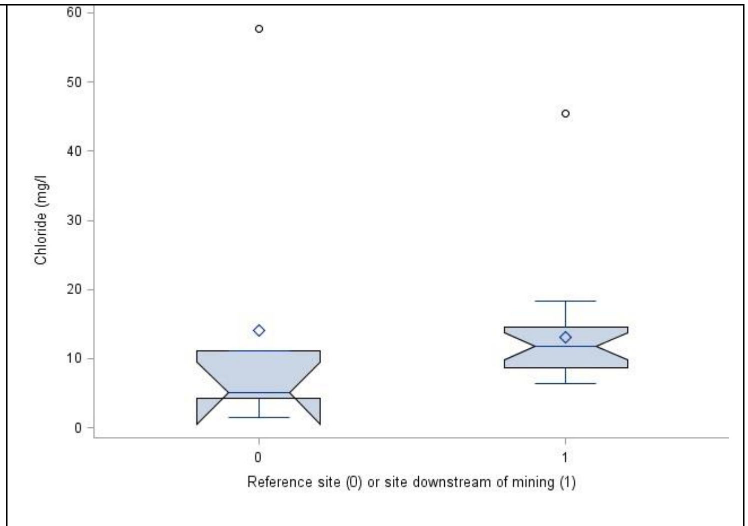


Fig. 39. Chloride concentrations were significantly greater ($P = 0.050$) at sites downstream of the tailings (n = 22) than at reference sites (n = 6) according to the Kruskal-Wallis test using combined 2015-2016 Iron R./Brule R. site and reference site data, with no site duplicates. For plot details, see Fig. 38.

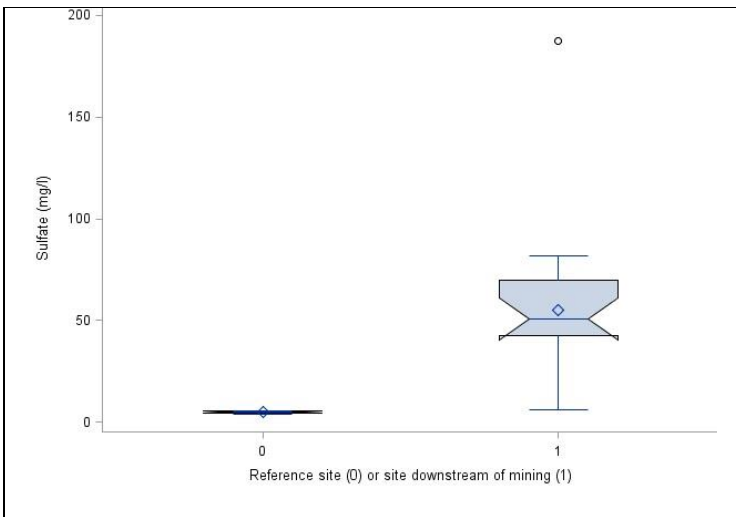


Fig. 40. Sulfate concentrations were significantly greater ($P < 0.005$) at sites downstream of the tailings (n = 17) than at reference sites (n = 4) according to the Kruskal-Wallis test using combined 2015-2016 Iron R./Brule R. site and reference site data, with no site duplicates. For plot details, see Fig. 38.

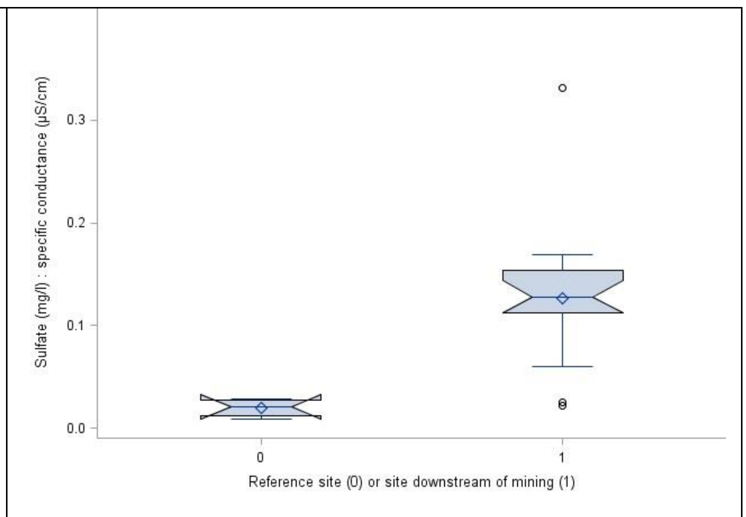


Fig. 41. The ratio of sulfate concentration to specific conductance was significantly greater ($P < 0.01$) at sites downstream of the tailings (n = 17) than at reference sites (n = 4) according to the Kruskal-Wallis test using combined 2015-2016 Iron R./Brule R. site and reference site data, with no site duplicates. For plot details, see Fig. 38.

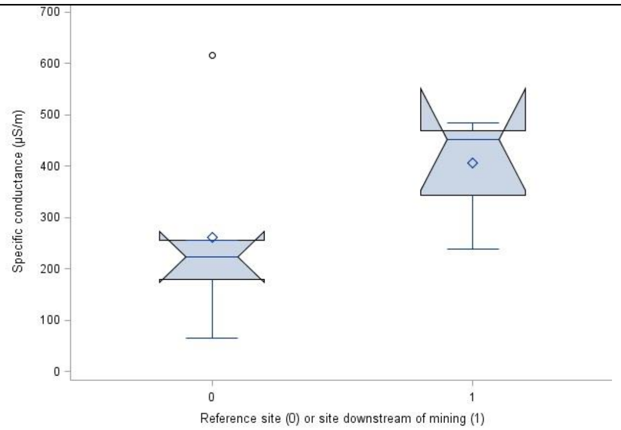


Fig. 42. Specific conductance measurements were not greater (P > 0.05) at the 4 sites the furthest downstream of the tailings (SC236, SC234, SC117, SC084) than at 6 reference sites (SC235, SC118, SC134, SC081, SC238, SC116) according to the Kruskal-Wallis test. This boxplot, however, indicated that those downstream measurements were greater. For plot details, see Fig. 38.

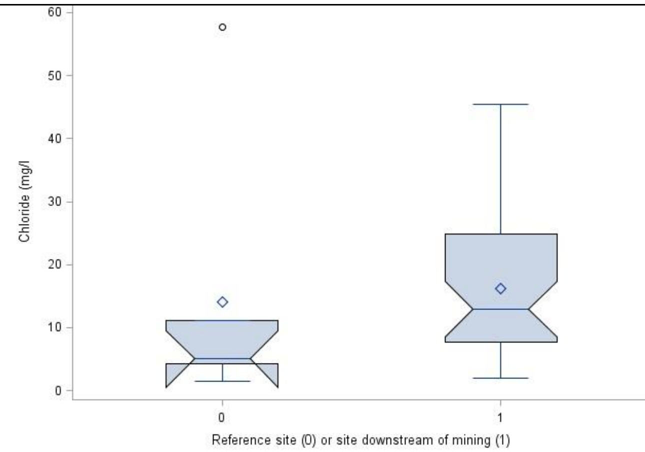


Fig. 43. Chloride concentrations were not greater (P > 0.05) at the 4 sites the furthest downstream of the tailings (SC236, SC234, SC117, SC084) than at 6 reference sites (SC235, SC118, SC134, SC081, SC238, SC116) according to the Kruskal-Wallis test. For plot details, see Fig. 38.

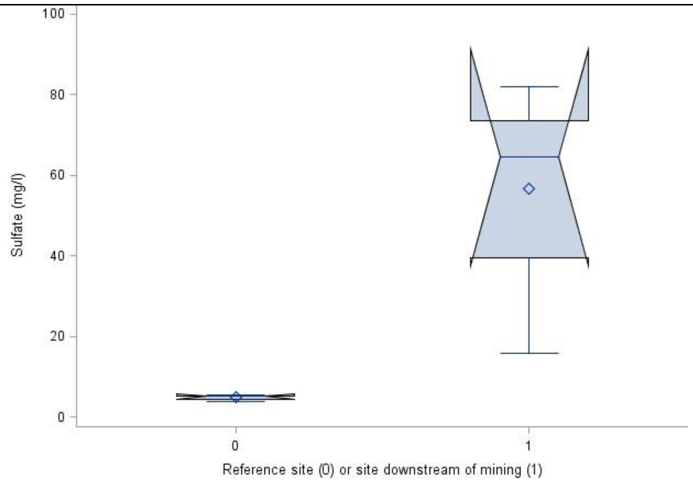


Fig. 44. Sulfate concentrations were greater (P < 0.05) at 4 sites the furthest downstream of the tailings (SC236, SC234, SC117, SC084) than at 4 reference sites (SC235, SC118, SC134, SC081) according to the Kruskal-Wallis test. For plot details, see Fig. 38.

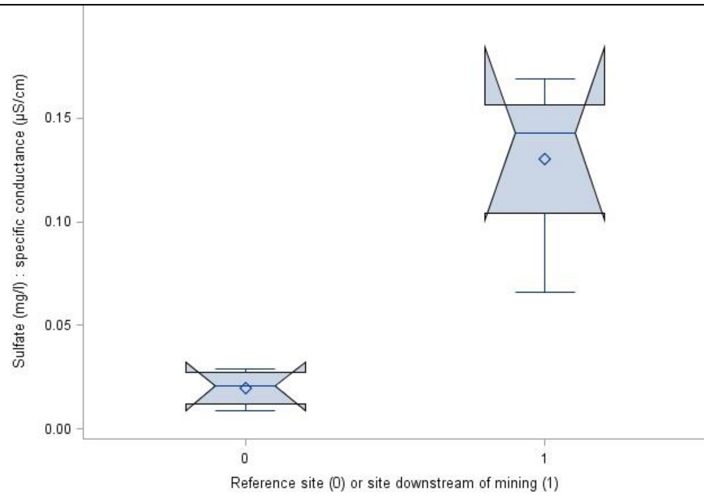


Fig. 45. The ratio of sulfate concentration to specific conductance was significantly greater (P < 0.05) at 4 sites the furthest downstream of the tailings (SC236, SC234, SC117, SC084) than at 4 reference sites (SC235, SC118, SC134, SC081) according to the Kruskal-Wallis test. For plot details, see Fig. 38.

Cluster analysis.

The cluster analyses, using specific conductance or sulfate and the ratios of chloride and sulfate to specific conductance for 2015-2016 data and just August 2016 data, indicated that reference sites clustered separately from sites downstream of mine zones but also clustered with sites between Sunset Creek and 7th Ave for 2015-2016 data (SC083 and SC224; Figs. 46, 47, 49). The Iron River reference site (SC081) also clustered separately from other sites using an analysis including trace element concentrations (Fig. 50). The Iron River site upstream (SC089) and downstream (SC088/88B) of the 7th-4th Ave pipes clustered separately for 2015-2016 data (Figs 46-47). Some sites, for which potential mine influence had been unclear, clustered with sites downstream of mine zones (Buck zone wetland SC246) and others clustered with sites not downstream of mine zones (stormwater outfall SC239, hillside stormwater/spring SC240, Nanaimo Park pipes SC224Z, SC225, and SC226, and Holmes Creek SC122; Figs. 46-49). A few Sunset Creek sites (SC079, SC238Z) remained ambiguous because we did not collect sulfate data at those sites and they clustered separately from the upstream Sunset Creek site but clustered with both the other Sunset Creek site downstream of the old mines (SC080) and most closely with the Iron River reference site (SC081; Fig. 49).

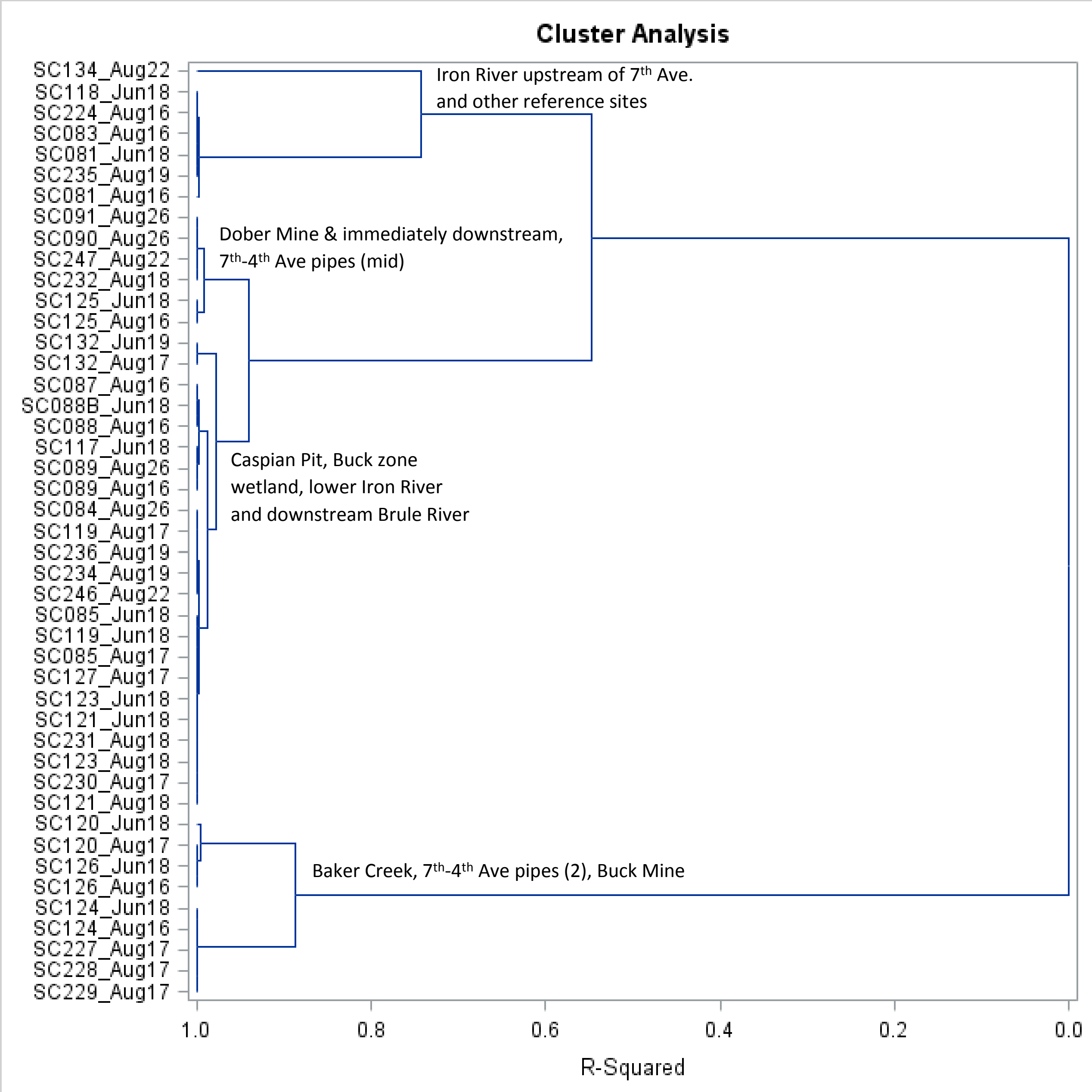


Fig. 46. For 2015 and 2016 data, cluster analysis of **specific conductance** and the **ratios of chloride and sulfate to specific conductance** indicated that reference sites (SC134, SC118, SC081, and SC235) clustered together along with the sites (SC083 and SC224) downstream of Sunset Creek but upstream of the 7th-4th Ave pipes. The sites upstream (SC089) and downstream (SC088/SC088B) of the 7th-4th Ave pipes were in different clusters. The reference site cluster was distinct from any other sites downstream of mines, but most closely clustered with other Iron River and Brule River downstream sites, a wetland site near the Buck Mine (SC246), and the discharges from the Dober Mine (SC091, SC232, SC247), Caspian Pit (SC132), and the middle pipe of the 7th-4th Ave pipes (SC125). In that group, the Dober Mine sites (SC091, SC232, SC247) clustered most closely with the middle 7th-4th Ave pipes (SC125), and the Caspian Pit (SC132) clustered more closely with wetland near the Buck site (SC246) and Iron River and Brule River downstream sites. The final cluster consisted of Baker Creek (SC120), two of the 7th-4th Ave pipes (SC124, SC126), and the Buck Mine discharges (SC227-229). Pseudo *F* and pseudo *T*-squared analysis indicated the optimal number of clusters was 14 (R^2 of 0.999) or 44 (R^2 of 1.0). All dates were in 2016 except Aug26 samples, which were in 2015.

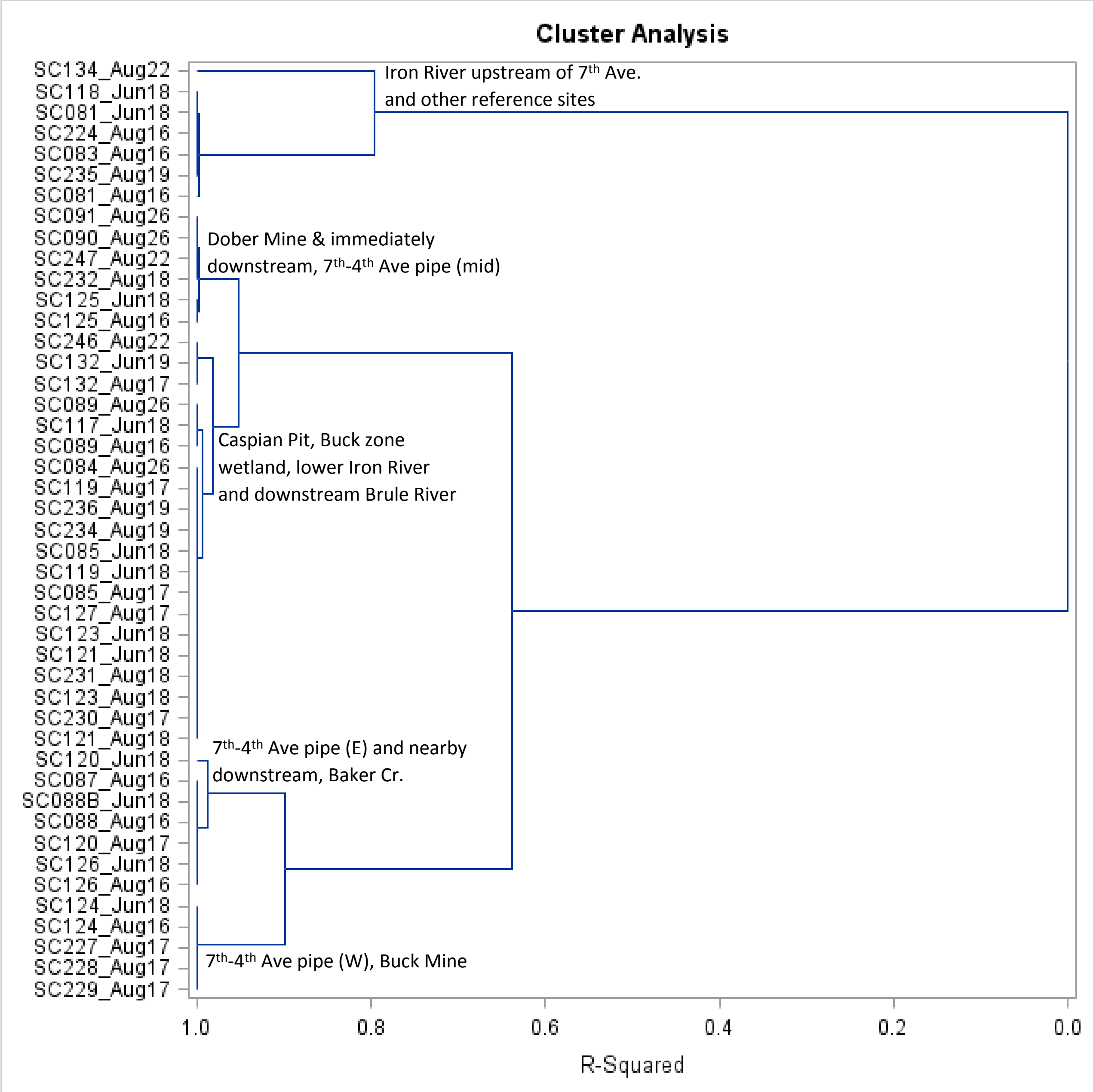


Fig. 47. For 2015 and 2016 data, cluster analysis of **sulfate** and the **ratios of chloride and sulfate to specific conductance** indicated that reference sites (SC134, SC118, SC081, and SC235) clustered together along with the sites (SC083 and SC224) downstream of Sunset Creek but upstream of the 7th-4th Ave pipes. The sites upstream (SC089) and downstream (SC088/SC088B) of the 7th-4th Ave pipes were in different clusters. The reference site cluster was distinct from any other sites downstream of mines. The Dober Mine sites (SC091, SC232, SC247) clustered most closely with the middle 7th-4th Ave pipes (SC125), and the Caspian Pit (SC132) clustered most closely with a wetland near the Buck site (SC246) and then Iron River and Brule River downstream sites. The final cluster consisted of Baker Creek (SC120), two of the 7th-4th Ave pipes (SC124, SC126), and the Buck Mine discharges (SC227-229). Pseudo *F* and pseudo *T*-squared analysis indicated the optimal number of clusters was 17 (R^2 of 1.0) or 44 (R^2 of 1.0). All dates were in 2016 except Aug26 samples, which were in 2015.

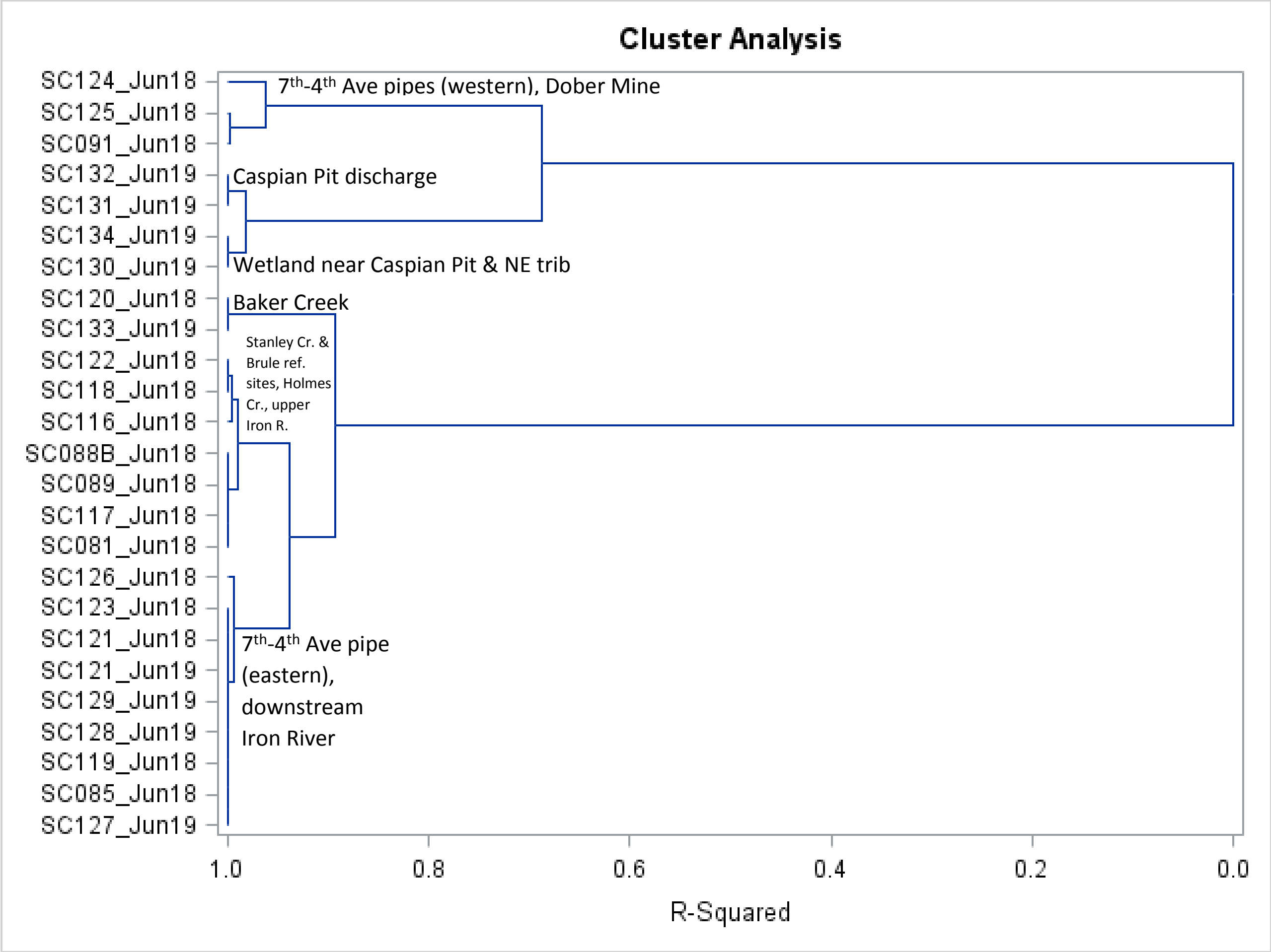


Fig. 48. Cluster analysis of **June 2016** data for **specific conductance** and **chloride** and the **ratio of chloride to specific conductance** indicated that the NE tributary site (SC134) clustered with the wetland near the Caspian pit flow (SC130), and those clustered with the Caspian Pit flow (SC131, SC132) and then the 7th-4th Ave pipes (SC124 and SC125) and the Dober Mine (SC091). The reference site in Stanley Creek (SC116) and the upstream Brule River site at SC118 clustered with Holmes Creek (SC122), and those sites clustered with the upstream Iron River reference site (SC081), the Iron River sites upstream and downstream of the 7th-4th Ave pipes (SC089 and SC088B), and the most downstream Brule River site (SC117). That set of sites clustered with the eastern 7th-4th Ave pipe (SC126), and other Iron River downstream sites (SC123, SC121, SC128, SC129, SC127, SC085, and SC119). That cluster and the previous clustered with the Baker Creek sites (SC120, SC133). Pseudo *T*-squared and pseudo *F* analysis indicated the optimal number of clusters was 9 (R^2 of 0.999) or 24 (R^2 of 1.0).

