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

Dark River, Minnesota

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Minntac processing facility

Dark River downstream of Minntac tailings

Sparse wild rice in Dark Lake downstream of tailings and Trout Stream sign on Dark River

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SUMMARY

The Dark River in Minnesota receives seepage waters from the tailings basin of the Minntac iron mine, which began operations ca. 1967. In spite of concern over the discharge and its sulfate concentrations, studies had yet to adequately document patterns of contaminants on the west side of the basin in the Dark, Sturgeon, and Little Fork Rivers downstream of the basin.

We studied water quality in those rivers to identify contaminants, determine their concentrations, and assess the downstream extent of contamination. After collecting preliminary data in August of 2015, we conducted additional anion and trace element sampling in the watersheds of those rivers in July of 2016.

We identified water quality characteristics apparently associated with tailings discharges. Several characteristics with measurements of potential concern were greatest at the site nearest the tailings and decreased downstream from there:

- **Specific conductance**[1] and **Total Dissolved Solids** (TDS)
- **Alkalinity** and **hardness**
- **Sulfate**, **chloride**, **fluoride**, and **bromide**
- **Manganese**
- **Selenium**

Uranium concentrations, though low, also decreased downstream of tailings, and phosphorus concentrations were greatest at the second site downstream of the tailings. Limited data on tailings discharges from Discharge Monitoring Reports and other documents also indicated high values for those and other constituents. Even though one of the four reference sites may have been impacted by discharges from Hibbing Taconite, comparisons with reference sites indicated that specific conductance, fluoride, chloride, sulfate, and bromide were greater in the Dark River than at reference sites, at least in the upstream reaches. In addition, comparison with limited historical data suggested that specific conductance, chloride, and sulfate increased after mining began.

The mine-influenced waters, especially those closest to the tailings, appeared to exceed state criteria or federal guidelines for **specific conductance, TDS, hardness, dissolved oxygen, sulfate, manganese, and selenium**. Sulfate was much greater than the 10 mg/l limit that applies in wild rice waters such as Dark Lake, which the sulfate-laden Dark River flows through. In addition, August 2015 sampling documented sulfate concentrations exceeding the state criterion of 250 mg/l in the trout stream reach of the Dark River. Although **fluoride** did not exceed state criteria or federal guidelines, it did exceed Canadian guidelines.

Our measurements also suggested a need for an improved understanding of the hydrogeology around the tailings basin. The 2016 NPDES reissuance document (MPCA 2016a) predicted lower concentrations of phosphorus, manganese, and selenium at the upstream end of the trout stream reach than what we measured ca. 1.8 km downstream of that point.

The influence of the Minntac tailings, perhaps combined downstream with an influence on fluoride of the Hibbing Taconite tailings in the Sturgeon River, extended far downstream. Kruskal-Wallis test comparisons with reference sites using specific conductance and chloride, Principal Components Analysis, and cluster analysis using ratios of anions to specific conductance suggested that the influence of the tailings on the Little Fork/Sturgeon River watershed extended 95 km downstream of the Minntac tailings. Ratios of anions, anions to specific conductance, and ratios with potassium, sodium, magnesium, and calcium appear to have some potential to serve as tracers of contamination.

This study provided new information on apparent mine tailings contamination that is important for protection of aquatic life in the river system and of the lifeways of wild rice harvesters. It seems that this study is the first documentation of downstream trends in sulfate in the Dark River, of contamination with constituents such as selenium and phosphorus in the river, of low concentrations of contaminants measured with sector-field ICP-MS, and of an estimated downstream extent of mine influence.

[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 Minntac iron mining facilities northwest of Virginia, Minnesota, in the Lake Superior Ojibwe 1854 Treaty-ceded Territory, consist of pits, waste rock piles, processing facilities, and tailings waste basins. The tailings basins receive tailings and waters from the ore processing facilities and from a domestic wastewater treatment plant (MPCA 2016a). The basins also contain a former demolition debris landfill and a dump site that contains scrap metal, mill grease, and waste oil (MPCA 2016a). The facilities began operating ca. 1967.

The tailings facility is mostly surrounded by Superior National Forest land. It is also upstream of several wild rice waters, including the Sandy Lakes on the east side and Dark Lake on the west side (1854 Treaty Authority 2016, MPCA 2016b). The tailings basin seepage drains to groundwater and to the Sand River on the east side and the Dark River on the west side (MPCA 2016a).