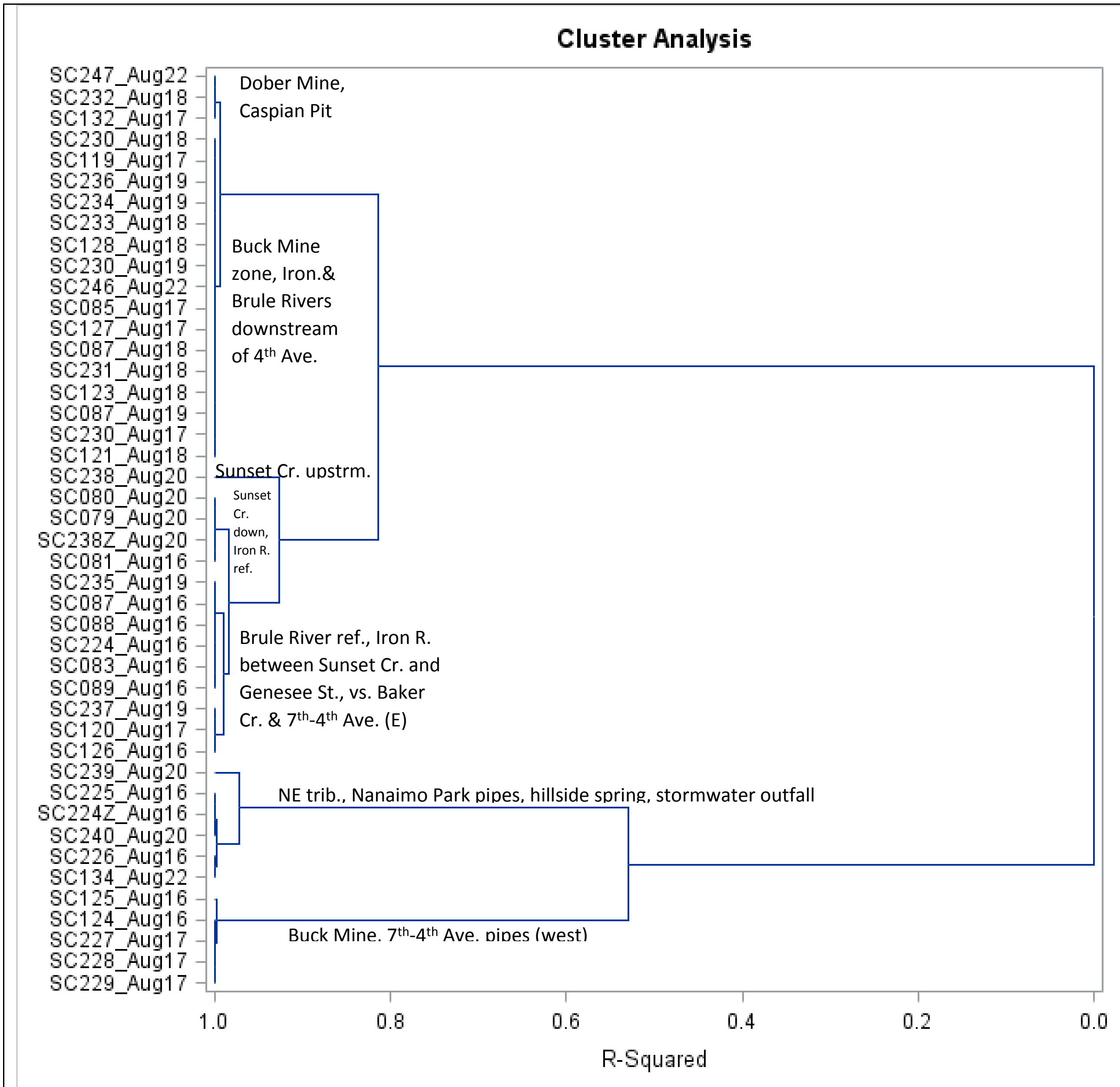


Fig. 49. Cluster analysis of **August 2016** data for **specific conductance** and **chloride** and the **ratio of chloride to specific conductance** indicated that the upstream Iron River reference site SC081 clustered with lower Sunset Creek sites (SC079, SC238Z, SC080), and that whole group clustered with a Brule River reference site (SC235), Baker Creek (SC237, SC120), the eastern 7th-4th Ave pipe (SC126), and some Iron River sites upstream of the Dober zone (SC083, SC224, SC089, SC088, SC087). The Sunset Creek upstream reference site (SC238) was distinct but formed a broader cluster with that mixed group. The reference site in the northeast tributary (SC134) formed a separate cluster with the Nanaimo Park pipes (SC225, SC224Z, and SC226), the stormwater or spring flow at SC240, and the stormwater outfall at SC239. The Buck Mine sites (SC227, SC228, SC229) clustered with the western 7th-4th Ave pipe sites (SC124, SC125). A final cluster (at top) consisted of a smaller group with the Dober Mine sites (SC247, SC232) and the Caspian Pit outfall (SC132) and a separate group of the wetland near the Buck Mine (SC246) and remaining downstream Iron River and Brule River sites. Pseudo *T*-squared and pseudo *F* analysis indicated the optimal number of clusters was 14 (R^2 of 1.0) or 43 (R^2 of 1.0).

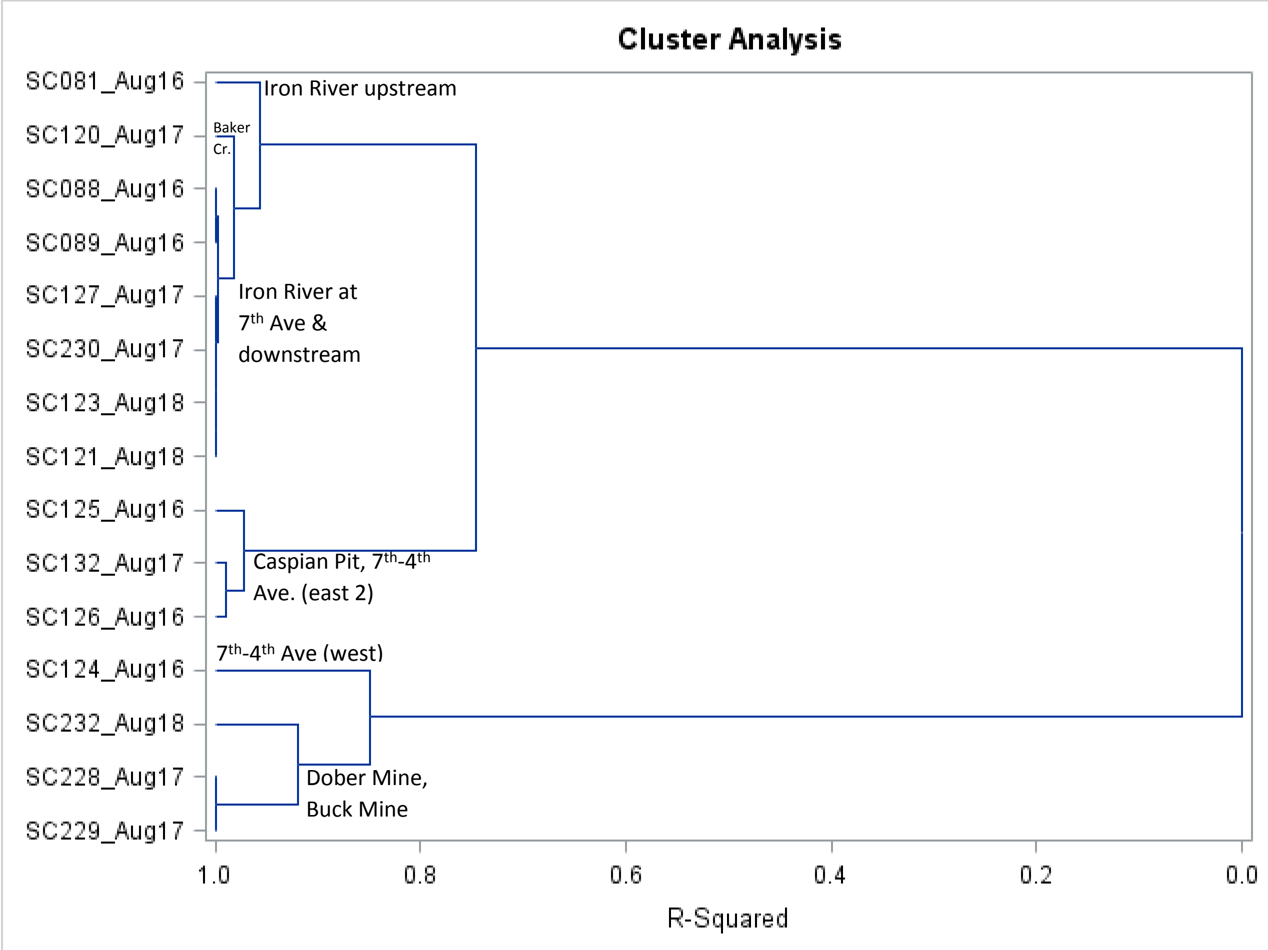


Fig. 50. Cluster analysis of **specific conductance, the ratios of chloride and sulfate to specific conductance, and concentrations of select metals** (lithium, boron, sodium, magnesium, potassium, calcium, manganese, iron, cobalt, nickel, zinc, selenium, rubidium, strontium, cadmium, barium, thallium, and uranium) indicated that the reference site at SC081 was distinct from other sites but mostly closely clustered with Baker Creek (SC120) and the sites in the Iron River (SC088-89, SC127, SC123, SC230, SC121). The Caspian Pit discharge (SC132) formed a cluster with two of the 7th-4th Ave pipes (SC125, SC126), and the third of those pipes (SC124) formed a cluster with the Dober and Buck Mine discharges (SC232, SC228, SC229). Pseudo *F* and pseudo *T*-squared analysis indicated the optimal number of clusters was 5 (R^2 of 0.95) or 14 (R^2 of 1). All dates were in 2016.

C) Temporal patterns

We found pre-2015 data for several of our study sites in part from MI DEQ Discharge Monitoring Reports, and from the MI SWIMS database (http://www.mcgi.state.mi.us/miswims/). Data for several sites was present in the MI SWIMS database but not in the Water Quality Portal (2017). Most of the historical data that we used came from other state agency reports or mine site-specific reports (Wagner 1963, Galbraith 1965, Willson 1973, Riley 1975, Johnson & Frantti 1978, Woods & Buda 1980, White 1983, Sayles 1989, Butler 1997, Butler 1999a,b,c,d,e, Butler 2000a,b,c,d,e,f,g,h, Butler 2001a,b,c,d,e, Butler 2002, Premo *et al*. 2005, PolyOne Corporation 2008, Weston Solutions 2009, Conroy 2012, Taft 2012a,b, Richard Sloat unpublished data from 2014).

Temporal patterns upstream in the Iron River and Sunset Creek

The reference site of SC081 demonstrated measurements in 2016 that were within the range of historical data from the 1960's and 1970's for specific conductance, pH, sulfate, phosphorus, and iron (Figs. A-1, A-9, A-27, A-45), but were greater than the historical range for chloride, the ratio of chloride to specific conductance, and manganese (Figs. A-17, A-18, A-48). The reference site of Stanley Creek in 2016 (SC116) was also within the historical range for specific conductance (Figs. A-1), but below the historical range for pH (Figs. A-9)

Sunset Creek sites downstream of the apparent former Homer-Wauseca and Sherwood Mine discharges (SC080, SC082) had specific conductance measurements in 2015-2016 that were lower than during the reported peak of the mine contamination in the 1970's (Figs. A-2). The 2015 pH, chloride, and chloride to specific conductance ratios at those sites, however, were within the historical range (Fig. A-10) except for decreased chloride measurements at SC082 (Figs. A-19, A-20). The upstream Sunset Creek sites, SC238Z and SC079, had specific conductance at least 11 % greater than measurements in the 1960's and 1970's (Figs. A-2) and SC238Z also had chloride measurements greater than all but the first historical value (though remaining still < 4 mg/l; Figs. A-19, A-20). Although we did not measure sulfate in Sunset Creek in 2015-2016, comparison of the historical data between sites indicated that the upstream SC238Z site had measurements of sulfate and the ratio of sulfate to specific conductance that were at least 85% lower than the downstream sites of SC080 or SC082 (Figs. A-29, A-30). That data also indicated that a peak of sulfate of 830 mg/l occurred in August 1976.

Sites in the Iron River downstream of Sunset Creek but upstream of 7th Ave. (SC083, SC224) demonstrated peaks of specific conductance, sulfate, and the ratio of sulfate to specific conductance in the 1960's and 1970's. The 2016 data were below those peaks (Figs. A-1, A-27, A-28). The pH measurements demonstrated a similar but inverse pattern, with pH minima occurring in the 1970's (Fig. A-9). Chloride concentration was greater in 2015-2016 than in the 1970's (Fig. A-17), and a minimum for the ratio of chloride to specific conductance occurred in 1979 (Fig. A-18).

Downstream of 4th Ave, the site near the US-2 road bridge (SC087) had 2015-2016 measurements for specific conductance (Fig. A-1) and sulfate (Fig. A-27) that were lower than the peak of the 1970's but greater than the lowest measurements of the 1970's (and 1989). Measurements for those sites had not declined as greatly over time as for the other sites further upstream (SC083, SC224). Chloride (and the ratio of chloride to specific conductance) at SC087 decreased between 1973 and 1988, a period during which the Iron River WWTP was shut down, but increased between 1988 and 2016 (Fig. A-17).

Temporal changes near Dober Mine site

The Dober Mine outfall water declined between the 1970's and 2016 in specific conductance (Fig. A-3), sulfate (Fig. A-31), the ratio of sulfate to specific conductance (Fig. A-32), manganese (Fig. A-49), and iron (Fig. A-53). The site also increased in pH between those years, but had **many dips below 6.5, and several below 6.0, between 2008 and 2016** (Fig. A-11). Chloride, the ratio of chloride to specific conductance, and phosphorus exhibited similar patterns, but also demonstrated peaks in 1997 (Fig. A-21, Fig. A-22, Fig. A-46). The outfall water was also lower in 2016 than peaks in the 1990's and early 2000's for nickel (Fig. A-56), copper (Fig. A-59), zinc (Fig. A-62), and thallium (Fig. A-65). Although lower than in the 1970's, the available data for outfall **specific conductance and concentrations of sulfate, manganese, and iron** have remained at high levels from the late 1990's to 2016 (Figs. A-3, A-31, A-49, A-53).

Comparing the history of the Iron River upstream (SC231, SC123) and downstream (SC121, SC233) of the Dober Mine outfall indicated that specific conductance, chloride, sulfate, and manganese were greater, and pH lower, downstream than upstream of the Dober Mine for almost all of the historical records (Fig. A-4, A-12, A-23, A-33, A-51). Manganese was greatest at SC233 in June 1976 (Fig. A-51). In that zone of the Iron River, specific conductance (Fig. A-4), sulfate (Fig. A-33), and iron (Fig. A-55) were mostly lower in 2015-2016 than during peaks in the 1970's, but chloride has increased over time (Fig. A-23). Recent measurements for nickel, copper, and zinc upstream of the Dober Mine were also lower than in 1999 (Figs. A-58, A-61, and A-64).

Temporal changes in the Caspian Pit outfall

The Caspian Mine Pit outfall measurements in 2016 were within the range of measurements from the 1970's for specific conductance (Fig. A-5). The pH in 2016 was higher than in the 1970's, when the pH was as low as 5.9 (Fig. A-13). For sulfate, 2016 concentrations were lower than in the 1970's but remained greater than 40 mg/l (Fig. A-35).

Temporal changes near the Buck site

The Buck Mine outfalls declined between the 1970's and 2016 in specific conductance (Fig. A-6), sulfate (Fig. A-37), the ratio of sulfate to specific conductance (Fig. A-38), manganese (Fig. A-50), and iron (Fig. A-54). The site also had a greater pH in 2016 than in earlier low points, but remained in the range of data from 1999-2001 (Fig. A-14). The pH was below 6.5 and 6.0 in the 1970's and 2006 (Fig. A-14). Although lower than in the 1970's, the outfall **specific conductance and concentrations of sulfate, manganese, and iron** have remained mostly at high levels between the late 1990's and 2016 (Figs. A-6, A-37, A-50, A-54). **Nickel** and **zinc** demonstrated similar patterns (Fig. A-57, A-63), but copper has decreased in one outfall and remained relatively low in another since 2006 (Fig. A-60).

Comparison of the history of the Iron River upstream (SC230) and downstream (SC127, SC085, SC119) of the Buck Mine outfalls indicated that specific conductance, sulfate, and manganese were greater downstream than upstream of the Buck Mine for almost all of the historical records (Fig. A-7, A-39, A-51). In that zone of the Iron River, specific conductance (Fig. A-7) remained at relatively high levels between the 1970's and 2016. At SC119, however, specific conductance has decreased since a peak in the 1960's, years for which data were unavailable for the other sites (Fig. A-7). Phosphorus decreased in more recent measurements (Fig. A-47). Sulfate, manganese, and iron also decreased but remained relatively high (Fig. A-39, A-51, A-55). Chloride has increased for most sites since the late 1970's (Fig. A-23).

Temporal changes near the confluence of the Iron River with the Brule River

For sites near the confluence of the Iron River with the Brule River, specific conductance has remained relatively constant except for an increase in the mixing zone site of SC234 (Fig. A-8). Chloride has increased for most of those sites since the 1970's (Fig. A-25). Sulfate and nitrate were lower in recent measurements than in 1969-1974 measurements for most sites, but sulfate decreased much more at the Iron River (SC236) and further downstream (SC117) sites (Fig. A-41, A-44). In contrast, sulfate and nitrate increased in the mixing zone site (SC234; Fig. A-41, A-44), but the sulfate to specific conductance ratio decreased there like for the other sites (Fig. A-42). Throughout the available historical record, the upstream Brule River sites (SC235, SC118) had the lowest levels, the Iron River upstream site (SC236) had the highest levels, and the downstream Brule River sites (SC234, SC117) had intermediate levels for specific conductance (Fig. A-8), chloride (Fig. A-25), and sulfate (Fig. A-41). A similar pattern occurred for nitrate, but the further downstream site (SC117) was within the range of concentrations of the upstream Brule River sites (SC235, SC118; Fig. A-44).

4. DISCUSSION

Contamination of concern

Analysis of outfall characteristics indicated that several mine-related waters discharging to the Iron River showed characteristics of concern. Those included: high specific conductance and temperature; low DO and pH; high concentrations of TDS, chloride, sulfate, manganese, iron, cobalt, nickel, zinc, and uranium; and moderately high concentrations of selenium, cadmium, and thallium. Although several of those water characteristics were of less concern than at their peaks in earlier decades, historical comparisons indicated that the Dober and Buck outfalls have still had pH dips in recent years, including 6.3 S.U. at Dober in June 2016. Those waters have also remained high in specific conductance, sulfate, Mn, Fe, Ni, and Zn (Buck).

Certain water characteristics appeared to exceed applicable or recommended surface, drinking, or groundwater-to-surface water criteria. Those characteristics and other high concentrations, by discharge site, were as follows:

- **7^{th}-4^{th} Ave pipes** (western two pipes): **TDS, DO, and pH** (June) did not meet Groundwater Surface Water Interface (GSI) criteria; **sulfate** and **manganese** exceeded MI and EPA residential/drinking water criteria; **selenium** (SC124) exceeded Canadian surface water criterion; **uranium** and **cadmium** occurred at relatively high concentrations.

- **Dober Mine**: **temperature** exceeded the MI mixing zone edge heat load limit criterion; **TDS, turbidity**, and **iron** exceeded MI or EPA surface water criteria; **manganese** exceeded MI and EPA residential/drinking criteria; **sulfate, nickel, cobalt,** and **thallium** occurred at relatively high concentrations and **DO** at a relatively low concentration.

- **Caspian Pit**: **temperature** exceeded the MI cold surface water criterion; **selenium** exceeded Canadian surface water criterion and approached the EPA lake criterion; **pH** was relatively high and **uranium** was present at concentrations greater than in the river;

- **Buck Mine**: **TDS** and **iron** exceeded MI or EPA surface water criteria; **uranium** exceeded EPA drinking water criteria; **sulfate** and **manganese** exceeded MI and EPA residential/drinking criteria; **fluoride** exceeded Canadian surface water criteria; **cobalt**, **nickel, zinc, cadmium**, and **thallium** occurred at relatively high concentrations.

Loading calculations suggest that the greatest measured load sources of sulfate to the Iron River were the 7^{th}-4^{th} Ave pipes, particularly SC124, and the Dober Mine discharge, but the Buck mine may represent a greater load than we estimated if we had sampled all observed discharges. We observed a similar pattern for manganese loading. For uranium, the Buck Mine discharges represented one of the greatest load sources. Obstructions by plant debris in the water at SC121, velocity meter malfunction, or flow into wetlands or groundwater may explain an unexpected measured decrease in flow and apparent decrease in loading between SC123 and SC121. The Dober Mine site does divert flow into the mine site in that zone, but the diversion is upstream of SC123. If no significant errors occurred in velocity measurements, then the load of sulfate, manganese, and uranium also increased in the section of the Iron River between SC088 and SC123. We did not, however, identify surface inputs of those constituents in that section. This would suggest that we missed some surface sources or that groundwater inflow in that zone was high in those constituents.

Downstream and historical trends

Comparison of downstream trends in the Iron River indicated that mine zone discharges were associated in certain reaches with measured changes in water quality. That influence on the Iron River included increases in specific conductance, alkalinity, TDS, TSS, turbidity, total hardness, sulfate, Li, B, Na, Mg, K, Ca, Mn, Fe, Co, Ni, Zn, Se, Rb, Sr, Cd, Tl, and U. Of those characteristics, specific conductance exceeded EPA Appalachian guidelines downstream of SC089, manganese exceeded MI residential health-based and EPA drinking water criteria, and iron exceeded MI and EPA drinking water, and Canadian criteria downstream of SC089. For the reaches receiving Dober and Buck mine waters, the influence on the Iron River, as assessed by upstream/downstream comparisons, was present also for almost all historical data for characteristics including specific conductance, sulfate, and manganese. Historical comparisons also indicated that many Iron River and Sunset Creek measurements in 2015-2016 were lower than in previous decades, but that specific conductance and sulfate have remained high downstream of the reach near the US-2 bridge. A decrease in sulfate at Iron River and Brule River upstream reference sites relative to certain measurements from the 1970's (Figs. A-27, A-41, A-42) could relate to a decrease in acid rain deposition (Nichols and McRoberts 1986, Lehmann *et al*. 2005). Chloride has increased at many sites since the 1960's and 1970's.

Potential effects of contaminants

Several of the contaminants that we detected are of particular concern because of their potential effects on aquatic life, wildlife, and humans. Although toxic effects depend on dose or concentration and it is unclear if concentrations we detected could cause the known toxic effects, understanding the risks of contamination requires understanding the potential toxicity of contaminants. Sulfate, in addition to affecting plants such as wild rice (Moyle 1944, 1945, Pastor *et al*. 2017), can increase the methylation of mercury, a process that increases concentrations of the more toxic methylmercury (Gilmour 1992, Jeremiason *et al*. 2006, Sonke *et al*. 2013, Bailey *et al*. 2014). This process could be of particular importance in the Dober and Buck wetlands. Total mercury was present in concentrations up to 1.7 ng/l in the Dober discharge in 2007, though hypothesized to come from the river inflow into the wetland (TRC 2011). Available documentation, however, reported only total mercury, not methylmercury, for these sites. The concentration of methylmercury could increase in the Dober and Buck wetlands. Fluoride is also of potential concern. It can disrupt the migration and reduce survival of fish, reduce invertebrate reproduction and survival, reduce algae growth, and cause skeletal fluorosis in humans (CCME 2001, ATSDR 2003). Chloride can also impact survival of fishes, amphibians, invertebrates, and algae (USEPA 1988, CCME 2011a). In humans, manganese can impair child brain development, and in large doses in the air is known to cause neurological (manganism) and reproductive effects (ATSDR 2012a). Although aquatic life toxicity data are limited for manganese, it is toxic to some fish and invertebrates (Borgmann *et al*. 2005, Harford *et al*. 2015, Kostich *et al*. 2017). Iron can reduce fish hatching and invertebrate growth and survival (CCME 2008). Cobalt is reasonably anticipated to be a human carcinogen according to the US National Toxicology Program, it affects the thyroid gland, and in lab animals it can cause heart, liver, kidney, blood, and testes effects (ATSDR 2004). Nickel is a potential concern because it can cause kidney and blood changes in humans (ATSDR 2005a), and can be toxic to aquatic organisms (Eisler 1998). Zinc can cause anemia and pancreatic and kidney damage in humans, and impact growth and survival of fish, amphibians, invertebrates, mammals, and birds (Eisler 1993, ATSDR 2005b, CCME 2008) Selenium can cause developmental deformities and death, particularly in fish and birds, and cause deformations, selenosis, and death in mammals (Eisler 1985, Hamilton 2004, Santos *et al*. 2015, USEPA 2016). Cadmium is a carcinogen that is toxic at relatively low concentrations, with effects in humans including vomiting, diarrhea, lung damage, kidney damage, fragile bones, and death (ATSDR 2012b). Effects in aquatic organisms include decreased growth and increased mortality (CCME 2014). Thallium can cause human hair loss, vomiting, diarrhea, and death at relatively low concentrations, and has caused heart, and nervous and reproductive system damage in laboratory animals (ATSDR 1992). Uranium exposure can result in kidney damage in humans, kidney and liver damage in fish, and decreased growth and increased mortality in fish and other aquatic organisms (CCME 2011b, ATSDR 2013). In addition, decay products of uranium (U-238) are radioactive isotopes that can cause radiological damage and are carcinogenic (CCME 2011b). High specific conductance, TDS, alkalinity, and hardness can also impact aquatic organism communities.

Extent of mine-influence

The combination of the mine-related discharges appeared to influence the Iron River far downstream. Based on comparisons with reference sites in the cluster analyses of specific conductance, chloride, sulfate, and the ratio of chloride and sulfate to specific conductance, as well as the Kruskal-Wallis tests using sulfate and the ratio of sulfate to specific conductance, the mine influence extended at least from the 7^{th}-4^{th} Ave. pipes to SC117 (at Damitz Road) in the Brule River downstream of the confluence. This indicates that mine zone waters influenced at least 16.5 river-kilometers in the Iron and Brule Rivers. These results also suggest that combinations of characteristics including specific conductance and concentrations of chloride and sulfate appear useful as tracers for mine influence. The REE analysis also indicated that REE concentrations may distinguish certain individual mine sources, particularly with concentrations of lanthanum and cerium relative to other REEs.

Remaining data gaps

Our study represents only a snapshot identifying contaminants, sources, and extent of contamination in select zones over a short time period. We did not sample in seasons outside of summer, or under conditions with stormwater runoff. In addition, we did not sample for such potentially important characteristics as total and methylmercury, asbestiform mineral fibers, and alpha and beta radioactivity. Several other sites that we did not sample might also provide insights into sources and contaminants in the zone, including additional Iron River sites between Sunset Creek and the 7^{th} Ave. bridge, additional Iron River sites near waste rock zones upstream of the Dober discharge, the stream/ditch northwest of Bachman Park, the stream/ditch at N River Ave. and Singler Street, and the WWTP discharge. We also did not sample groundwater or drinking water wells. We did not sample in the middle of contaminated sites either, and wildlife such as ducks may access those zones.

Although we characterized the discharges between 7^{th} and 4^{th} Avenues, we did not link them to a definite source. Those discharges may stem from a header pipe diverting groundwater on the north side of Franklin Street and the groundwater gradient may flow downhill towards that zone from possible mining areas (Stuart *et al*. 1948). The Mineral Hills area mines apparently stopped pumping water to the west (Sunset Creek) in the 1970's or 1980's and it is possible that groundwater rebound since then is leading to mine water discharge in the Franklin Street area that then flows out the 7^{th}-4^{th} Ave pipes. Recent flooding from groundwater has happened south of Franklin Street at Jackson and 8^{th} Ave (MI DEQ 2016). The sulfate concentrations in the water in those pipes are a potential indication of mine influence. Uraninite was also known from the Sherwood Mine as well as the Buck Mine (James *et al*. 1968), and the 7^{th}-4^{th} Ave discharges had significant uranium in our water samples. Further work could assess the source of the nitrate present in those discharges, and also use the sulfate to specific conductance ratio or patterns of REE concentrations (relatively low cerium) to relate potential sources to the pipe discharges.

Conclusion

This study has provided new information on water quality and contaminant sources in the Iron River system. It appears to be the first documentation of water quality in the discharge from the 7th-4th Ave pipes or Baker Creek, and the first to use sector-field ICP-MS to detect low concentrations of contaminants in this zone. In addition, information was previously lacking for several contaminants (e.g. cobalt, selenium, and uranium) for several outfalls and Iron River sites, and recent information was lacking for others (e.g. cadmium and thallium at Dober). This study estimated the extent of contamination for the first time since the 1970's, and suggested that mine-related contamination remains extensive and incompletely remediated to this day.

5. ACKNOWLEDGEMENTS

Esteban Chiriboga, Steve Ventura, and Jim Hurley helped with the planning and implementation of this work. We thank Emma Cassidy for her invaluable assistance with the field work. We are also grateful to Michael Golas, John Reed, Rick Shelthrow, and Richard Sloat for documents and orientation on the Iron River watershed, and Megan McConville, Chris Worley, Alex Liu, and Jacqueline Mejia for their insights on ion chromatography. For facilitating the trace element analysis at the Wisconsin State Laboratory of Hygiene, we thank Pat Gorski, Pam Skaar, and Martin Shafer. We are appreciative of the support of the staff of the Great Lakes Indian Fish and Wildlife Commission, and the Nelson Institute for Environmental Studies, the Land Information and Computer Graphics Facility, and the Department of Soil Science of the University of Wisconsin-Madison, in particular Dan Capacio, Tom McClintock, and Math Heinzel. For information that was helpful for planning our methods, we are grateful to Joe Duris. This work was possible through the support of the Great Lakes Indian Fish and Wildlife Commission, an EPA STAR Fellowship, and a University of Wisconsin-Madison Graduate School Student Research Travel Grant.

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7. APPENDIX A. Temporal trends figures

Data from this study and from MI DEQ Discharge Monitoring Reports, the MI SWIMS database (http://www.mcgi.state.mi.us/miswims/), Wagner 1963, Galbraith 1965, Willson 1973, Riley 1975, Johnson & Frantti 1978, Woods & Buda 1980, White 1983, Sayles 1989, Butler 1997, Butler 1999a,b,c,d,e, Butler 2000a,b,c,d,e,f,g,h, Butler 2001a,b,c,d,e, Butler 2002, Premo *et al*. 2005, PolyOne Corporation 2008, Weston Solutions 2009, Conroy 2012, Taft 2012a,b, and Richard Sloat unpublished data from 2014.

Specific Conductance

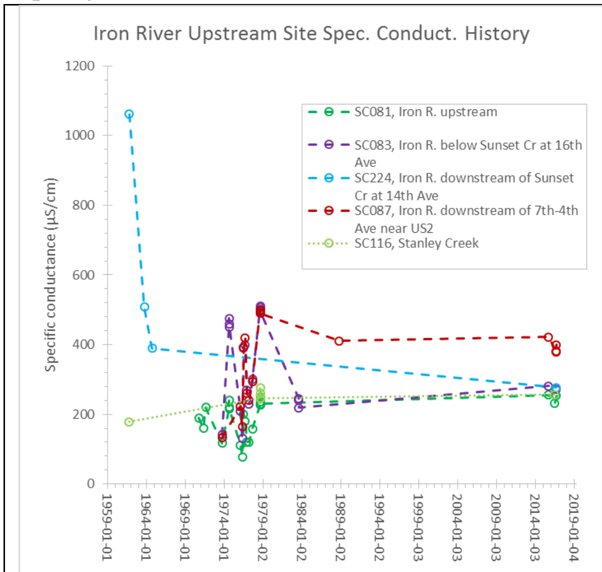


Fig. A-1. Iron River sites between Sunset Creek and 7th Ave. demonstrated lower specific conductance in recent years than in the 1960's (SC224) and 1970's (SC083), but the site downstream of 7th-4th Ave (SC087) has not changed greatly (< 30%) in specific conductance since high measurements in the 1970's. Specific conductance at the upstream Iron River reference site (SC081) and Stanley Creek site (SC116) was within the historical range from the 1960's and 1970's. Certain historical data may have been of conductivity, not specific conductance. Specific conductance at SC081 was also 201 µS/cm in ca. 2000 and SC083 was 246 µS/cm in ca. 2000 (Bond 2001).

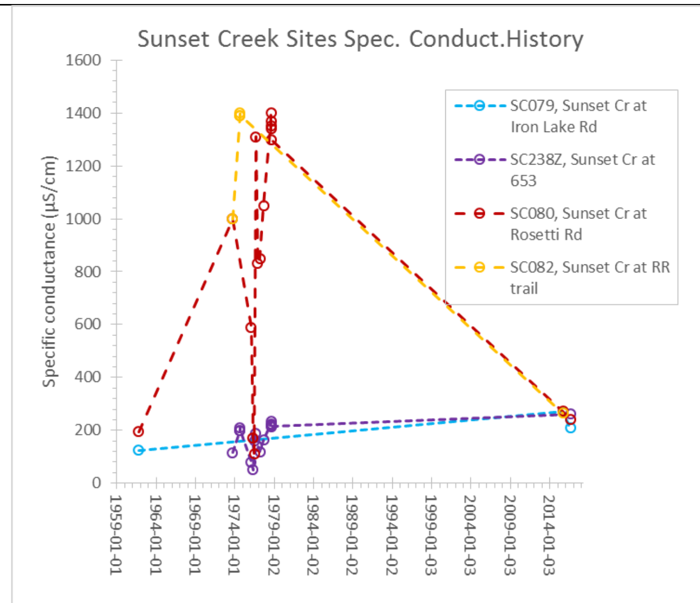
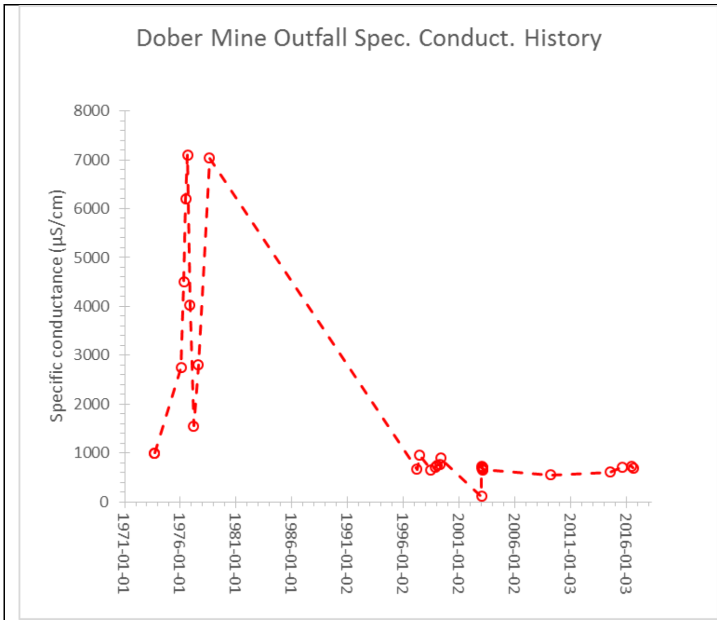


Fig. A-2. Sunset Creek sites (SC080, SC082) downstream of the former discharge zone from the former Homer-Wauseca/Sherwood mine discharges demonstrated high specific conductance in the 1970's but lower specific conductance in recent years and in 1961 (SC080). At the site upstream of there (SC238Z), measurements were < 8% greater in 2016 than in 1973. Measurements at SC080 and SC082 exceeded 1000 µS/cm but we displayed 1000 µS/cm as the measurement. Certain historical data may have been of conductivity, not specific conductance.



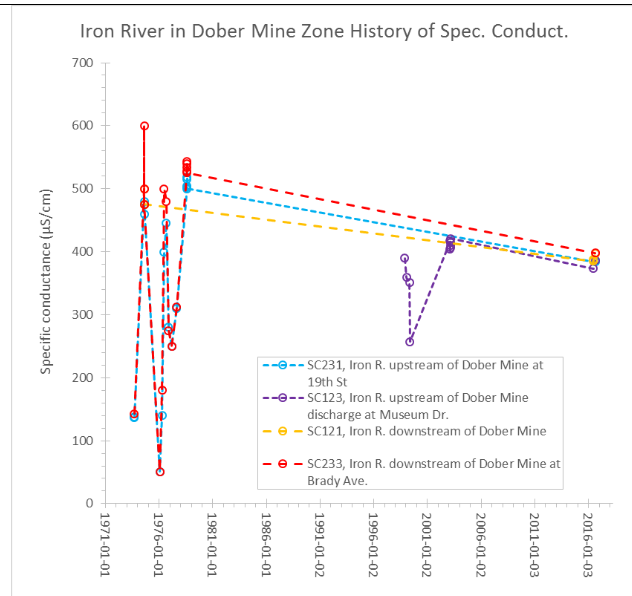
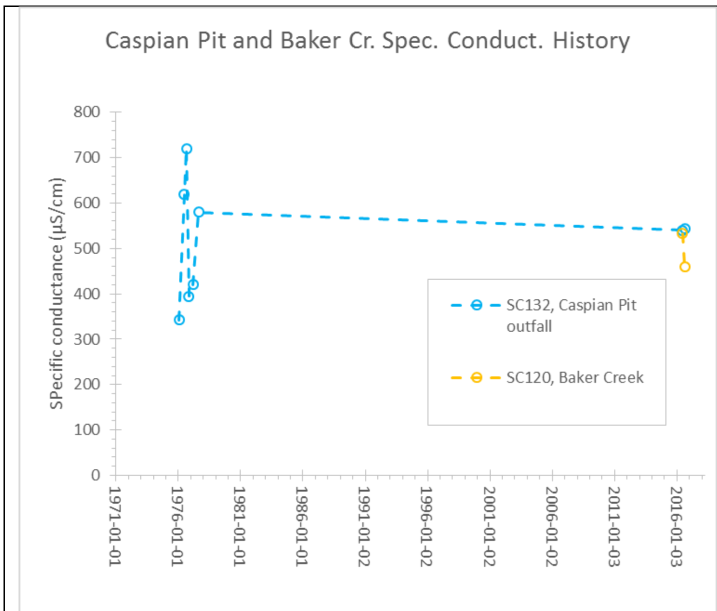


Fig. A-3. The Dober Mine discharge was lower in specific conductance in recent years than in the 1970's. Except for one low measurement in January 2003, however, all measurements remained greater than 550 µS/cm between 1997 and 2016. Certain historical data may have been of conductivity, not specific conductance.

Fig. A-4. Iron River sites upstream and downstream of the Dober Mine discharge were within the historic range of specific conductance. Certain historical data may have been of conductivity, not specific conductance. Specific conductance at SC233 was also 405 µS/cm in ca. 2000 (Bond 2001).



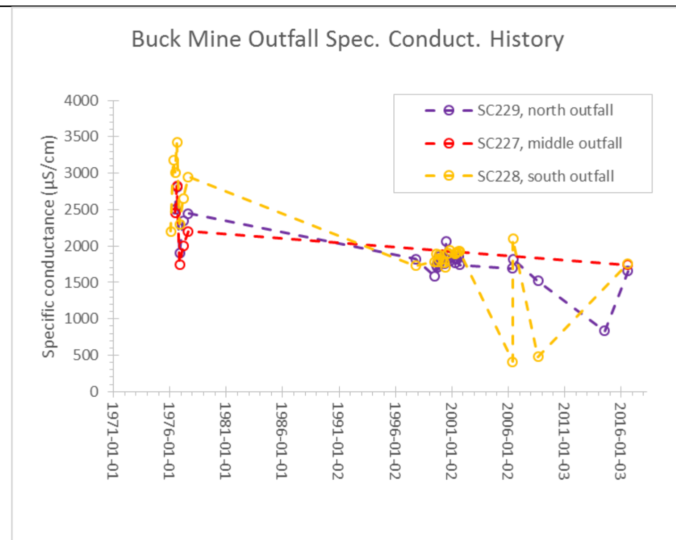


Fig. A-5. The Caspian Pit outfall demonstrated specific conductance within the historic range of 1976-1977. Certain historical data may have been of conductivity, not specific conductance.

Fig. A-6. The Buck Mine outfalls in recent years were lower in specific conductance than measurements from 1976-1977, but remained within the range of values measured in 1997-2008 (SC228 and SC229). Certain historical data may have been of conductivity, not specific conductance.

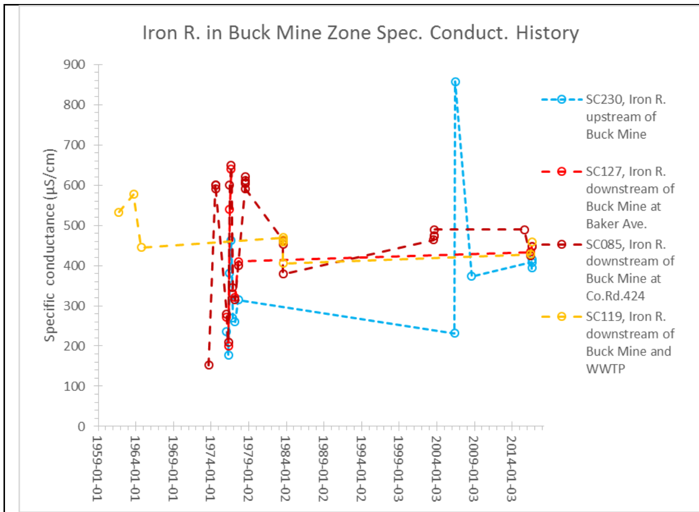


Fig. A-7. Specific conductance at Iron River sites upstream and downstream of the Buck Mine outfalls in recent years remained within the range of historical values. The upstream site (SC230) was lower in specific conductance than downstream sites when data were from the same dates. Certain historical data may have been of conductivity, not specific conductance. Specific conductance at SC119 was also 445 µS/cm in ca. 2000 (Bond 2001).

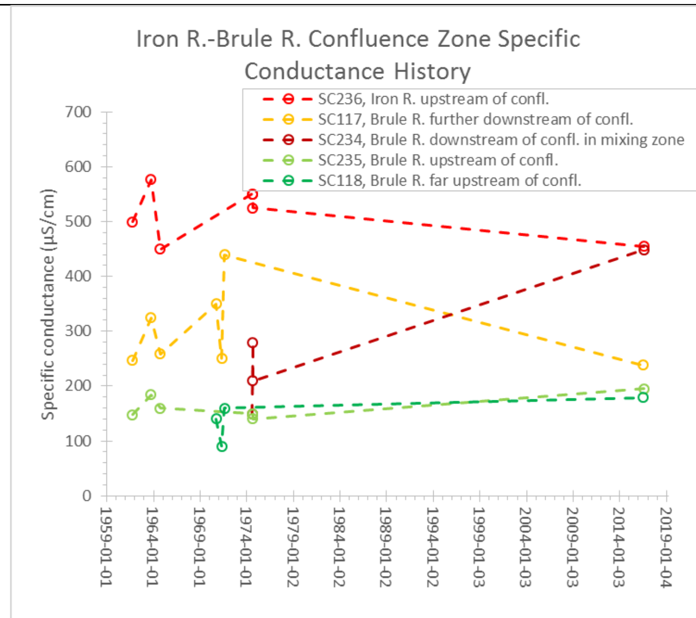


Fig. A-8. Specific conductance was consistently lowest at Brule River upstream reference sites (SC235 and SC118) and highest in the Iron River upstream of the confluence (SC236). Specific conductance was within the historical range only for the Iron River site (SC236) upstream of the confluence with the Brule River. The upstream Brule River were higher in specific conductance in 2016 than the maximum historical data by < 15 %, and the site downstream of the confluence (SC117) was lower than the historical minimums by < 4 %. The mixing zone site of SC234 was higher in specific conductance in 2016 than in 1974.

pH

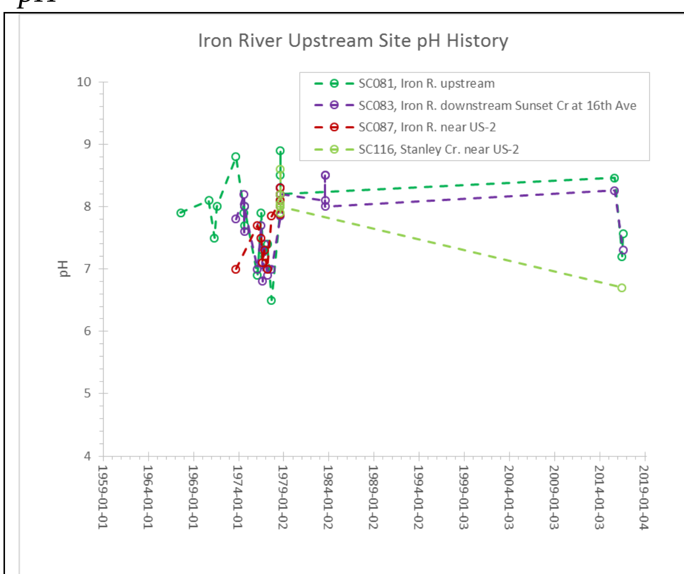


Fig. A-9. Upstream Iron River sites had pH measurements in 2015-2016 that were within the range of historical measurements. No pH was below 6.5 SU. No site had a consistently higher or lower pH than the other sites.

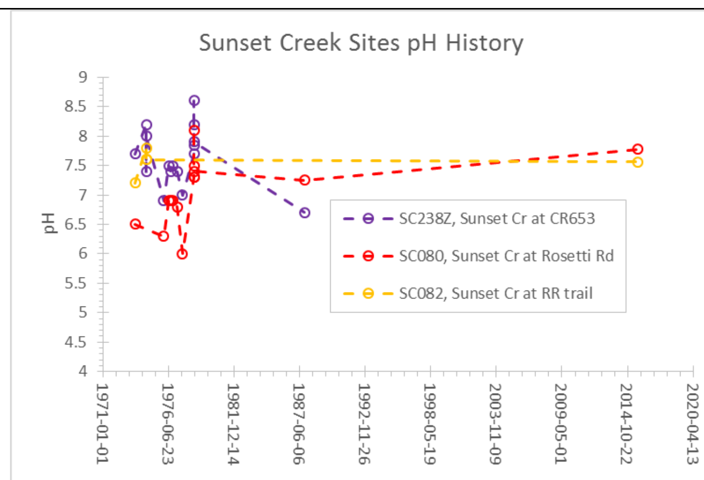


Fig. A-10. Sunset Creek site pH measurements in 2015-2016 were within the range of historical measurements. The lowest historical pH was 6.0 in 1977 at SC080. In the 1970's, SC080 had a lower pH than did the other two sites.

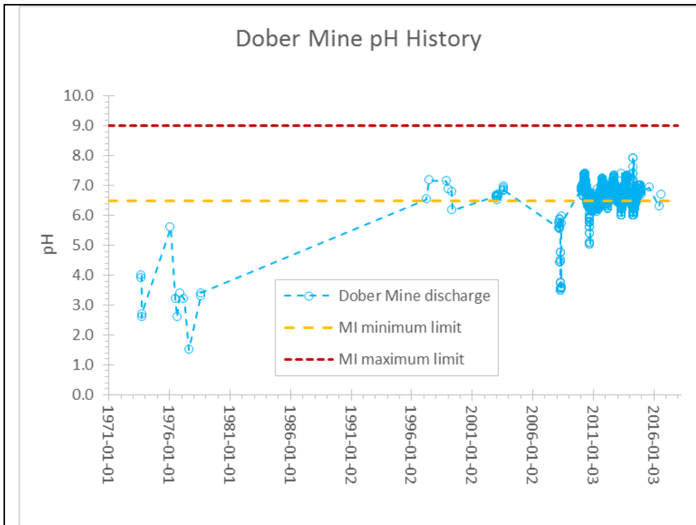


Fig. A-11. Dober Mine pH measurements in 2015-2016 were within the historical range of the last 10 years but in June 2016 was below 6.5 SU. Measurements of pH below 5 SU occurred in the 1970's and in 2008. Measurements of pH below 6.0 SU, the permit limit until the DEQ lowered it to 5.5 in 2014, occurred in the 1970's, 2008, and 2010.

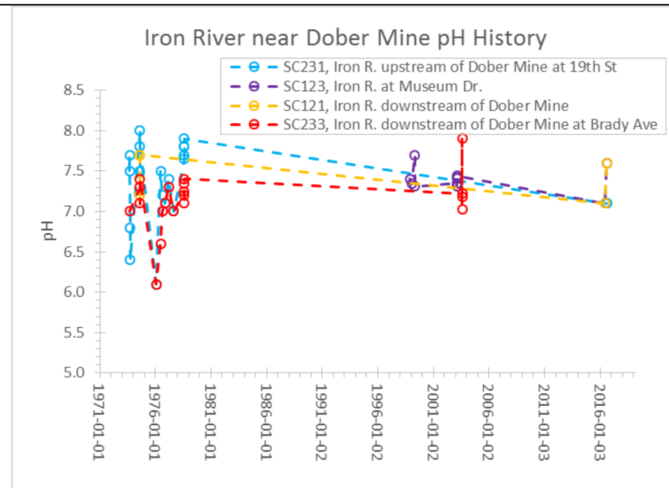


Fig. A-12. Iron River sites downstream of the Dober Mine had lower pH measurements than upstream sites in the 1970's. Measurements in 2015-2016 were within the historical range for the respective sites.

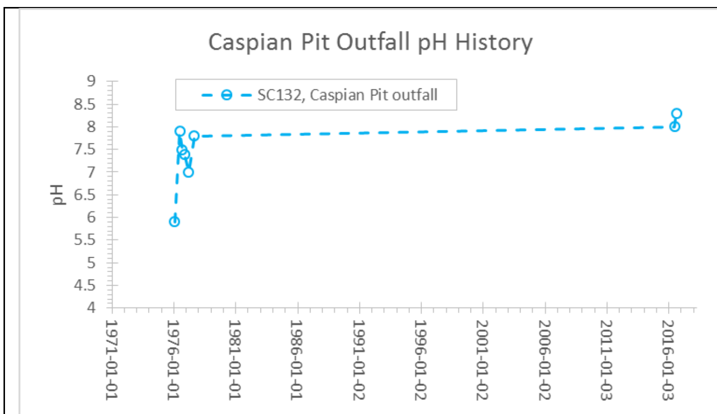


Fig. A-13. The Caspian Pit outfall had a higher pH in 2016 than it did in the 1970's.

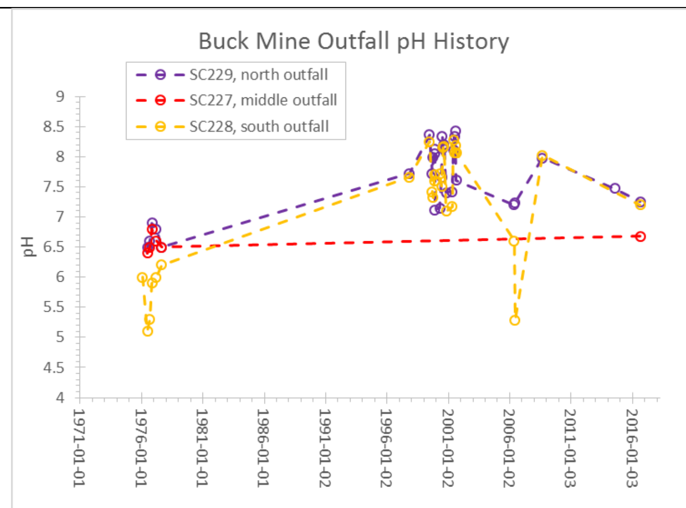


Fig. A-14. Buck Mine outfall pH measurements in 2016 were within the historical range for the respective sites. The south outfall had a lower pH than the others in the 1970's, but the middle outfall had a lower pH than the others in 2016. The pH dropped below 5.5 in the 1970's and in 2006.

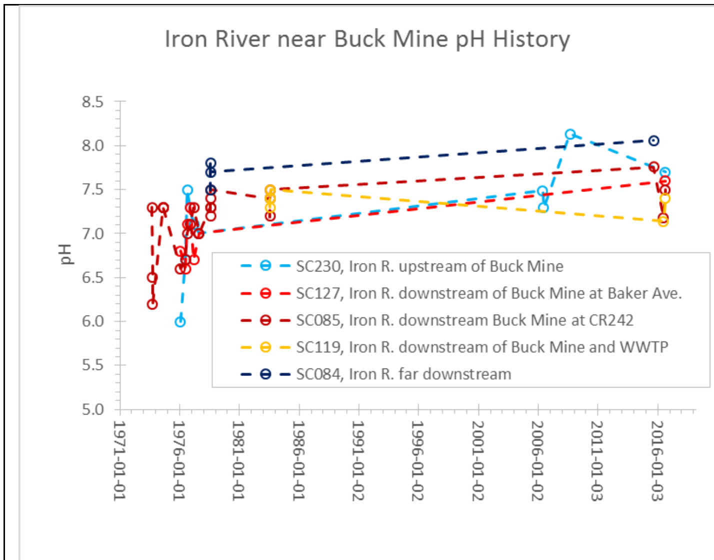


Fig. A-15. Measurements of pH in 2015-2016 were within the historical range for SC230 upstream of the Buck Mine and SC119 downstream of the Buck Mine and the WWTP, but measurements were greater in 2015-2016 than in earlier years for the other sites downstream of the Buck Mine. The pH at SC084 far downstream was higher than at other sites when measured on the same date.

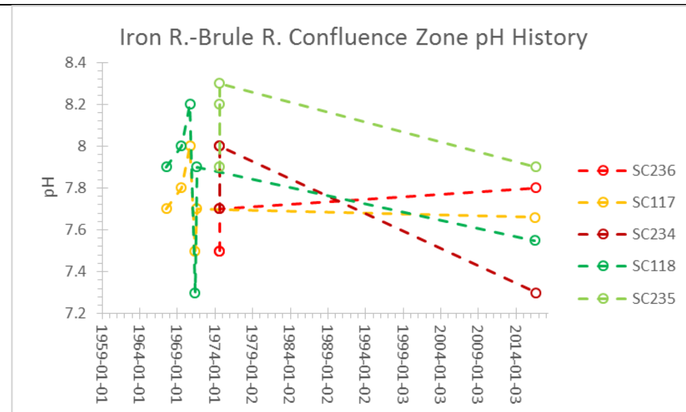


Fig. A-16. Around the confluence of the Iron River and the Brule River, 2015-2016 pH measurements were within the historical range except for the Iron River site (SC236), which had a higher pH than in the 1970's, and the mixing zone site (SC234), which had a lower pH than in the 1970's. The Brule River site immediately upstream of the confluence (SC235) had a pH consistently higher than at the other sites when measured on the same date.

Chloride

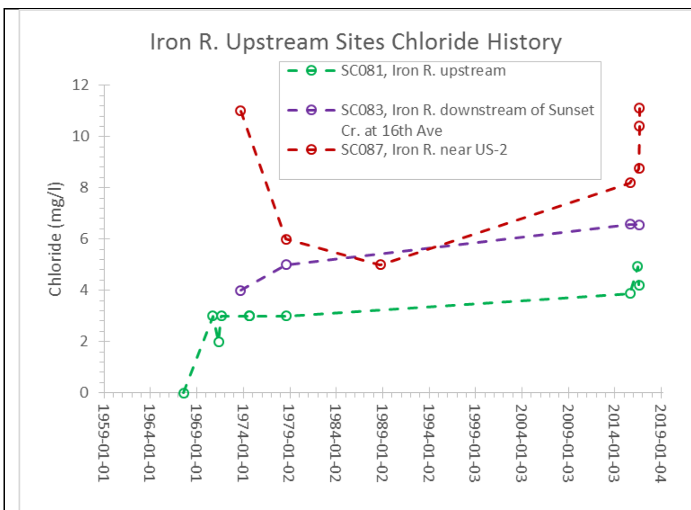


Fig. A-17. Chloride concentrations were less than 12 mg/l at upstream Iron River sites. Chloride concentrations have increased over time at all three sites, but decreased between 1973 and 1988 near US-2 (SC087), a site apparently downstream of a former WWTP. When measured on the same dates, concentrations were greatest at SC087 and lowest at SC081.

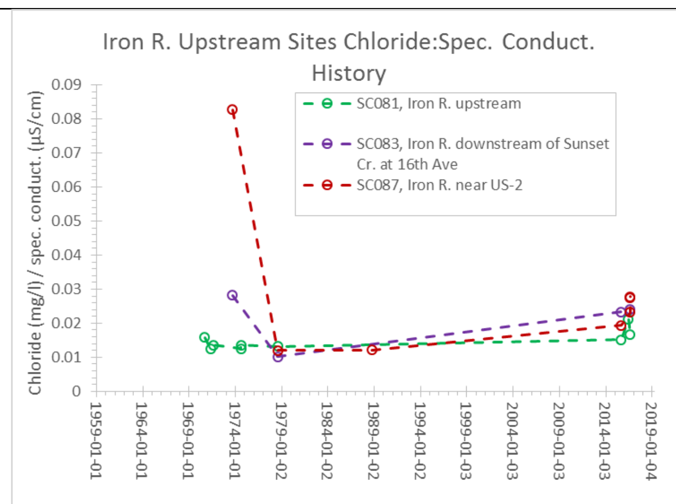
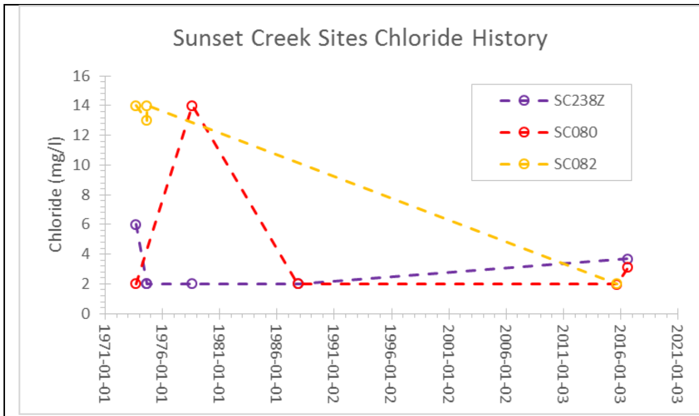


Fig. A-18. The ratio of chloride to specific conductance remained relatively constant at the upstream Iron River site (SC081). The ratio declined between 1973 and 1978 at sites downstream of Sunset Creek (SC083 and SC087) before increasing by < 30% between 1978 and 2015-2016.



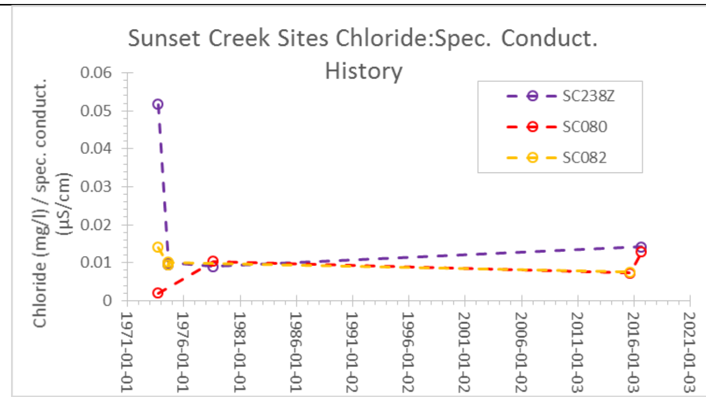
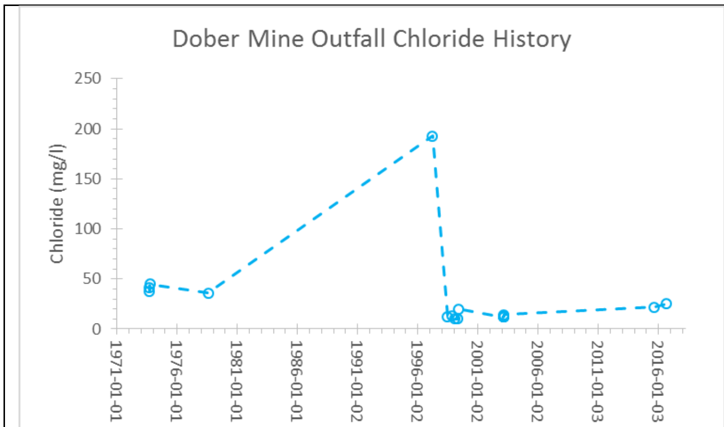


Fig. A-19. Chloride concentration were less than 15 mg/l at Sunset Creek sites. 2015-2016 concentrations were with the historical ranges except for SC082, where concentrations were lower than in the 1970's.

Fig. A-20. The ratio of chloride to specific conductance remained relatively constant in Sunset Creek except at the upstream site (SC238Z), where the ratio decreased between 1973 and 1974.



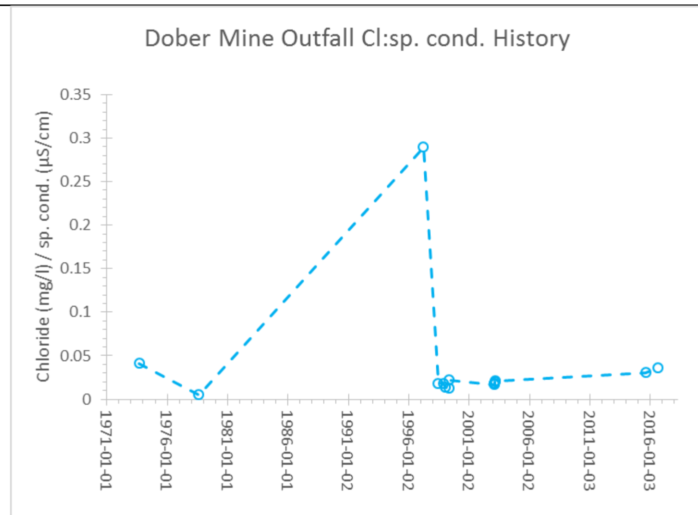
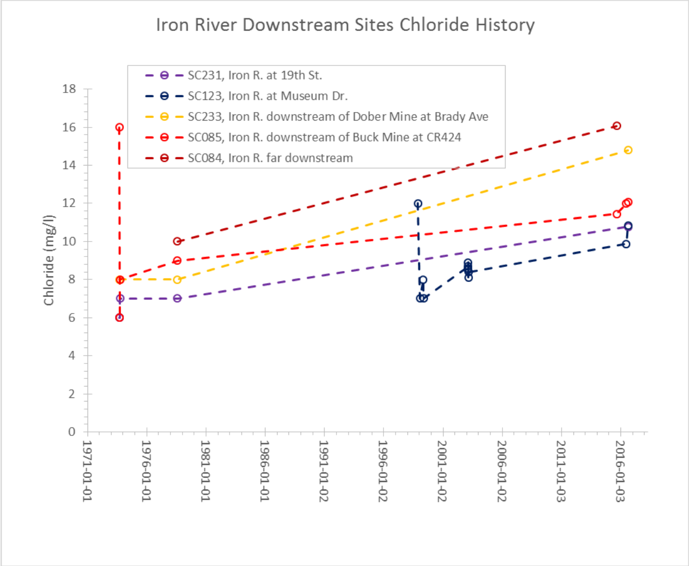


Fig. A-21. In the Dober Mine outfall, chloride was less than 50 mg/l except for a measurement of 193 mg/l in 1997. 2015-2016 measurements were within the historical range.

Fig. A-22. The ratio of chloride to specific conductance in the Dober Mine outfall demonstrated a pattern comparable to that of the concentration of chloride.



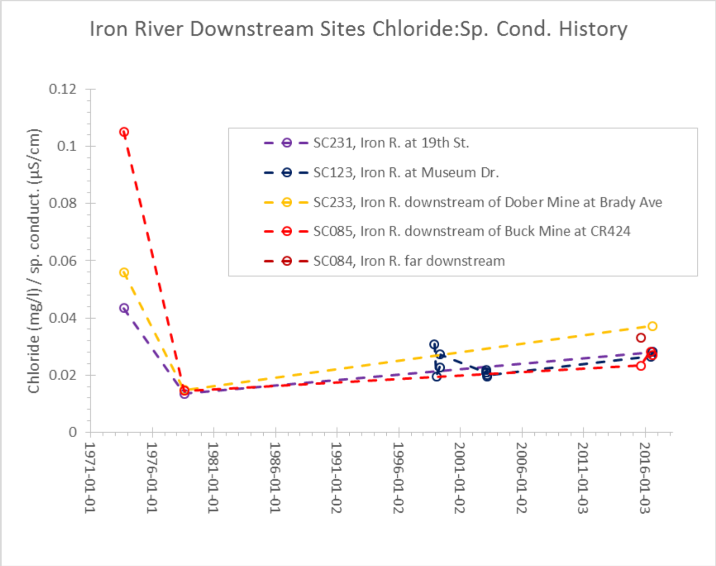
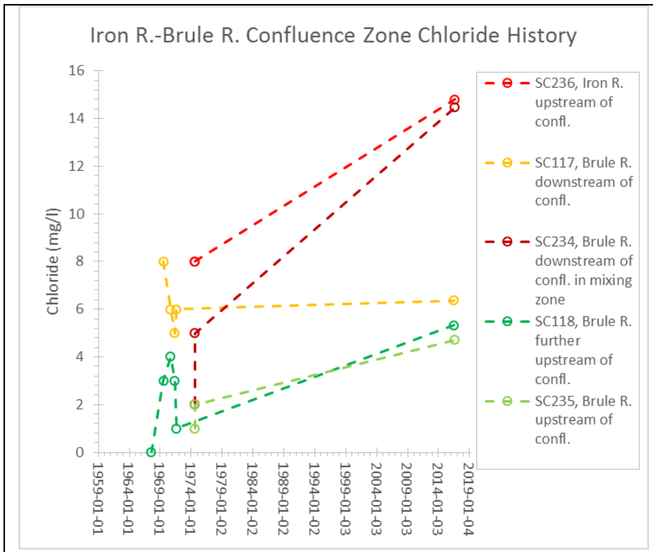


Fig. A-23. Downstream Iron River sites demonstrated chloride concentrations less than 17 mg/l. Concentrations increased over time except for decreases at Museum Dr. (SC123) in 1973, and decreases downstream of the Buck Mine (SC085) in 1998-1999. 2015-2016 concentrations were greater than the historical range for all but SC123 and SC085. The downstream site SC084 had chloride concentrations greater than the other sites when measured on the same date.

Fig. A-24. The ratio of chloride to specific conductance decreased between 1973 and 1978 at all three Iron River sites measured during that time. 2015-2016 ratios were within the historical ranges but greater than in 1978.



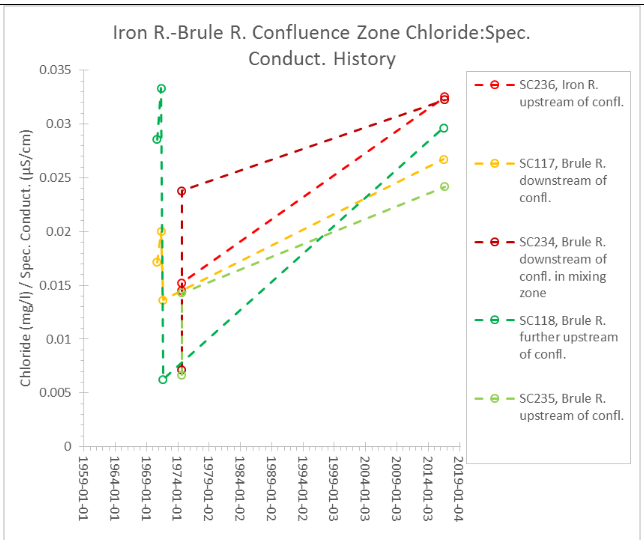


Fig. A-25. Chloride concentrations around the Iron River-Brule River confluence were greater in 2015-2016 than the historical range for the Iron River (SC236), mixing zone (SC234), and Brule River (SC235) sites. The sites further upstream (SC118) and downstream (SC117) demonstrated decreases in chloride in 1969-1971. The Brule River upstream sites (SC118 and SC235) had less chloride than the other sites and the Iron River site (SC236) had more chloride than other sites when measured on the same date.

Fig. A-26. The ratio of chloride to specific conductance was greater in 2015-2016 than in the 1970's for all sites except the Brule River further upstream site (SC118).

Sulfate

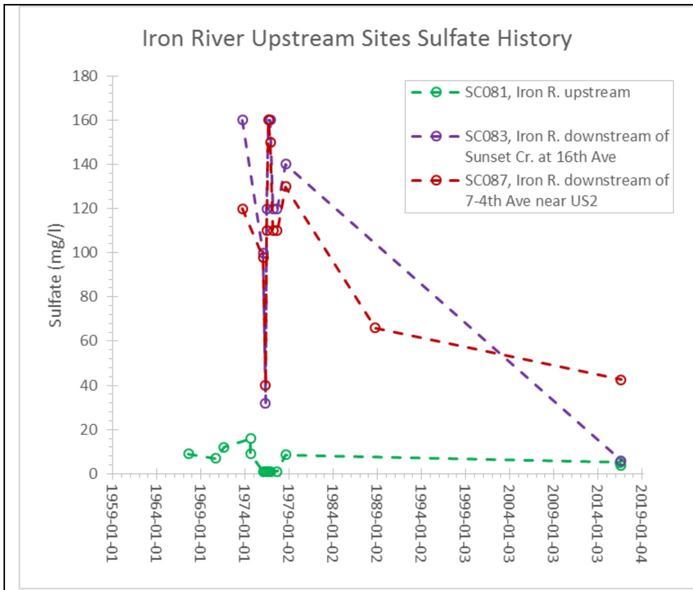


Fig. A-27. Sulfate concentrations in 2015-2016 at the upstream sites of the Iron River were within the historical range for SC081 and SC087, but were lower than the historical range for SC083. Sulfate decreased in 2016 relative to most 1970's measurements, but remained greater than 40 mg/l at SC087. In contrast, sulfate at SC083 decreased to 6 mg/l. Sulfate at the upstream site SC081 remained less than the other sites and less than 20 mg/l.

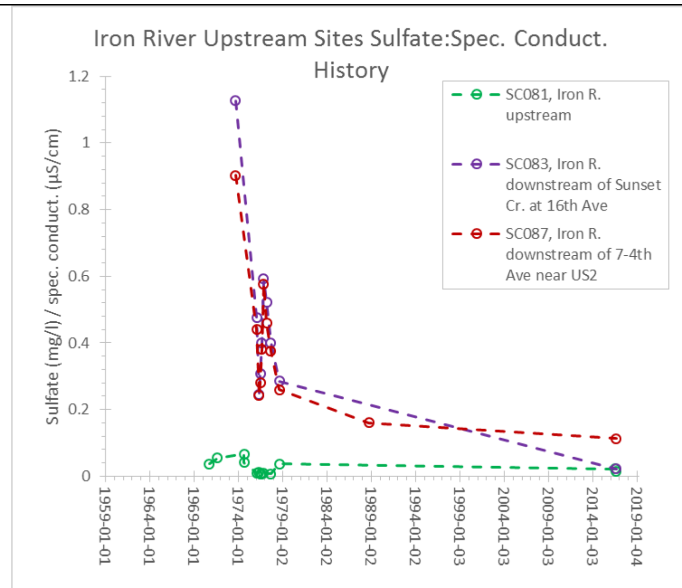


Fig. A-28. The ratio of sulfate to specific conductance in 2015-2016 was within the historical range for the SC081 reference site and decreased for the other sites since the 1970's. The ratio was < 0.03 $mg*l^{-1}*cm*\mu S^{-1}$ for SC083 in 2016, and remained < 0.07 $mg*l^{-1}*cm*\mu S^{-1}$ for SC081 in the 1970's and < 0.03 $mg*l^{-1}*cm*\mu S^{-1}$ in 2016.

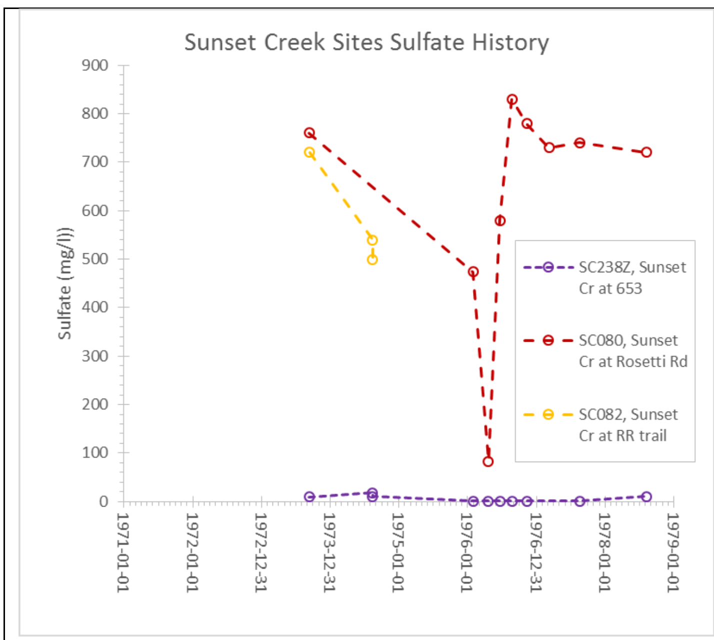


Fig. A-29. In the 1970's, sulfate concentrations in Sunset Creek was low (< 20 mg/l) at the upstream SC238Z, and greater at the other downstream sites (SC080, SC082).

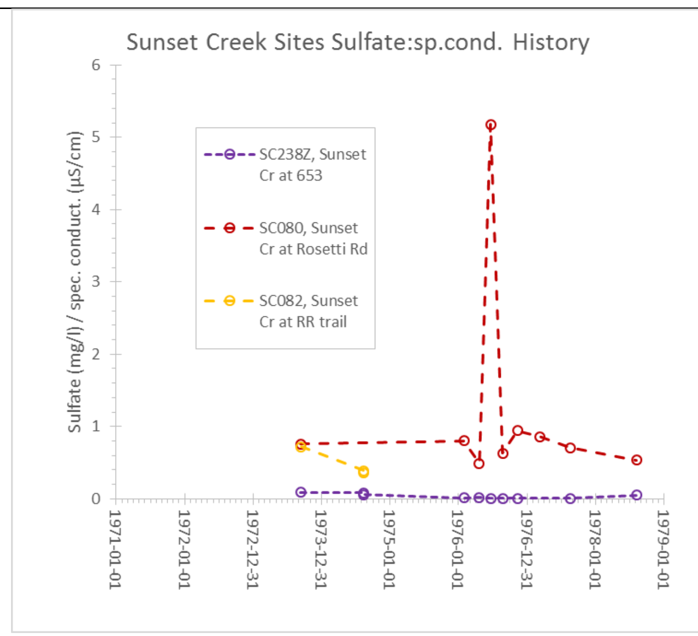


Fig. A-30. In the 1970's, the ratio of sulfate to specific conductance was low (< 0.09 $mg*l^{-1}*cm*\mu S^{-1}$) at the upstream SC238Z site, and greater at the other downstream sites (SC080, SC082).

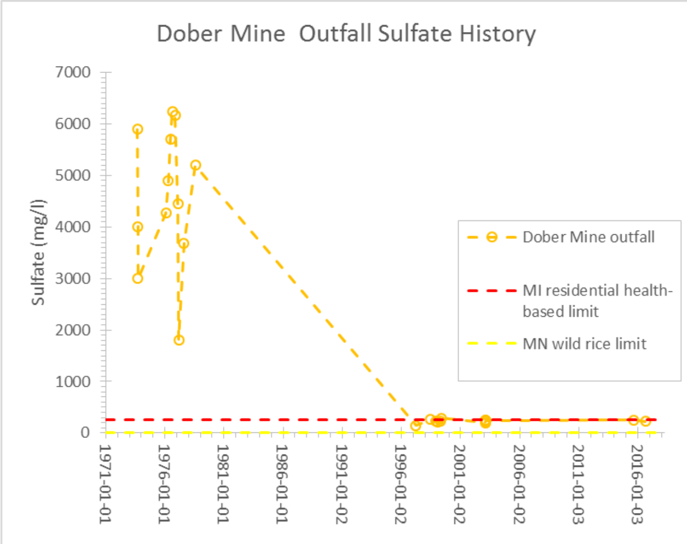


Fig. A-31. The Dober Mine outfall sulfate concentrations in 2015-2016 were within the range of values reported since the late 1990's. Those concentrations were lower than in the 1970's but remained greater than 140 mg/l and exceeded the MI residential health-based 250 mg/l criterion in the late 1990's.

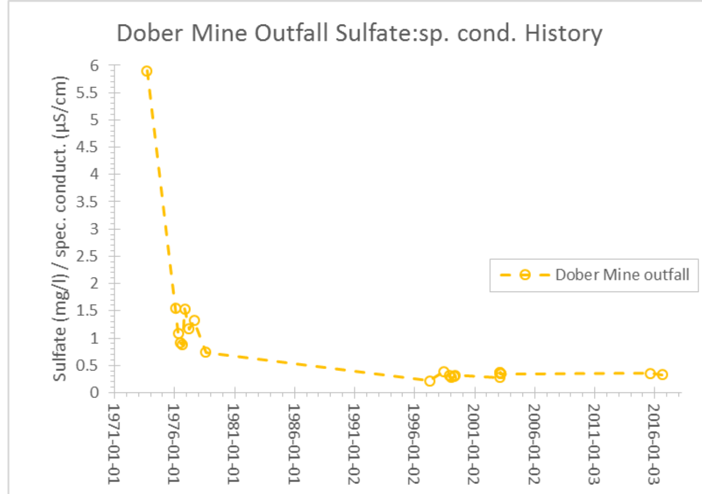


Fig. A-32. The Dober Mine outfall ratio of sulfate to specific conductance decreased since the 1990's but remained greater than 0.2 $mg*l^{-1}*cm*\mu S^{-1}$.

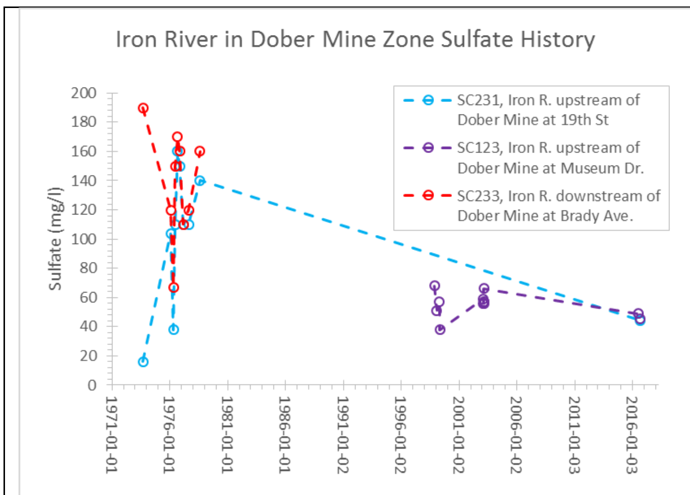


Fig. A-33. Sulfate concentrations upstream of the Dober Mine were within the historical range but lower than the values reported from the late 1970's. In the 1970's, downstream (SC233) sulfate concentrations were consistently greater than upstream (SC231) sulfate concentrations.

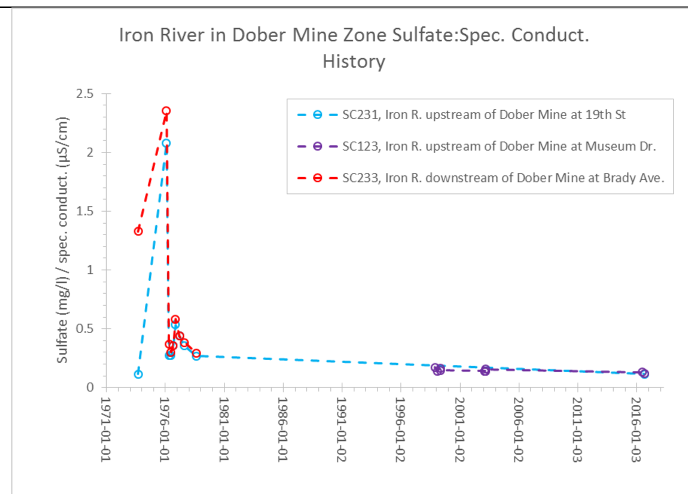


Fig. A-34. Sulfate to specific conductance ratios in the Iron River near the Dober Mine for 2016 were lower than the late 1970's (SC231) and the late 1990's (SC123). Ratios for all sites remained > 0.1 $mg*l^{-1}*cm*\mu S^{-1}$.

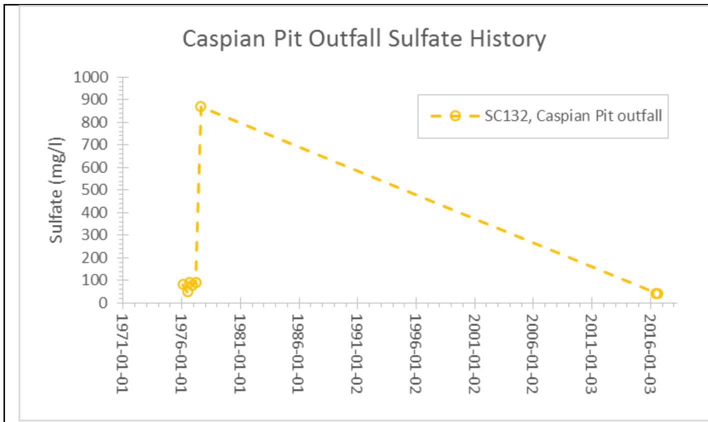


Fig. A-35. Sulfate concentrations in the Caspian Pit outfall were lower than historical measurements but remained > 40 mg/l.

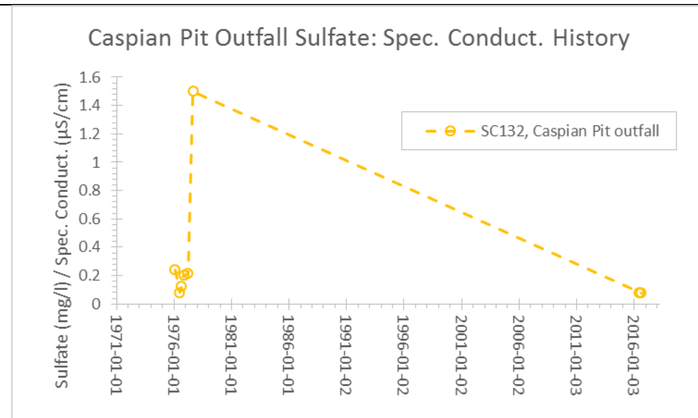


Fig. A-36. The ratio of sulfate to specific conductance in the Caspian Pit outfall was lower than historical measurements but remained > 0.07 mg*l^{-1}*cm*µS^{-1}.

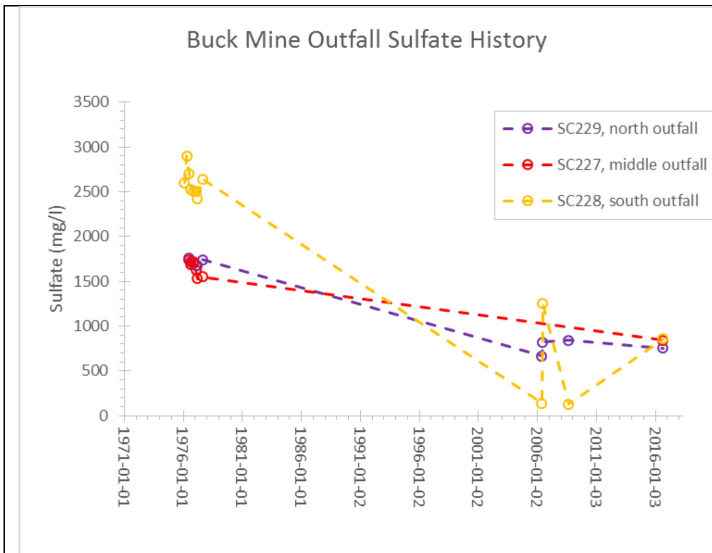


Fig. A-37. Sulfate concentrations in the Buck Mine outfall in 2016 were within the historical range, except for SC227, which demonstrated concentrations lower than in the 1970's. All measurements were > 120 mg/l.

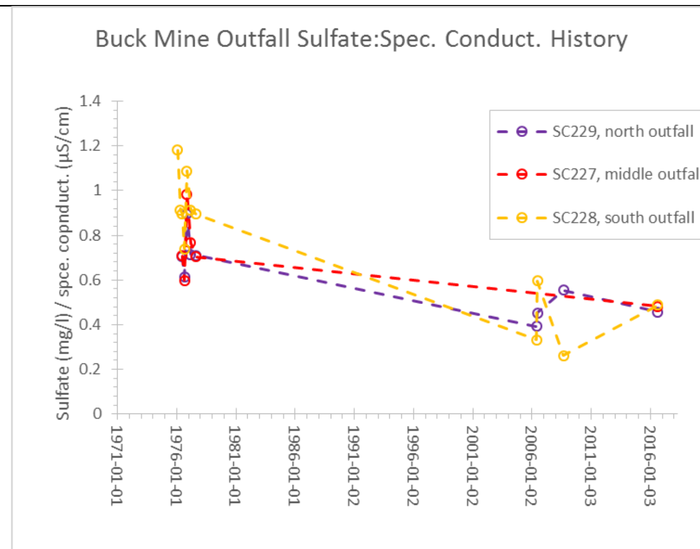


Fig. A-38. The ratios of sulfate to specific conductance in the Buck Mine outfall in 2016 were within the historical range, except for SC227, which demonstrated ratios lower than in the 1970's. All measurements were > 0.2 mg*l^{-1}*cm*µS^{-1}.

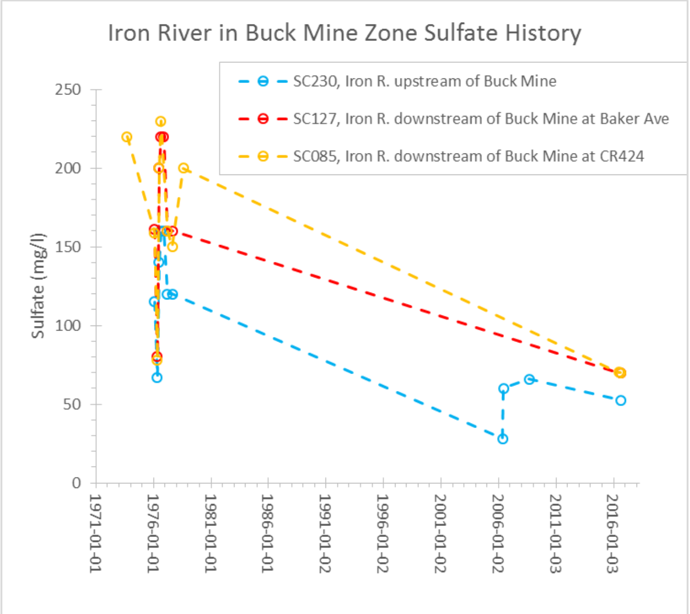


Fig. A-39. The Iron River sites near the Buck Mine outfall in 2016 were lower in sulfate than historical records, except for SC230, the sulfate of which was within the historical range. The upstream SC230 site was consistently lower in sulfate than the downstream sites when data were from the same dates, but sulfate at that upstream site remained greater than 25 mg/l.

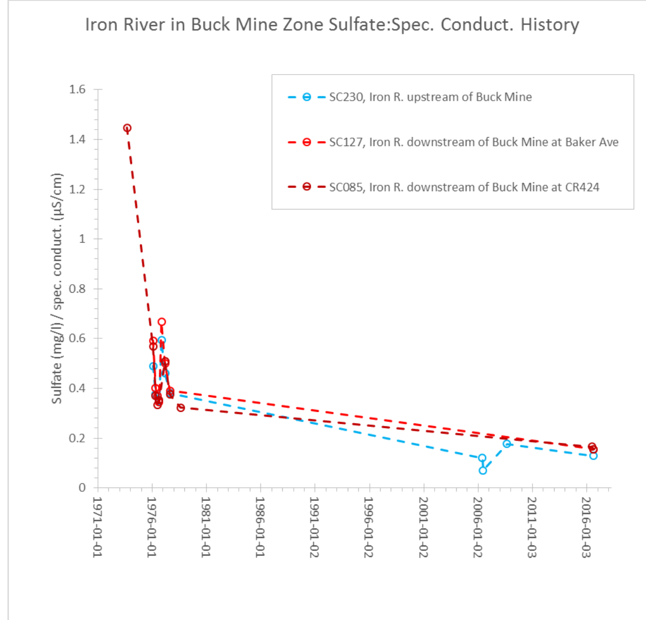


Fig. A-40. The Iron River sites near the Buck Mine outfall in 2016 were lower in the sulfate to specific conductance ratio, except for SC230, the ratio of which was within the historical range. The ratio remained greater than 0.07 mg*l^{-1}*cm*µS^{-1}

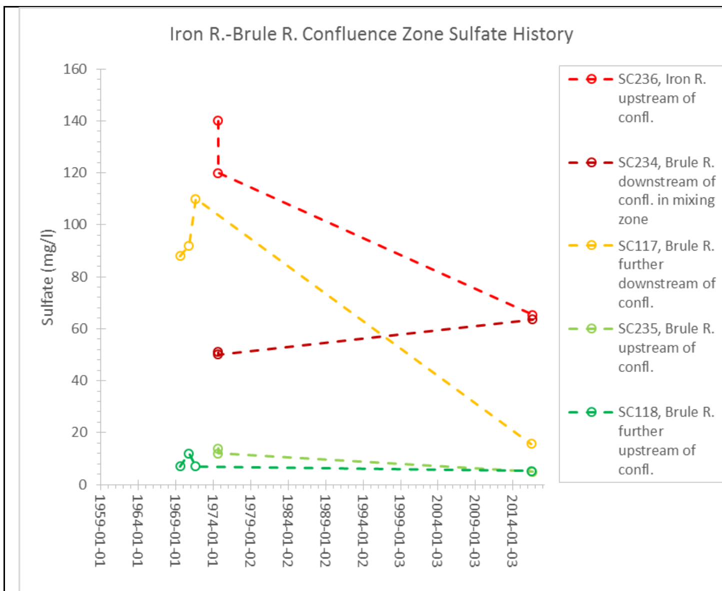


Fig. A-41. Sulfate concentrations in 2016 were lower than historical ranges for all Iron-Brule River confluence sites except for the mixing zone site (SC234), which had greater sulfate concentration in 2016 than in 1974. Upstream Brule River sites were consistently lower in sulfate than the Iron River and downstream sites.

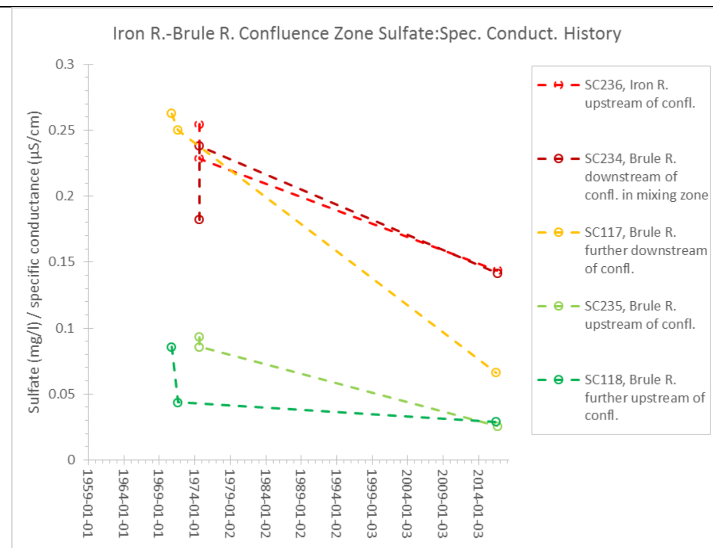


Fig. A-42. Sulfate to specific conductance ratios in 2016 were lower than historical ranges for all Iron-Brule River confluence sites. Ratios for the upstream Brule River sites were consistently lower than the Iron River and downstream sites and did not exceed 0.1 mg*l^{-1}*cm*µS^{-1} (1970's) or 0.03 mg*l^{-1}*cm*µS^{-1} (2016).

Nitrate

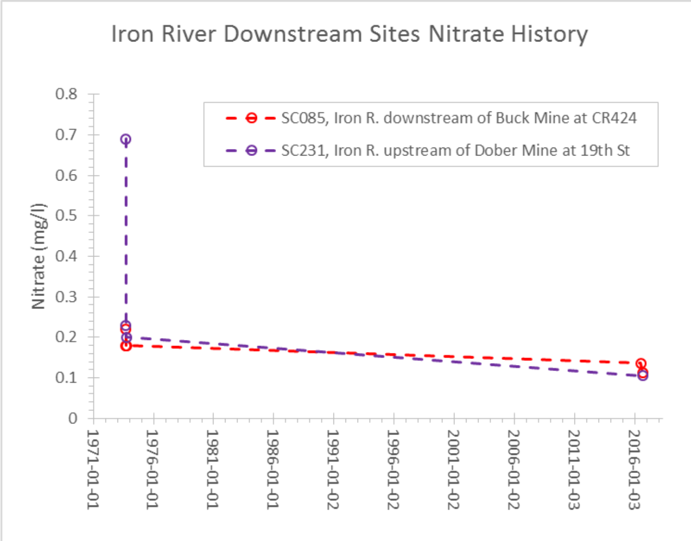


Fig. A-43. Nitrate concentrations were lower in the Iron River upstream and downstream of the Dober-Buck zones in 2016 than in the 1970's. 2016 measurements exceeded holding times.

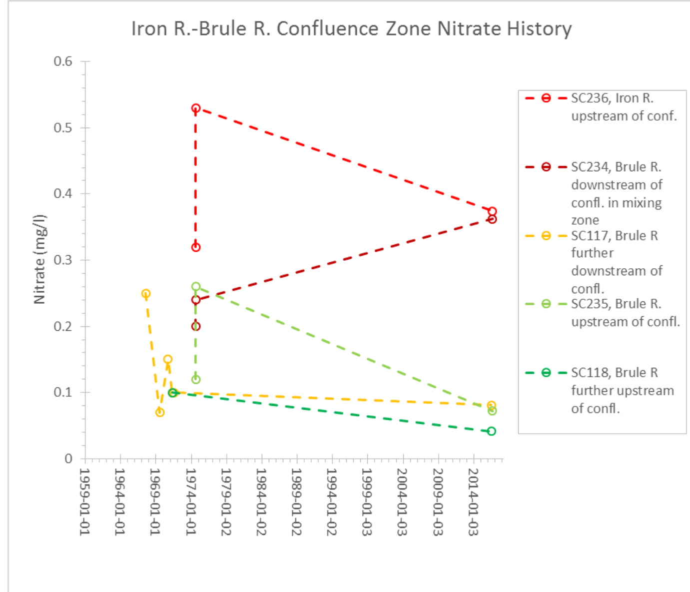


Fig. A-44. Nitrate concentrations near the Iron River-Brule River confluence were within historical ranges except for the Brule River upstream sites (SC235, SC118), for which nitrate concentrations were lower than in the 1970's. For all measured dates, the Iron River concentrations (at SC236) were greater than the concentrations at the Brule River sites. 2016 measurements exceeded holding times.

Phosphorus

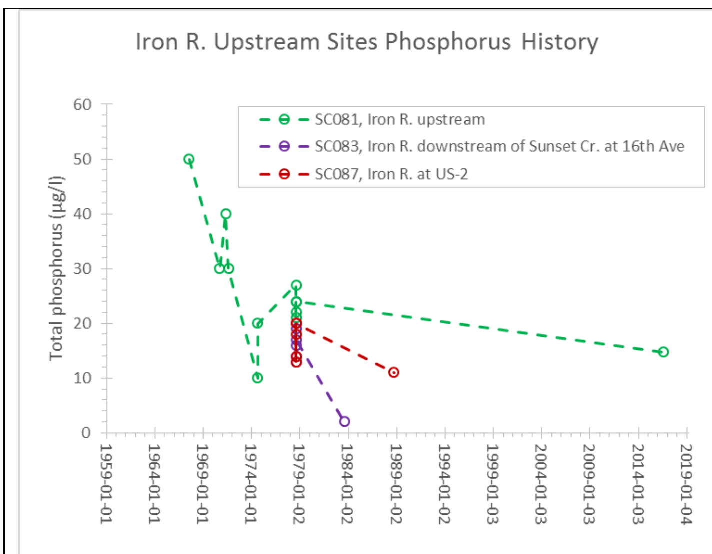


Fig. A-45. For upstream Iron River sites downstream of Sunset Creek, phosphorus concentrations were lower in the 1980's than in the late 1970's, but concentrations at SC081 in 2016 were within the historical range for that site.

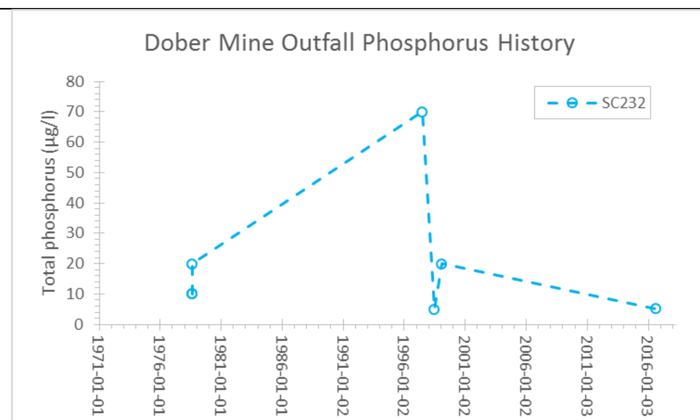


Fig. A-46. The Dober Mine outfall phosphorus concentration in 2016 was one of the two lowest concentrations of the available record. The other was actually a record in 1998 of < 10 µg/l but displayed as 5 µg/l.

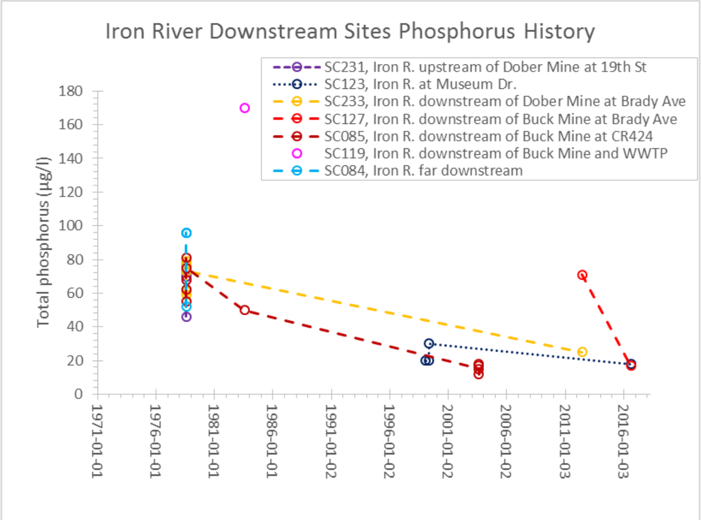


Fig. A-47. 2016 measurements of phosphorus at Iron River downstream sites were lower than historical measurements. The highest phosphorus measurement occurred at SC199, downstream of the current WWTP (and other past WWTPs) in 1983.

Manganese

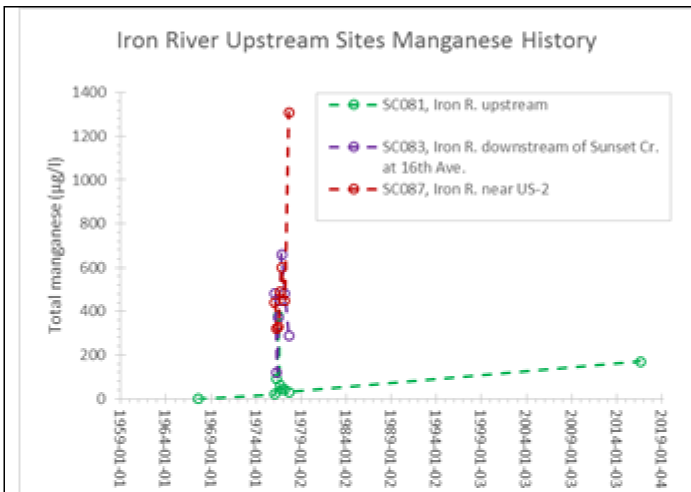


Fig. A-48. Manganese concentrations at the reference site of SC081 in 2016 were greater than in the 1960's and 1970's. Manganese concentrations at SC083 and SC087 were greater than those at the SC081 reference site in the 1970's. The maximum of 1310 µg/l occurred at the location of SC087 in 1977.

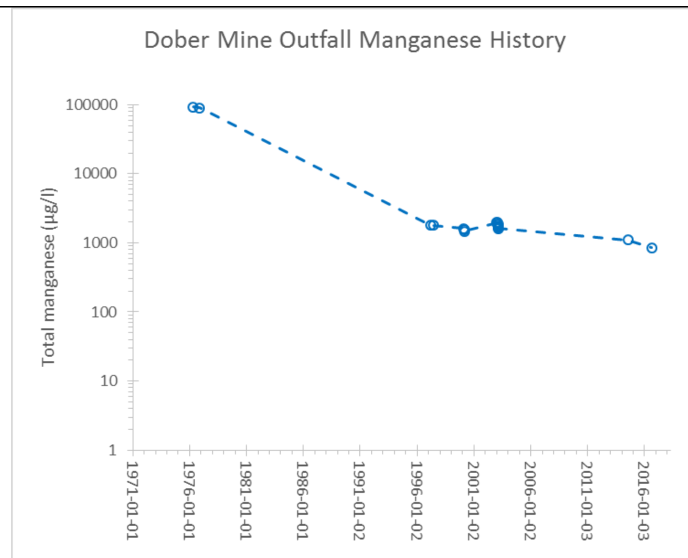
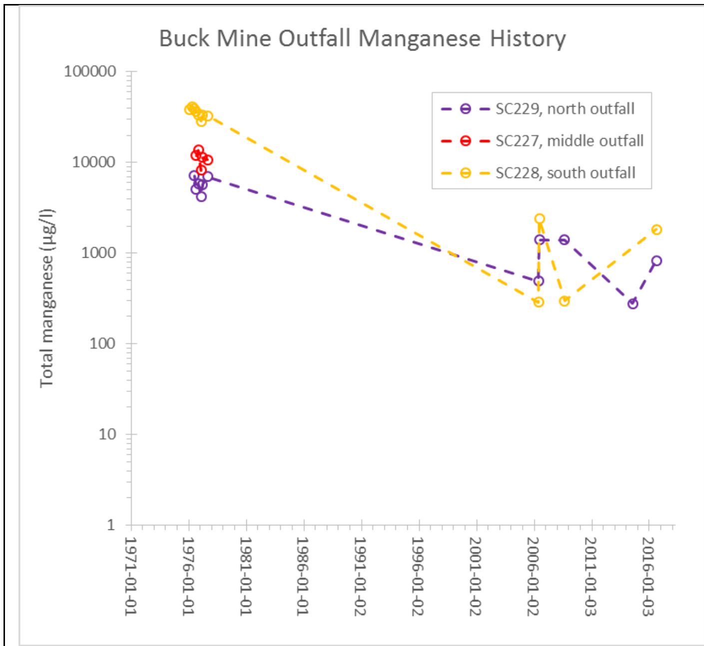


Fig. A-49. Manganese at the Dober Mine outfall was lower in 2016 than in previous years, but remained > 800 µg/l. Dependent axis is on $\log_{10}$ scale.



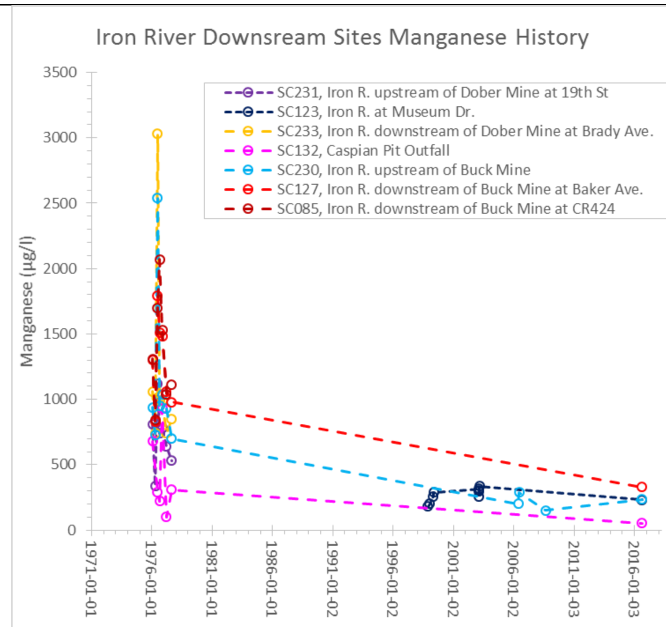
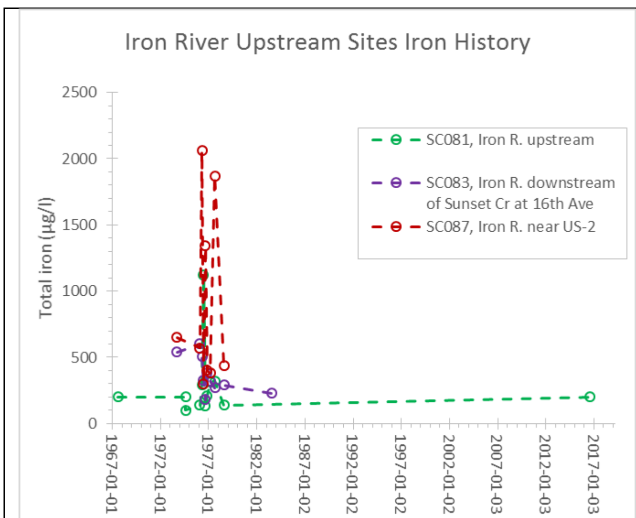


Fig. A-50. Manganese in the Buck Mine outfalls in 2016 was within the range of values reported since 2006. That range was lower than the values from the 1970's. Measurements have remained > 280 µg/l. Dependent axis is on $\log_{10}$ scale.

Fig. A-51. Manganese in measured downstream Iron River sites in 2016 was lower than in the 1970's, but within the historical range from the past 20 years for SC123 and SC230. Manganese in the Caspian Pit outfall has remained lower than at other sites, and manganese upstream of the Buck Mine (SC230) has remained lower than downstream (SC127) for all but June 1976, when measured on the same dates. Manganese at these sites was greater than 50 µg/l for all reported data and was greatest at SC233 in June 1976 (3030 µg/l).

Iron



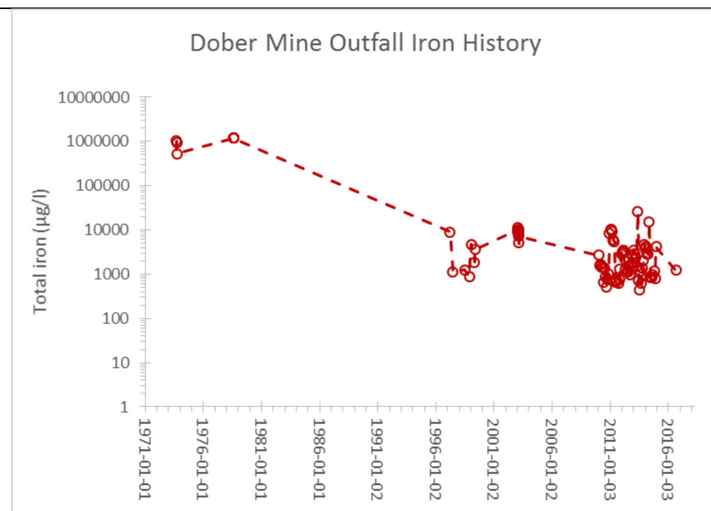


Fig. A-52. Total iron at the SC081 reference site in 2016 was within the historical range for that site. This site was lower in total iron than most measurements for the Iron River sites downstream of Sunset Creek in the 1970's and early 1980's, except for a high value in June 1976.

Fig. A-53. Total iron at the Dober Mine outfall in 2016 was within the range of measurements from the previous 10 years. Those values were lower than those from the 1970's. Dependent axis is on $\log_{10}$ scale.

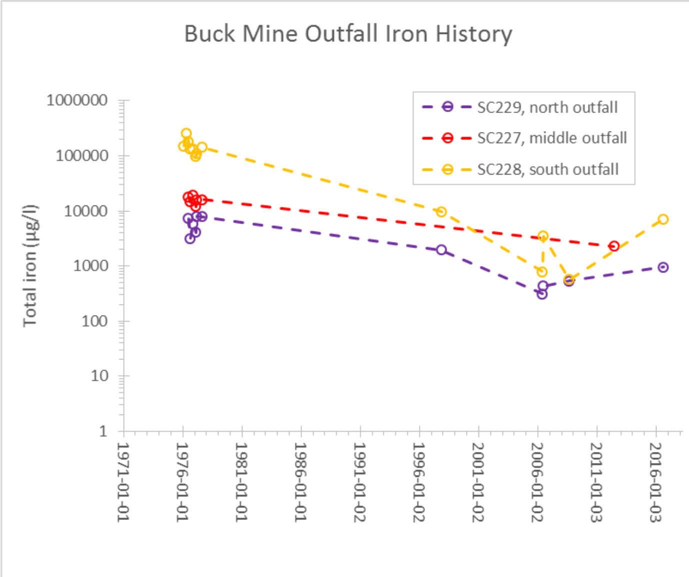


Fig. A-54. Total iron in the Buck Mine outfalls in 2016 was within the range of measurements from the previous 10 years. The south outfall (SC228) has had higher concentrations than the north outfall (SC229). Within a given outfall series, concentrations were greater in the 1970's than measurements since the 1990's. Dependent axis is on log_{10} scale.

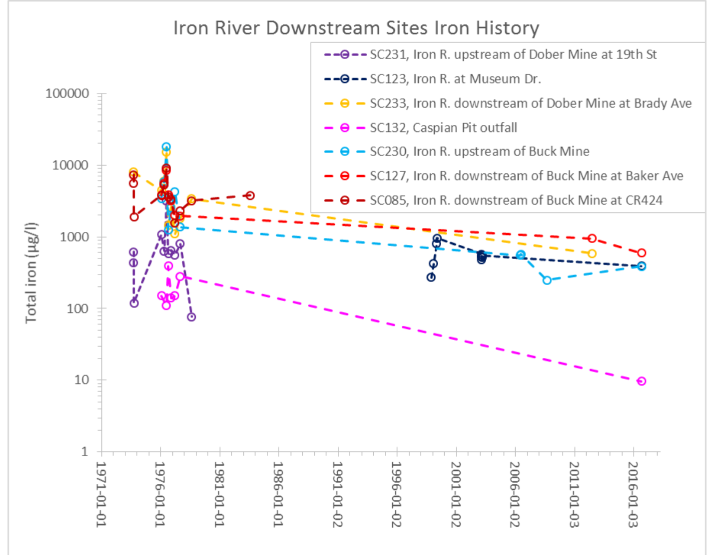


Fig. A-55. Total iron concentrations at downstream Iron River sites and in the Caspian Pit outfall were lower in 2016 than the historical range. The site upstream of the Dober Mine was lower in iron in the 1970's than the site downstream (SC233). Dependent axis is on log_{10} scale.

Nickel

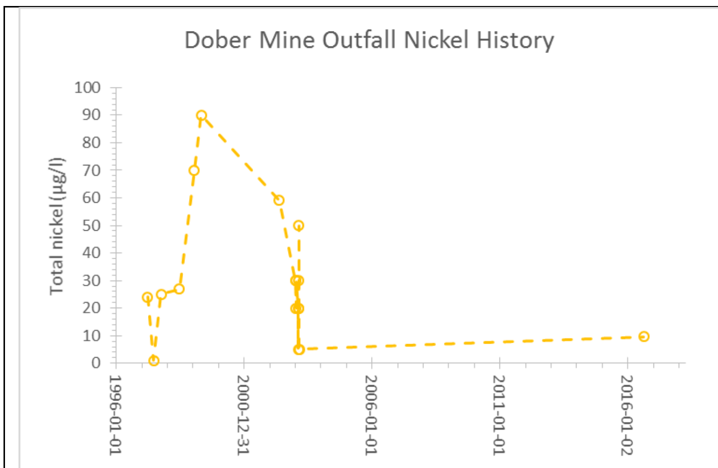


Fig. A-56. The Dober Mine outfall nickel concentrations were lower in 2016 than for most of the historical records since 1997. The maximum concentration of 90 µg/l occurred in April 1999. Historical measurements displayed as 1, 5, and 25 µg/l were actually < double those values.

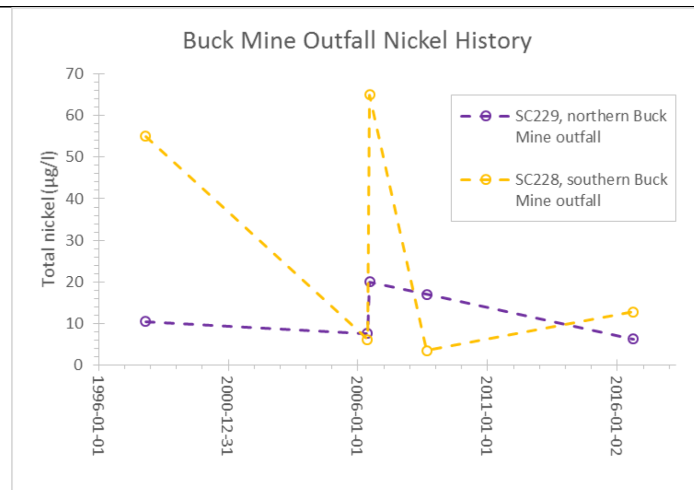


Fig. A-57. The Buck Mine outfall nickel concentrations were lower than the post-1997 historical range at the north outfall (SC229) but within the post-1997 range at the south outfall. The highest nickel concentration of 65 µg/l occurred in June of 2006.

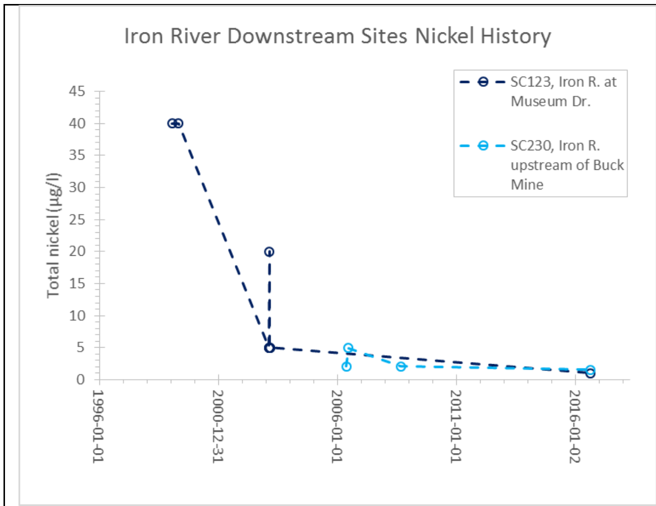


Fig. A-58. Nickel concentrations in the Iron River at SC123 and SC230 were lower in 2016 than in previous years. Measurements displayed as 5 µg/l in February 2003 were actually < 10 µg/l.

Copper

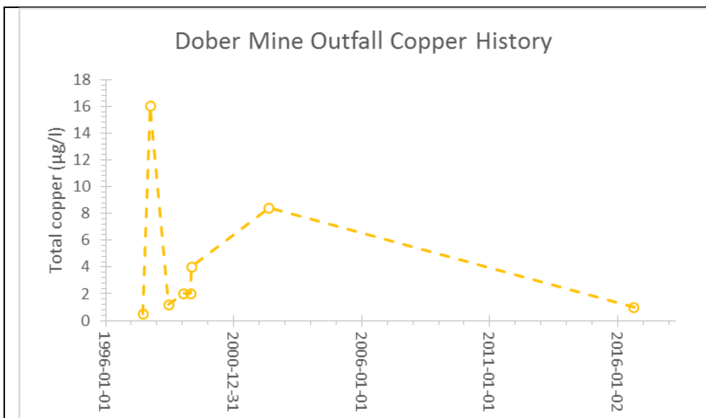


Fig. A-59. Total copper concentrations in the Dober Mine outfall were with the range of measurements from previous years. The highest concentration (16 µg/l) occurred in October 1997. A measurement displayed as 0.5 µg/l (1997) was actually < 1 µg/l.

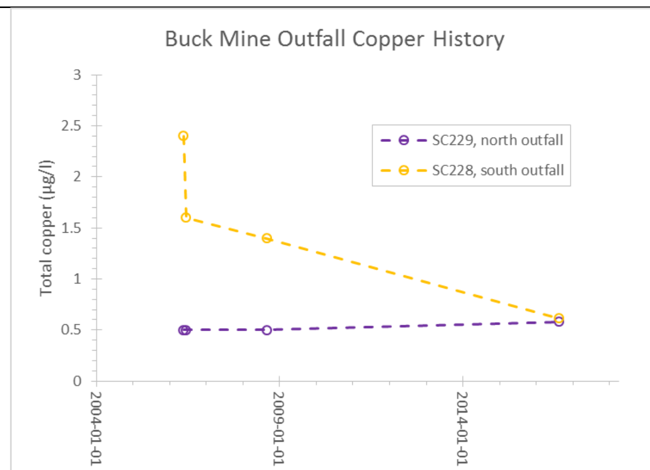


Fig. A-60. Total copper concentrations in the Buck Mine outfalls in 2016 were less than measurements in 2006 and 2008 for the southern outfall (SC228). Measurements displayed as 0.5 µg/l (2006 and 2008) were actually < 1 µg/l.

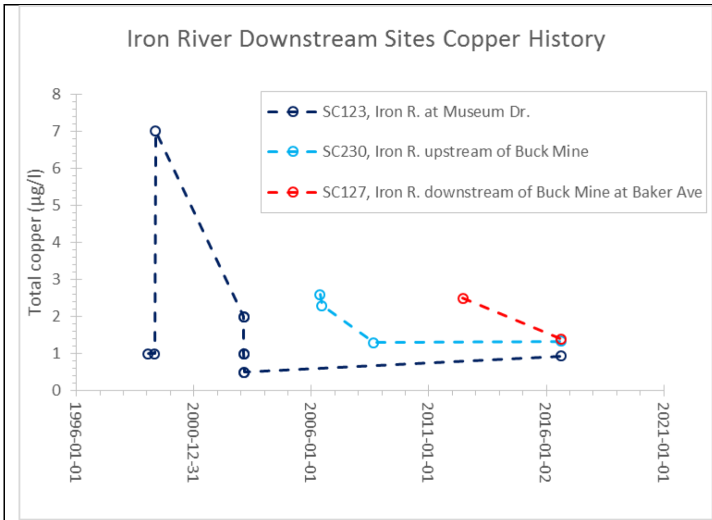


Fig. A-61. Total copper measurements in 2016 at downstream Iron River sites were at the low end of historical ranges for SC123 and SC230, and lower than in 2012 for SC127.

Zinc

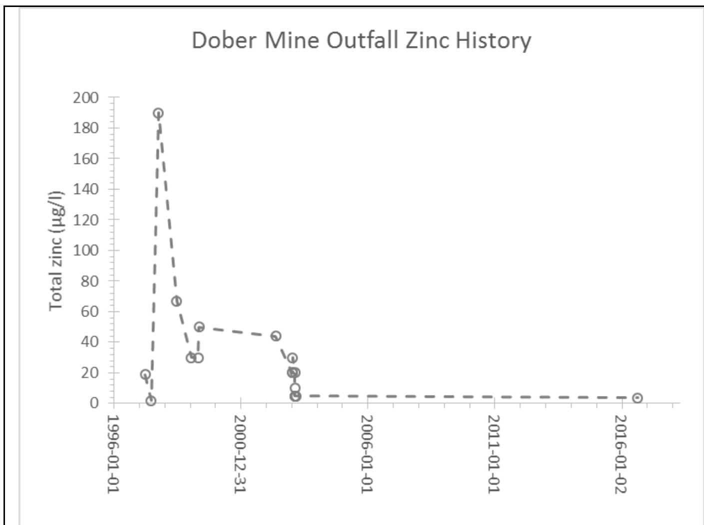


Fig. A-62. Dober Mine outfall zinc concentration in 2016 was at the low end of the historical range since 1997. The highest concentration of 190 µg/l occurred in October 1997. Measurements displayed as 2 µg/l (1997) and 5 µg/l (2003) were actually < 4 µg/l and < 10 µg/l, respectively.

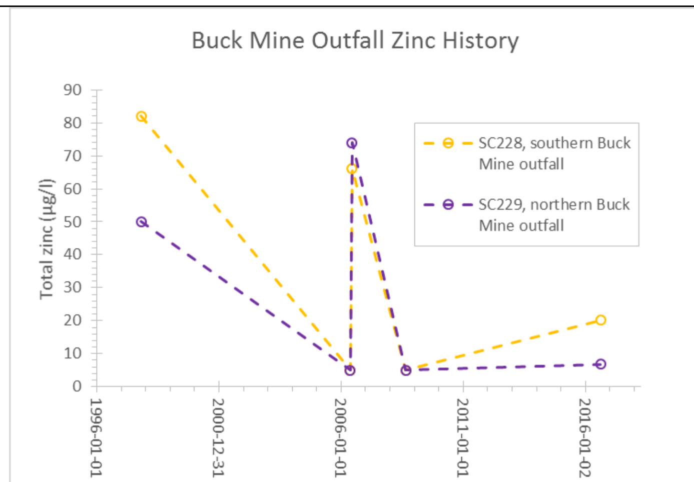


Fig. A-63. Buck Mine outfall zinc concentrations in 2016 were at the low end of the historical range since 1997. The highest concentration of 82 µg/l occurred in October 1997. Measurements displayed as 5 µg/l (2006 and 2008) were actually < 10 µg/l.

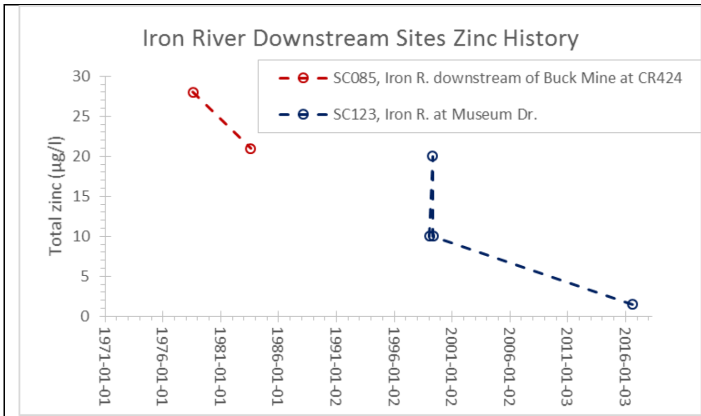


Fig. A-64. Total zinc concentrations in the Iron River at Museum Dr. (SC123) were lower in 2016 than in the winter and spring of 1999.

Thallium

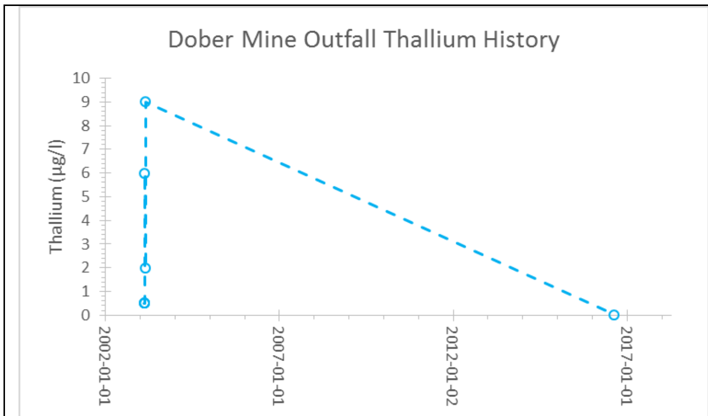


Fig. A-65. The Dober Mine outfall thallium concentration was lower in 2016 than it was late February 2003, when the highest concentration of 9 µg/l occurred. Measurements displayed as 0.5 µg/l (2003) were actually < 1 µg/l.

8. APPENDIX B. Additional site photos

Fig. B-1. SC081, upstream reference site on the Iron River, facing upstream. 16 AUG 2016. Photo Emma Cassidy.

Fig. B-2. SC238, upstream reference site on Sunset Creek, facing upstream. 20 AUG 2016. Photo Emma Cassidy.

Fig. B-3. SC079, upstream site on Sunset Creek, facing upstream. 20 AUG 2016. Photo Emma Cassidy.

Fig. B-4. SC238Z, upstream site on Sunset Creek, facing upstream. 20 AUG 2016. Photo Emma Cassidy.

Fig. B-5. SC080, downstream site on Sunset Creek, facing upstream. 20 AUG 2016. Photo Emma Cassidy.

Fig. B-6. SC082, downstream site on Sunset Creek, facing upstream. 26 AUG 2015.

Fig. B-7. SC116 on Stanley Creek, facing upstream. 18 JUN 2016.

Fig. B-8. SC083 on Iron River, facing upstream. 16 AUG 2016. Photo Emma Cassidy.

	
Fig. B-9. SC224 on Iron River, facing upstream. 16 AUG 2016. Photo Emma Cassidy.	Fig. B-10. SC089 on Iron River, facing upstream. 16 AUG 2016. Photo Emma Cassidy.

	
Fig. B-11. SC124 pipe outfall between 7th and 6th Aves., viewed from above pipe (center) and water flowing to river (left). 18 JUN 2016.	Fig. B-12. SC125 pipe outfall (submerged) between 6th and 5th Ave. 16 AUG 2016. Photo Emma Cassidy.

	
Fig. B-13. SC126 pipe outfall east of 5th Ave., view of pipe where water enters Iron River. 16 AUG 2016.	Fig. B-14. SC126 pipe outfall east of 5th Ave., view from pipe towards center of Iron River. 16 AUG 2016.

Fig. B-15. SC088 Iron River at 4th Ave, viewed from north side facing south. 16 AUG 2016.

Fig. B-16. SC224Z Nanaimo Park pipe to Iron River, view towards the pipe and park. 16 August 2016. Photo Emma Cassidy.

Fig. B-17. SC225 Nanaimo Park pipe to Iron River, view towards the pipe and park. 16 August 2016. Photo Emma Cassidy.

Fig. B-18. SC226 Nanaimo Park pipe to Iron River, view towards the pipe and park. 16 August 2016. Photo Emma Cassidy.

Fig. B-19. SC087, Iron River at E Genesee Street bridge facing upstream. 16 August 2016. Photo Emma Cassidy.	Fig. B-20. SC239, stormwater outfall to pond adjacent to Iron River, facing downstream. 20 August 2016. .

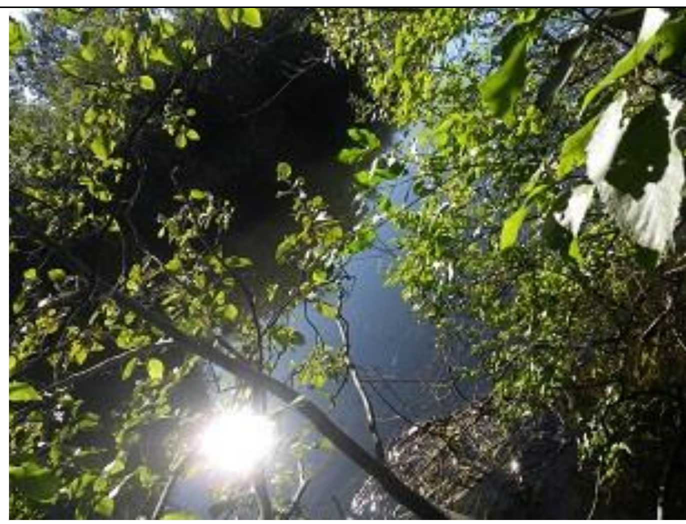


Fig. B-21. SC240, stormwater or spring uphill of Iron River. 20 August 2016.	Fig. B-22. SC086. Iron River upstream of 19th St. bridge adjacent to trail, facing west across river. 26 August 2015.

	
Fig. B-23. SC231, Iron River on upstream side of 19th St. bridge, facing upstream. 18 August 2016. Photo Emma Cassidy.	Fig. B-24. SC123, Iron River on upstream side of Museum Dr, facing upstream. 18 August 2016. Photo Emma Cassidy.

	
Fig. B-25. SC122, Holmes Creek, facing upstream. 18 June 2016.	Fig. B-26. SC247, Dober Mine flow into ponds at Museum Dr., facing west across direction of flow. 22 August 2016.

Fig. B-26. SC232, Dober Mine outfall, facing across/upstream. 18 August 2016.	Fig. B-27. SC091, Dober Mine outfall, facing across/upstream. 18 June 2016.

Fig. B-28. SC121. Iron River downstream of Dober Mine outfall. 18 August 2016. Photo Emma Cassidy	Fig. B-29. SC233. Iron River at Brady Ave., facing upstream. 18 August 2016.

Fig. B-30. SC132, Caspian Pit outfall, facing upstream. 17 August 2016.

Fig. B-31. SC128, Iron River at Caspian Ave upstream of Caspian Pit outfall, facing across/upstream. 19 June 2016.

Fig. B-32. SC120, Baker Creek, facing downstream from boardwalk above. 18 June 2016.

Fig. B-33. SC237, Baker Creek upstream wetland, facing upstream. 19 August 2016.

	
Fig. B-34. SC246, north Buck Mine zone wetland, from boardwalk above. 22 August 2016.	Fig. B-35. SC229, north Buck Mine outfall, facing east. 17 August 2016.

	
Fig. B-36. SC227, middle Buck Mine outfall, facing east. 17 August 2016.	Fig. B-37. SC228, south Buck Mine outfall, facing east. 17 August 2016.

Fig. B-38. SC127, Iron River at Baker Ave., facing upstream. 17 August 2016. Photo Emma Cassidy.

Fig. B-39. SC085, Iron River at Cty Rd. 424, facing across/upstream. 18 June 2016.

Fig. B-40. SC119, Iron River downstream of WWTP, facing upstream. 18 June 2016.

Fig. B-41. SC084, Iron River at State Line Trail near Scott Lake Road, facing

Fig. B-42. SC118, Brule River at State Highway 189, facing upstream. 18 June 2016.

Fig. B-43. SC235, Brule River upstream of confluence with Iron River, viewed from downstream bridge on the Brule River. 19 August 2016. The Iron River is to the right, the upstream Brule River to the left. Photo Emma Cassidy.

Fig. B-44. SC236, Iron River upstream of confluence with Brule River, facing upstream and viewed from downstream bridge on the Brule River.

Fig. B-45. SC234, Brule River downstream of confluence with Iron River, facing south across the river. 19 August 2016.

	
Fig. B-46. SC117, Brule River downstream of confluence with Iron River at Damitz Road, in channel on south side of island and facing upstream. 18 June 2016.	Fig. B-47. SC134, unnamed northeast tributary to Iron River at North Lay Ave, facing upstream. 22 August 2016.

9. APPENDIX C. Data collected in 2015 and 2016.

Date	SC Site Code	Time	Water Temptr. (°C)	Specific conduct. (µS/cm)	DO (mg/l)	DO (%)	pH	ORP (mV)	Temptr. of air (°C)	Total water depth (m)	Stream width (m)	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)	Bromide (mg/l)	Nitrate (mg/l)	Field QAQC sample type
2015-08-26	SC079	11:27	13.3	271.1	6.2	62	7.3	192	18.5	0.3	5		2.3				
2015-08-26	SC080	12:03	15.0	272	8.2	85	7.8	157	21.7	0.2	4		2.0				
2015-08-26	SC081	12:47	14.1	255.5	12.6	128	8.5	197	21.2	0.8	6		3.9				
2015-08-26	SC082	13:29	18.2	265.9	7.2	80	7.6	62	20.9	0.2	5		2.0				
2015-08-26	SC083	13:51	14.4	281.1	11.0	114	8.3	167	19.6	0.3	10		6.6				
2015-08-26	SC084	15:04	14.7	484.4	10.8	112	8.1	178	21.5	0.6	12	0.151	16.1	82.0	< 0.01	0.37	
2015-08-26	SC085	16:07	14.3	489.7	10.3	106	7.8	117	22.2	0.8	12		11.4				
2015-08-26	SC086	16:55	14.3	425.3	10.3	105	7.8	99	20.9	1.1	12		9.8				
2015-08-26	SC087	17:37	14.6	421.7						0.5	12		8.2				
2015-08-26	SC088	17:49	14.9	420.6									7.0				
2015-08-26	SC089	18:42	15.6	331.5	10.5	110	8.1	118	21.4		12	0.062	8.1	25.1	< 0.01	0.08	
2015-08-26	SC090	19:51	16.2	566.6	9.4	99	7.4	91	13.2	0.5	10	0.137	18.4	187.7	< 0.01	0.07	
2015-08-26	SC091	20:16	17.7	715	8.8	97	6.9	117	11.3	0.1	4	0.128	21.9	250.3	< 0.01	0.04	
2016-06-18	SC081	10:27	17.6	231.8	8.7	96	7.2	170	25.6	0.8	5	0.132	4.9	5.2	0.001	0.12	
2016-06-18	SC116	11:00	21.9	256.2	4.7	56	6.7	167	27.6	0.3	2						
2016-06-18	SC117	13:46	20.9	238	10.2	119	7.7	137	27.1	0.2	20	0.073	6.4	15.7	0.001	0.08	
2016-06-18	SC118	14:51	21.3	179.6	9.9	116	7.6	118	28.1	0.3	20	0.065	5.3	5.2	0.001	0.04	
2016-06-18	SC119	15:35	19.4	428	9.4	107	7.1	121	29.9	0.7	6	0.087	12.7	70.2	0.003	0.21	
2016-06-18	SC085	16:15	19.5	425.4	9.3	106	7.2	111	30.2	0.8	8	0.086	12.0	70.2	0.003	0.14	
2016-06-18	SC120	16:52	22.8	533	7.1	86	7.3	122	30.8	0.1	0.5	0.143	5.3	80.9	0.012	0.06	
2016-06-18	SC121	18:16	20.0	385	9.4	108	7.1	99	28.4	0.9	6	0.078	10.5	53.7	0.001	0.13	
2016-06-18	SC091	18:45	24.3	735	7.8	97	6.3	117		0.2	4						
2016-06-18	SC122	19:22	22.2	194					26.8	0.1	1						
2016-06-18	SC123	19:43	20.0	373	9.2	106	7.1	110		0.8	6	0.076	9.9	48.9	0.001	0.13	
2016-06-18	SC089	20:07	21.1	281						0.8	6						
2016-06-18	SC124	20:26	10.3	2586	1.8	17	6.3	149	25.1	0.2	0.2	0.091	38.7	1342.7	0.001	0.29	
2016-06-18	SC125	20:42	9.1	1280	4.8	44	6.4	157		0.4	0.2	0.102	30.0	431.3	0.002	0.52	
2016-06-18	SC126	20:59	8.0	624	6.8	60	7.0	138	23.8	0.1	0.3	0.075	11.1	109.9	0.002	0.69	
2016-06-18	SC088B	21:26	20.1	360	8.1	93	7.4	110		0.4	6	0.072	7.6	46.6	0.001	0.13	
2016-06-18	SC088B	21:27										0.071	7.6	46.7	0.001	0.13	Dup
2016-06-19	SC127	11:55	19.1	434					28.5		6						
2016-06-19	SC121	12:21	19.3	388					28.0								
2016-06-19	SC128	12:45	19.3	390					27.1	1	6						
2016-06-19	SC129	12:58	19.8	416					27.4	0.5	6						
2016-06-19	SC130	13:13	26.3	567					29.6		4						
2016-06-19	SC131	13:28	22.0	540	9.5	114	8.0	78	28.7	0.3	3						
2016-06-19	SC132	14:06	22.1	540	9.2	111	8.0	84	29.8	0.1	2	0.118	26.3	44.3	0.070	0.07	
2016-06-19	SC132	14:07															Blank
2016-06-19	SC133	15:11	22.5	453						0.2	2						

Date	SC Site Code	Time	Water Temptr. (°C)	Specific conduct. (µS/cm)	DO (mg/l)	DO (%)	pH	ORP (mV)	Temptr. of air (°C)	Total water depth (m)	Stream width (m)	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)	Bromide (mg/l)	Nitrate (mg/l)	Field QAQC sample type
2016-06-19	SC134	16:20	20.6	660					29.6	0.2	1						
2016-08-16	SC081	10:55	18.3	253	8.9	100	7.6	81	27.9	1.1	5.5	0.048	4.2	3.9	< 0.005	0.06	
2016-08-16	SC083	12:17	18.0	271.8	9.8	110	7.3	109	26.5	0.3		0.051	6.6	5.9	< 0.005	0.08	
2016-08-16	SC224	12:45	18.1	277	9.9	110	7.7	101	27.4	1.2	12	0.052	6.8	7.0	< 0.005	0.12	
2016-08-16	SC087	13:18	17.3	378	9.2	101	7.3	106	26.4	1	10	0.049	8.8	42.6	< 0.005	0.10	
2016-08-16	SC089	14:36	18.6	310	9.6	108	7.8	111	24.6	0.8	10	0.049	6.8	18.8	< 0.005	0.08	
2016-08-16	SC088	15:53	18.5	369	9.5	107	7.6	114	25.7	0.8	8	0.053	7.5	43.1	< 0.005	0.09	
2016-08-16	SC224Z	16:35	13.0	450					24.3								
2016-08-16	SC225	16:43	12.9	483					24.3								
2016-08-16	SC226	16:46	13.3	608					24.3								
2016-08-16	SC124	17:08	10.8	2642	0.8	8	6.6	159	24.4	0.2	0.28	0.077	42.2	1301.0	< 0.005	0.29	
2016-08-16	SC125	17:55	9.7	1332	4.3	39	6.9	152	25.4	0.3	0.4	0.038	37.4	438.1	0.006	0.51	
2016-08-16	SC126	18:42	9.0	636	9.0	88	7.3	144	23.3	0.15	0.31	0.053	11.8	109.7	< 0.005	0.66	
2016-08-17	SC119	10:39	17.6	459	9.0	98	7.4	129	25.1	0.7		0.071	14.6	70.3	< 0.005	0.28	
2016-08-17	SC119	10:40							25.1	0.7		0.064	13.7	70.1	< 0.005	0.23	Dup
2016-08-17	SC119	10:41											< 0.05	< 0.05	< 0.005	< 0.002	Blank
2016-08-17	SC085	11:07	17.7	448	8.7	96	7.5	119	26.3	0.9		0.052	12.1	70.0	< 0.005	0.11	
2016-08-17	SC127	11:24	18.0	448	9.1	101	7.6	132	25.0	0.6	7	0.052	12.0	69.7	< 0.005	0.11	
2016-08-17	SC227	13:15	17.9	1744	6.7	74	6.7	42	27.0			0.296	27.1	840.7	0.006	0.00	
2016-08-17	SC228	14:07	18.9	1759	7.0	79	7.2	26	25.2			0.296	26.9	859.0	0.006	0.00	
2016-08-17	SC229	14:42	21.0	1655	6.6	78	7.3	32	26.4		0.4	0.289	26.7	754.4	0.008	< 0.002	
2016-08-17	SC230	17:38	19.0	408	9.1	103	7.7	101	24.3	0.73	10	0.045	11.4	52.4	0.003	0.11	
2016-08-17	SC132	18:35	23.6	543	9.2	114	8.3	91	23.4	0.12	1.3	0.079	26.4	43.1	0.092	< 0.002	
2016-08-17	SC132	18:36							23.4	0.12	1.3						Dup
2016-08-17	SC120	19:40	20.4	460	7.3	84	8.0	108	20.8	0.12	0.8	0.089	6.8	47.5	0.015	0.04	
2016-08-17	SC120	19:41															Blank
2016-08-18	SC087	14:17	19.0	380					27.1								
2016-08-18	SC230	14:45	19.3	394					29.1								
2016-08-18	SC128	14:52	19.3	393					29.1								
2016-08-18	SC231	15:27	19.2	384	8.7	100	7.1	127	29.0	1.2		0.050	10.8	44.2	0.003	0.10	
2016-08-18	SC123	15:57	19.4	386	8.4	96	7.6	113	28.3	0.85	7.5	0.053	10.8	45.3	< 0.005	0.10	
2016-08-18	SC121	17:07	19.5	397	8.5	98	7.6	121	24.7	0.46	9	0.053	11.3	50.8	< 0.005	0.10	
2016-08-18	SC232	18:09	23.0	696	6.8	83	6.7	140	23.8	0.27	3	0.080	24.9	229.4	0.003	0.04	
2016-08-18	SC233	19:04	19.6	398					23.4	0.9							
2016-08-19	SC087	12:22	17.7	400					23.1								
2016-08-19	SC230	12:45	17.9	416					22.5								
2016-08-19	SC234	14:05	18.0	449	8.9	99	7.3	138	21.2	0.8		0.086	14.5	63.6	0.003	0.36	
2016-08-19	SC234	14:06											14.2	62.2	0.003	0.36	Dup
2016-08-19	SC235	14:35	20.2	195	9.3	109	7.9	102	19.6	0.3		0.039	4.7	5.0	0.003	0.07	

Date	SC Site Code	Time	Water Temptr. (°C)	Specific conduct. (µS/cm)	DO (mg/l)	DO (%)	pH	ORP (mV)	Temptr. of air (°C)	Total water depth (m)	Stream width (m)	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)	Bromide (mg/l)	Nitrate (mg/l)	Field QAQC sample type
2016-08-19	SC236	14:53	17.9	455	8.9	99	7.8	108	19.6	0.6		0.071	14.8	65.4	0.003	0.37	
2016-08-19	SC237	17:40	21.1	501					20.7								
2016-08-20	SC238	15:15	16.8	65.1					16.0								
2016-08-20	SC079	15:42	15.4	209					16.2								
2016-08-20	SC238Z	15:56	17.9	261					15.7								
2016-08-20	SC080	16:37	18.6	243					16.3								
2016-08-20	SC239	17:35	10.4	916					15.8	0.1							
2016-08-20	SC240	18:10	16.5	328					15.7								
2016-08-22	SC134	11:06							20.5				< 0.05	< 0.05	< 0.005	< 0.002	Blank
2016-08-22	SC134	11:07	12.2	616					20.5			0.149	57.7	5.5	0.022	0.04	
2016-08-22	SC246	11:57	15.1	437					23.8			0.342	17.0	46.2	0.012	0.00	
2016-08-22	SC247	12:31	17.1	683	4.1	46	5.8	118	26.2			0.175	27.8	223.8	0.009	0.11	

Date	SC Site Code	Time	Field QAQC sample type	Turbidity (FNU)	Flow (cfs)	Total alkalinity (mg/l as CaCO3)	TDS (mg/l)	TSS (mg/l)	Li7 (µg/l)	Li7 std. dev.	B11 (µg/l)	B11 std. dev.	Na23 (µg/l)	Na23 std. dev.
2016-08-16	SC081	10:55		0.87	18.1	118			1.18	0.02	7.94	0.02	3495	61
2016-08-16	SC089	14:36		1.25	27.8	128	198	< 2	1.37	0.03	11.7	0.2	4536	33
2016-08-16	SC088	15:53		1.46	25.4	132	222	< 2	1.64	0.02	17.1	0.3	4996	50
2016-08-16	SC124	17:08		0.02	0.27	386	2340	< 2	19.87	0.30	292	3	31271	557
2016-08-16	SC125	17:55		0.00	0.29	271	1000	< 2	7.74	0.07	91.1	0.4	25486	488
2016-08-16	SC126	18:42		0.01	0.60	209	390	< 2	3.64	0.07	26.1	0.2	7498	162
2016-08-17	SC127	11:24		3.40	46.1	140	268	3	3.65	0.03	34	0	6528	206
2016-08-17	SC228	14:07		2.90	0.02	173	1460	3.2	44.14	0.28	385	4	8344	127
2016-08-17	SC229	14:42		2.15	0.07	202	1350	< 2	42.39	0.25	374	3	7686	244
2016-08-17	SC230	17:38		2.69	31.9	137	252	2.4	2.62	0.05	25.5	0.4	6716	148
2016-08-17	SC132	18:35		0.93	1.1	201			3.64	0.04	141	2	10597	196
2016-08-17	SC132	18:36	Dup		1.1	201			3.70	0.03	142	1	10363	190
2016-08-17	SC120	19:40		1.93	0.08	182			4.33	0.10	40.3	0.5	4322	109
2016-08-17	SC120	19:41	Blank		0.08	< 2.55			0.02	0.01	0.8	0.0	1.0	0.3
2016-08-18	SC123	15:57		1.65	49.9	135			2.00	0.02	19	0	5938	159
2016-08-18	SC121	17:07		2.37	27.5	133			2.37	0.02	20	0	6206	182
2016-08-18	SC232	18:09		10.37	0.54	85.2	518	< 2	13.26	0.06	78	1	10444	241

Date	SC Site Code	Time	Mg25 (µg/l)	Mg25 std. dev.	Al27 (µg/l)	Al27 std. dev.	P31 (µg/l)	P31 std. dev.	S32 (µg/l)	S32 std. dev.	K39 (µg/l)	K39 std. dev.	Ca44 (µg/l)	Ca44 std. dev.	Sc45 (µg/l)	Sc45 std. dev.
2016-08-16	SC081	10:55	12482	247	13.2	0.1	14.8	0.5	1586	43	892	21	31864	506	0.004	0.004
2016-08-16	SC089	14:36	15642	325	25.1	1.1	17.5	0.9	6402	123	988	24	37731	409	0.006	0.006
2016-08-16	SC088	15:53	19652	129	26.8	1.0	17.2	0.3	15602	131	1066	10	45219	230	0.021	0.004
2016-08-16	SC124	17:08	212050	2414	1.56	0.14	6.20	0.34	476015	14172	5330	82	376607	3202	0.056	0.007
2016-08-16	SC125	17:55	80724	517	1.28	0.04	7.86	0.42	156009	3878	2901	69	154103	2762	0.023	0.005
2016-08-16	SC126	18:42	36921	490	0.63	0.04	7.34	0.36	37353	660	1925	29	79716	671	0.020	0.007
2016-08-17	SC127	11:24	23939	304	78.3	1.0	16.9	1.2	25481	282	1429	27	53658	333	0.019	0.006
2016-08-17	SC228	14:07	120755	2403	41.3	0.8	5.81	0.48	310370	7486	5927	153	239093	4122	0.022	0.005
2016-08-17	SC229	14:42	116710	1283	15.0	0.3	3.61	0.21	278419	5299	6256	53	219924	2451	0.019	0.007
2016-08-17	SC230	17:38	21274	127	67.3	2.0	14.7	0.4	19369	135	1247	45	49198	573	0.011	0.004
2016-08-17	SC132	18:35	31643	402	1.80	0.07	4.19	0.40	15385	72	2211	44	60099	344	0.005	0.006
2016-08-17	SC132	18:36	31518	286	1.44	0.18	4.80	0.23	15445	393	2239	30	59851	658	0.002	0.004
2016-08-17	SC120	19:40	26356	483	10.7	0.2	21.4	1.0	17326	376	2121	39	56735	1180	0.008	0.005
2016-08-17	SC120	19:41	3.1	1.1	0.0	0.0	0.03	0.03	3.9	2.0	0.4	0.2	9.0	2.5	0.000	0.006
2016-08-18	SC123	15:57	19399	290	54.5	2.3	17.7	0.6	16030	198	1125	1	44736	872	0.008	0.004
2016-08-18	SC121	17:07	19771	370	65.7	0.8	17.7	0.9	17679	282	1134	17	46102	442	0.011	0.006
2016-08-18	SC232	18:09	31396	551	38.1	1.1	5.17	0.52	78444	2274	2140	36	87406	1364	0.007	0.004

Date	SC Site Code	Time	Ti49 (µg/l)	Ti49 std. dev.	V51 (µg/l)	V51 std. dev.	Cr52 (µg/l)	Cr52 std. dev.	Mn55 (µg/l)	Mn55 std. dev.	Fe56 (µg/l)	Fe56 std. dev.	Co59 (µg/l)	Co59 std. dev.	Ni60 (µg/l)	Ni60 std. dev.
2016-08-16	SC081	10:55	0.424	0.205	0.833	0.022	0.493	0.024	169.0	2.4	201.3	1.4	0.051	0.008	0.146	0.008
2016-08-16	SC089	14:36	0.591	0.144	0.916	0.051	0.614	0.035	83.2	1.2	297.8	11.0	0.160	0.020	0.877	0.095
2016-08-16	SC088	15:53	0.645	0.051	0.928	0.020	0.453	0.025	157.3	1.3	322.6	6.1	0.182	0.016	0.325	0.064
2016-08-16	SC124	17:08	0.049	0.035	0.614	0.033	0.228	0.018	3283.4	72.2	21.3	0.4	0.770	0.040	3.72	0.15
2016-08-16	SC125	17:55	0.016	0.021	0.601	0.037	0.652	0.022	279.1	0.5	14.9	0.2	0.032	0.006	0.428	0.036
2016-08-16	SC126	18:42	0.003	0.009	0.727	0.019	1.015	0.058	16.0	0.4	0.7	0.0	0.040	0.003	0.432	0.034
2016-08-17	SC127	11:24	1.017	0.137	0.744	0.036	0.402	0.029	328	3	591	11	0.668	0.015	1.72	0.13
2016-08-17	SC228	14:07	0.095	0.058	0.055	0.002	0.044	0.008	1835	23	7142	117	5.83	0.29	12.7	0.4
2016-08-17	SC229	14:42	1.646	0.147	0.165	0.020	0.073	0.011	832.8	12.0	963.6	10.1	3.86	0.15	6.19	0.17
2016-08-17	SC230	17:38	0.707	0.220	0.716	0.043	0.436	0.021	235.7	2.9	388.8	13.4	0.463	0.033	1.56	0.04
2016-08-17	SC132	18:35	0.036	0.027	0.205	0.016	0.083	0.011	54.1	0.7	9.7	0.4	0.026	0.005	0.151	0.036
2016-08-17	SC132	18:36	0.023	0.009	0.194	0.010	0.111	0.005	58.8	0.6	10.7	0.2	0.049	0.006	0.341	0.043
2016-08-17	SC120	19:40	0.142	0.060	0.166	0.016	0.115	0.007	15.1	0.5	421.6	6.2	0.109	0.008	1.80	0.11
2016-08-17	SC120	19:41	0.004	0.016	0.000	0.001	0.000	0.001	0.0	0.0	0.2	0.0	0.000	0.001	0.013	0.016
2016-08-18	SC123	15:57	0.673	0.082	0.725	0.034	0.373	0.038	231	4	393	12	0.441	0.018	0.981	0.042
2016-08-18	SC121	17:07	0.642	0.120	0.772	0.034	0.390	0.028	241	2	419	16	0.507	0.015	1.40	0.07
2016-08-18	SC232	18:09	0.068	0.022	0.093	0.007	0.120	0.016	855	11	1214	21	2.37	0.100	9.71	0.25

Date	SC Site Code	Time	Cu63 (µg/l)	Cu63 std. dev.	Zn66 (µg/l)	Zn66 std. dev.	As75 (µg/l)	As75 std. dev.	Se82 (µg/l)	Se82 std. dev.	Rb85 (µg/l)	Rb85 std. dev.	Sr88 (µg/l)	Sr88 std. dev.	Y89 (µg/l)	Y89 std. dev.
2016-08-16	SC081	10:55	0.168	0.022	0.448	0.065	1.32	0.07	0.283	0.040	0.484	0.005	43.3	0.7	0.028	0.001
2016-08-16	SC089	14:36	0.580	0.053	0.513	0.096	1.46	0.17	0.319	0.025	0.449	0.008	52.1	0.6	0.059	0.002
2016-08-16	SC088	15:53	0.567	0.030	0.581	0.034	1.29	0.10	0.334	0.017	0.456	0.009	61.7	0.6	0.069	0.002
2016-08-16	SC124	17:08	0.463	0.035	0.489	0.067	0.152	0.076	2.40	0.07	0.634	0.008	485.9	3.3	0.398	0.003
2016-08-16	SC125	17:55	0.176	0.011	0.103	0.028	0.238	0.049	0.966	0.039	0.368	0.005	222.0	1.4	0.146	0.004
2016-08-16	SC126	18:42	0.251	0.021	0.068	0.026	0.279	0.016	0.858	0.040	0.229	0.006	94.5	0.7	0.066	0.001
2016-08-17	SC127	11:24	1.40	0.04	2.30	0.20	1.05	0.11	0.410	0.029	0.629	0.017	111.1	0.6	0.215	0.002
2016-08-17	SC228	14:07	0.616	0.033	20.1	0.3	0.481	0.073	0.727	0.032	3.52	0.05	1762	16	0.239	0.004
2016-08-17	SC229	14:42	0.579	0.043	6.87	0.29	0.232	0.040	0.764	0.050	3.50	0.04	1860	46	0.058	0.001
2016-08-17	SC230	17:38	1.34	0.08	1.69	0.14	1.20	0.12	0.445	0.034	0.534	0.007	73.1	0.9	0.186	0.006
2016-08-17	SC132	18:35	0.155	0.030	0.089	0.017	0.578	0.127	1.32	0.04	0.327	0.005	142.3	1.0	0.007	0.001
2016-08-17	SC132	18:36	0.193	0.013	0.118	0.027	0.557	0.051	1.32	0.06	0.325	0.006	141.0	0.8	0.007	0.000
2016-08-17	SC120	19:40	1.93	0.06	0.670	0.108	1.64	0.17	0.695	0.030	1.65	0.02	115.0	1.7	0.048	0.001
2016-08-17	SC120	19:41	0.002	0.004	0.001	0.009	0.001	0.005	0.075	0.008	0.004	0.002	0.1	0.0	0.000	0.000
2016-08-18	SC123	15:57	0.938	0.027	1.47	0.20	1.23	0.08	0.379	0.021	0.500	0.015	63.4	1.4	0.179	0.003
2016-08-18	SC121	17:07	1.18	0.09	1.75	0.10	1.27	0.06	0.363	0.018	0.568	0.010	67.3	0.5	0.201	0.003
2016-08-18	SC232	18:09	0.991	0.048	3.77	0.17	0.338	0.026	0.359	0.027	2.04	0.05	215.0	2.8	0.169	0.002

Date	SC Site Code	Time	Nb93 (µg/l)	Nb93 std. dev.	Mo95 (µg/l)	Mo95 std. dev.	Rh103 (µg/l)	Rh103 std. dev.	Pd108 (µg/l)	Pd108 std. dev.	Ag109 (µg/l)	Ag109 std. dev.	Cd111 (µg/l)	Cd111 std. dev.	Sn118 (µg/l)	Sn118 std. dev.
2016-08-16	SC081	10:55	0.001	0.001	0.249	0.010	0.0028	0.0003	0.001	0.000	0.0005	0.0003	0.0044	0.0012	0.004	0.003
2016-08-16	SC089	14:36	0.003	0.005	0.438	0.018	0.0039	0.0004	0.001	0.000	0.0005	0.0004	0.0065	0.0022	0.008	0.006
2016-08-16	SC088	15:53	0.007	0.002	0.330	0.013	0.0058	0.0004	0.002	0.000	0.0019	0.0005	0.0099	0.0041	0.009	0.002
2016-08-16	SC124	17:08	0.005	0.001	0.617	0.011	0.0521	0.0024	0.0109	0.0009	0.0047	0.0005	0.0888	0.0077	0.010	0.003
2016-08-16	SC125	17:55	0.003	0.001	0.549	0.016	0.0260	0.0012	0.0033	0.0005	0.0045	0.0004	0.0191	0.0029	0.031	0.004
2016-08-16	SC126	18:42	0.001	0.001	0.707	0.017	0.0120	0.0003	0.0021	0.0006	0.0010	0.0004	0.0095	0.0023	0.004	0.003
2016-08-17	SC127	11:24	0.0042	0.0013	0.456	0.011	0.0127	0.0005	0.0018	0.0005	0.0013	0.0004	0.0125	0.0023	0.014	0.006
2016-08-17	SC228	14:07	0.0017	0.0013	0.240	0.005	0.182	0.001	0.0019	0.0002	0.0008	0.0004	0.0584	0.0032	0.009	0.006
2016-08-17	SC229	14:42	0.0085	0.0014	0.464	0.014	0.220	0.002	0.0013	0.0003	0.0009	0.0003	0.0305	0.0021	0.018	0.008
2016-08-17	SC230	17:38	0.0023	0.0013	0.467	0.013	0.0100	0.0002	0.0019	0.0004	0.0010	0.0003	0.0125	0.0016	0.002	0.002
2016-08-17	SC132	18:35	0.0008	0.0013	0.992	0.033	0.0183	0.0010	0.0015	0.0003	0.0005	0.0003	0.0083	0.0026	0.041	0.014
2016-08-17	SC132	18:36	0.0009	0.0013	0.995	0.023	0.0186	0.0008	0.0019	0.0002	0.0003	0.0003	0.0095	0.0029	0.000	0.002
2016-08-17	SC120	19:40	0.0022	0.0013	2.08	0.06	0.0148	0.0008	0.0057	0.0009	0.0008	0.0003	0.0211	0.0022	0.006	0.004
2016-08-17	SC120	19:41	0.0002	0.0018	0.002	0.002	0.0009	0.0002	0.0000	0.0002	0.0001	0.0004	0.0000	0.0002	0.006	0.006
2016-08-18	SC123	15:57	0.0022	0.0013	0.446	0.010	0.0090	0.0004	0.0017	0.0003	0.0008	0.0003	0.0134	0.0019	0.007	0.005
2016-08-18	SC121	17:07	0.0023	0.0013	0.452	0.013	0.0091	0.0007	0.0016	0.0004	0.0008	0.0003	0.0130	0.0020	0.027	0.008
2016-08-18	SC232	18:09	0.0009	0.0013	0.229	0.007	0.0263	0.0008	0.0008	0.0004	0.0003	0.0003	0.0127	0.0018	0.001	0.002

Date	SC Site Code	Time	Sb121 (µg/l)	Sb121 std. dev.	Cs133 (µg/l)	Cs133 std. dev.	Ba137 (µg/l)	Ba137 std. dev.	La139 (µg/l)	La139 std. dev.	Ce140 (µg/l)	Ce140 std. dev.	Pr141 (µg/l)	Pr141 std. dev.	Nd146 (µg/l)	Nd146 std. dev.
2016-08-16	SC081	10:55	0.019	0.007	0.0028	0.0004	13.9	0.2	0.0274	0.0007	0.0508	0.0004	0.0065	0.0003	0.0271	0.0008
2016-08-16	SC089	14:36	0.029	0.008	0.0028	0.0005	13.5	0.3	0.0451	0.0017	0.0955	0.0032	0.0112	0.0006	0.0466	0.0034
2016-08-16	SC088	15:53	0.031	0.006	0.0065	0.0055	13.9	0.2	0.0543	0.0018	0.0985	0.0011	0.0130	0.0008	0.0558	0.0013
2016-08-16	SC124	17:08	0.009	0.004	0.0020	0.0003	23.8	0.6	0.2829	0.0079	0.1290	0.0022	0.0342	0.0007	0.1432	0.0022
2016-08-16	SC125	17:55	0.023	0.008	0.0014	0.0004	25.5	0.3	0.0779	0.0022	0.0162	0.0010	0.0104	0.0002	0.0458	0.0023
2016-08-16	SC126	18:42	0.032	0.013	0.0008	0.0002	24.4	0.5	0.0242	0.0013	0.0021	0.0002	0.0044	0.0002	0.0201	0.0028
2016-08-17	SC127	11:24	0.031	0.011	0.0046	0.0004	16.6	0.3	0.1071	0.0045	0.2193	0.0046	0.0282	0.0010	0.1203	0.0027
2016-08-17	SC228	14:07	0.022	0.008	0.0109	0.0005	9.16	0.26	0.1413	0.0054	0.2290	0.0045	0.0216	0.0006	0.0890	0.0024
2016-08-17	SC229	14:42	0.023	0.010	0.0123	0.0006	7.12	0.29	0.0212	0.0012	0.0382	0.0015	0.0045	0.0004	0.0199	0.0021
2016-08-17	SC230	17:38	0.037	0.013	0.0038	0.0003	15.7	0.4	0.0892	0.0046	0.1814	0.0057	0.0229	0.0010	0.0996	0.0030
2016-08-17	SC132	18:35	0.016	0.007	0.0022	0.0005	13.2	0.1	0.0039	0.0015	0.0056	0.0003	0.0005	0.0001	0.0029	0.0004
2016-08-17	SC132	18:36	0.026	0.004	0.0020	0.0003	13.5	0.2	0.0042	0.0002	0.0065	0.0005	0.0008	0.0001	0.0037	0.0005
2016-08-17	SC120	19:40	0.058	0.018	0.0029	0.0004	14.3	0.3	0.0270	0.0009	0.0506	0.0017	0.0073	0.0004	0.0354	0.0028
2016-08-17	SC120	19:41	0.000	0.004	0.0004	0.0004	0.01	0.01	0.0000	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0001
2016-08-18	SC123	15:57	0.036	0.012	0.0034	0.0004	16.2	0.4	0.0883	0.0037	0.1792	0.0057	0.0224	0.0007	0.0983	0.0028
2016-08-18	SC121	17:07	0.031	0.010	0.0040	0.0003	16.4	0.4	0.0987	0.0033	0.2015	0.0039	0.0254	0.0008	0.1091	0.0035
2016-08-18	SC232	18:09	0.016	0.007	0.0202	0.0009	10.8	0.4	0.0245	0.0009	0.0614	0.0020	0.0097	0.0004	0.0530	0.0020

Date	SC Site Code	Time	Sm149 (µg/l)	Sm149 std. dev.	Eu151 (µg/l)	Eu151 std. dev.	Dy163 (µg/l)	Dy163 std. dev.	Ho165 (µg/l)	Ho165 std. dev.	Yb173 (µg/l)	Yb173 std. dev.	Lu175 (µg/l)	Lu175 std. dev.	W184 (µg/l)	W184 std. dev.
2016-08-16	SC081	10:55	0.0052	0.0006	0.0040	0.0004	0.005	0.001	0.001	0.000	0.003	0.000	0.000	0.000	0.014	0.001
2016-08-16	SC089	14:36	0.0115	0.0040	0.0062	0.0009	0.009	0.001	0.002	0.000	0.004	0.001	0.001	0.000	0.033	0.002
2016-08-16	SC088	15:53	0.0114	0.0014	0.0074	0.0005	0.010	0.001	0.002	0.000	0.005	0.001	0.001	0.000	0.008	0.003
2016-08-16	SC124	17:08	0.0244	0.0013	0.0147	0.0006	0.028	0.000	0.007	0.000	0.018	0.001	0.003	0.000	0.055	0.002
2016-08-16	SC125	17:55	0.0080	0.0012	0.0120	0.0007	0.0097	0.0006	0.0025	0.0002	0.0069	0.0016	0.0014	0.0001	0.004	0.001
2016-08-16	SC126	18:42	0.0042	0.0005	0.0106	0.0004	0.0048	0.0007	0.0013	0.0001	0.0035	0.0005	0.0009	0.0001	0.028	0.002
2016-08-17	SC127	11:24	0.0278	0.0007	0.0140	0.0009	0.0311	0.0004	0.0061	0.0004	0.0146	0.0005	0.0023	0.0002	0.007	0.001
2016-08-17	SC228	14:07	0.0202	0.0017	0.0087	0.0005	0.0199	0.0011	0.0041	0.0004	0.0073	0.0008	0.0012	0.0001	0.001	0.001
2016-08-17	SC229	14:42	0.0042	0.0005	0.0042	0.0004	0.0047	0.0008	0.0010	0.0001	0.0028	0.0002	0.0005	0.0001	0.007	0.001
2016-08-17	SC230	17:38	0.0225	0.0006	0.0128	0.0008	0.0266	0.0018	0.0053	0.0004	0.0127	0.0010	0.0020	0.0001	0.013	0.001
2016-08-17	SC132	18:35	0.0006	0.0003	0.0062	0.0004	0.0006	0.0000	0.0002	0.0000	0.0007	0.0002	0.0002	0.0001	0.005	0.001
2016-08-17	SC132	18:36	0.0007	0.0002	0.0059	0.0003	0.0007	0.0003	0.0002	0.0001	0.0006	0.0002	0.0001	0.0001	0.021	0.002
2016-08-17	SC120	19:40	0.0088	0.0005	0.0080	0.0003	0.0080	0.0006	0.0016	0.0001	0.0048	0.0010	0.0006	0.0001	0.014	0.001
2016-08-17	SC120	19:41	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.001	0.001
2016-08-18	SC123	15:57	0.0226	0.0024	0.0126	0.0007	0.0247	0.0013	0.0054	0.0001	0.0123	0.0012	0.0019	0.0001	0.006	0.001
2016-08-18	SC121	17:07	0.0255	0.0035	0.0136	0.0003	0.0295	0.0008	0.0059	0.0003	0.0141	0.0007	0.0020	0.0001	0.006	0.001
2016-08-18	SC232	18:09	0.0164	0.0019	0.0095	0.0006	0.0182	0.0007	0.0041	0.0002	0.0095	0.0009	0.0017	0.0002	0.016	0.001

Date	SC Site Code	Time	Pt195 (µg/l)	Pt195 std. dev.	Tl205 (µg/l)	Tl205 std. dev.	PbSum (µg/l)	Pb_ std. dev.	Th232 (µg/l)	Th232 std. dev.	U238 (µg/l)	U238 std. dev.	Total hardness (mg/l, calculated from total Ca and Mg)
2016-08-16	SC081	10:55	0.0009	0.0002	0.0014	0.0002	0.033	0.001	0.0017	0.0011	0.191	0.003	131
2016-08-16	SC089	14:36	0.0009	0.0003	0.0018	0.0002	0.053	0.002	0.0026	0.0016	0.387	0.005	159
2016-08-16	SC088	15:53	0.0013	0.0003	0.0027	0.0009	0.061	0.003	0.0047	0.0011	0.561	0.008	194
2016-08-16	SC124	17:08	0.0007	0.0002	0.0088	0.0003	0.002	0.000	0.0033	0.0013	6.653	0.059	1815
2016-08-16	SC125	17:55	0.0004	0.0001	0.0018	0.0002	0.001	0.000	0.0027	0.0012	4.416	0.039	718
2016-08-16	SC126	18:42	0.0006	0.0002	0.0010	0.0002	0.001	0.000	0.0012	0.0011	3.095	0.045	351
2016-08-17	SC127	11:24	0.0011	0.0003	0.0041	0.0003	0.174	0.003	0.0056	0.0011	1.304	0.030	233
2016-08-17	SC228	14:07	0.0005	0.0003	0.0389	0.0015	0.032	0.002	0.0055	0.0013	22.635	0.367	1095
2016-08-17	SC229	14:42	0.0011	0.0004	0.0243	0.0011	0.016	0.001	0.0041	0.0013	35.582	0.347	1031
2016-08-17	SC230	17:38	0.0010	0.0003	0.0029	0.0002	0.136	0.003	0.0030	0.0011	0.786	0.024	211
2016-08-17	SC132	18:35	0.0006	0.0002	0.0018	0.0003	0.008	0.001	0.0005	0.0010	1.963	0.052	281
2016-08-17	SC132	18:36	0.0004	0.0002	0.0018	0.0001	0.010	0.001	0.0006	0.0010	2.002	0.051	279
2016-08-17	SC120	19:40	0.0009	0.0002	0.0027	0.0003	0.038	0.002	0.0023	0.0011	3.058	0.043	250
2016-08-17	SC120	19:41	0.0002	0.0002	0.0000	0.0000	0.000	0.000	0.0000	0.0015	0.002	0.000	0
2016-08-18	SC123	15:57	0.0023	0.0004	0.0022	0.0002	0.088	0.003	0.0034	0.0011	0.721	0.024	192
2016-08-18	SC121	17:07	0.0009	0.0004	0.0030	0.0003	0.098	0.003	0.0047	0.0012	0.755	0.016	197
2016-08-18	SC232	18:09	0.0002	0.0001	0.0232	0.0003	0.006	0.000	0.0015	0.0011	0.539	0.016	348

10. APPENDIX D. Site locations

SC code	Location name	Location description	Latitude (°,WGS84)	Longitude (°,WGS84)	GPS precision (m)
SC079	Sunset Creek at Iron Lake Road	upstream side of bridge	46.13	-88.63767	5
SC080	Sunset Creek at Rosotti Road	ca 3m upstream of culvert in 2015 and at upstream end of culvert in	46.1076	-88.66572	5
SC081	Iron River at McNutt Road		46.12593	-88.68959	3
SC082	Sunset Creek at Iron County ORV Snowmobile Trail	ca 15m downstream of beaver dam	46.10192	-88.6711	6
SC083	Iron River at 16th Avenue (County Hwy 653)	ca 15m upstream of bridge	46.09356	-88.65884	4
SC084	Iron River at State Line Trail near Scott Lake Road		46.02398	-88.58875	5
SC085	Iron River at County Road 424 and Brady Avenue	ca 10m upstream of bridge	46.05842	-88.62685	5
SC086	Iron River upstream of W 19th Street		46.07531	-88.63948	5
SC087	Iron River at E Genesee Street	ca 10m upstream of bridge	46.09167	-88.63542	6
SC088	Iron River at N 4th Avenue	ca 4m upstream of bridge	46.09683	-88.64211	7
SC088B	Iron River at 4th Avenue downstream side of bridge		46.09661	-88.64182	5
SC089	Iron River at N 7th Avenue	ca 4m upstream of bridge	46.0973	-88.64619	4
SC090	Iron River at bike trail SE of Museum Drive	ca 4m downstream of Dober outfall channel	46.06845	-88.63201	
SC091	Dober mine site wetland outfall	outfall channel ca 1m upstream of confluence with river	46.06844	-88.63202	7
SC116	Stanley Creek at Lundin Drive	ca 3m upstream of culvert	46.09283	-88.67337	4
SC117	Brule River at Damitz Road	ca 5m downstream of where road ends on south side	46.01537	-88.56616	3
SC118	Brule River at Michigan State Highway 189	ca 10m upstream of bridge	45.98769	-88.65276	
SC119	Iron River adjacent to Caspian Cutoff Road		46.05648	-88.63136	5
SC120	Baker Creek at trail south of Caspian Road near confluence with Iron River	downstream side of foot bridge	46.06528	-88.62161	3
SC121	Iron River at Dober dock by trail west of Brady Ave.		46.06764	-88.63042	6
SC122	Holmes Creek south of Museum Drive	ca 20m upstream of confluence with Iron River	46.07015	-88.63511	5
SC123	Iron River at Museum Drive	below north side of bridge	46.07058	-88.63528	
SC124	Pipe outfall to north side of Iron River at alley between 6th and 7th Avenues		46.09716	-88.6455	
SC125	Pipe outfall to north side of Iron River at alley between 5th and 6th Avenues		46.09707	-88.64433	6
SC126	Pipe outfall to north side of Iron River at alley east of 5th Avenue		46.09729	-88.64294	5
SC127	Iron River at Baker Avenue	ca 6m upstream of bridge	46.05962	-88.62328	4
SC128	Iron River at Caspian Road on NW side of bridge	ca 4m upstream of bridge	46.06569	-88.62344	5
SC129	Iron River at Caspian Road on SE side of bridge	downstream side of bridge	46.06549	-88.62315	3
SC130	Wetland pond adjacent to Iron River at Caspian Road on NE side of bridge		46.06571	-88.62317	3
SC131	Wetland and old pit flow into Iron River north of Caspian Road	in pit flow wetland stream at its confluence with Iron River	46.06573	-88.62334	4
SC132	Pit outfall to wetland and Iron River north of Caspian Road	20 cm downstream of outfall from pit lake	46.06584	-88.62338	3
SC133	Baker Creek at Bengal Road		46.06747	-88.62025	4
SC134	Unnamed NE tributary to Iron River at North Lay Ave	ca 6m upstream of culvert and ca 2m downstream of cattail wetland and ca 560 m upstream confluence IronR	46.09732	-88.63292	5
SC224	Iron River at W Minkler Street (14th Ave)	ca 10m upstream of bridge	46.09488	-88.6535	3
SC224Z	Below-pipe western outfall to Iron River in Nanaimo Park in Iron River town	flow below dry pipe in park	46.0969	-88.64128	3
SC225	Central pipe outfall to Iron River in Nanaimo Park in Iron River town	pipe outfall in park	46.09685	-88.64083	3
SC226	East pipe outfall to Iron River in Nanaimo Park in Iron River town	pipe outfall in park	46.09678	-88.6404	3
SC227	Buck mine wetland central outfall to Iron River	in Buck mine wetland outfall ca 0.5m before flows down to Iron River	46.06125	-88.6203	3
SC228	Buck mine wetland southern outfall to Iron River	in Buck mine wetland outfall ca 0.5m before flows down to Iron River	46.06088	-88.62078	3
SC229	Buck mine wetland northern outfall to Iron River	in N Buck mine wetland outfall ca 0.5m before flows down to Iron	46.06252	-88.62022	3

SC code	Location name	Location description	Latitude (°,WGS84)	Longitude (°,WGS84)	GPS precision (m)
SC230	Iron River at Caspian Road	ca 15m downstream of bridge	46.06536	-88.62326	3
SC231	Iron River at Iron County ORV and Snowmobile Trail north of W 19th Street	ca 2m north of ATV bridge	46.07368	-88.63811	3
SC232	Dober mine site wetland outfall ca 6m upstream of confluence with Iron River	ca 15m downstream of outfall pipe under trail and ca 5m upstream of SC091	46.06851	-88.63201	3
SC233	Iron River at Brady Ave parking lot	ca 40m upstream of bridge and adjacent to parking lot	46.06687	-88.62822	3
SC234	Brule River at ATV trail to Scott Lake Rd and downstream of confluence with Iron River	ca 10m upstream of bridge	46.00993	-88.57787	3
SC235	Brule River upstream of confluence with Iron River	ca 20m upstream of confluence	46.00954	-88.57898	3
SC236	Iron River upstream of confluence with Brule River	ca 15m upstream of confluence	46.00973	-88.57936	3
SC237	Wetland in Baker Creek north of Lovers Lane near Baker Road	ca 3m E of dirt road path	46.07408	-88.61506	3
SC238	Sunset Creek at W Sunset Lake Road	upstream end of culvert	46.138	-88.60998	3
SC238Z	Sunset Creek at Homer Road (County Road 653)	upstream end of culvert	46.12428	-88.65843	3
SC239	Stormwater outfall to wetland adjacent Iron River at trail	downstream end of culvert and ca 140m upstream of confluence with IronR	46.089	-88.63728	3
SC240	Spring or storm water flow near dirt path uphill from Iron River		46.08242	-88.63772	3
SC246	Wetland stream upstream of Buck mine	North side of trail boardwalk	46.06491	-88.61976	3
SC247	Dober mine wetland stream at Museum Drive	ca 1m downstream of culvert	46.07077	-88.63315	3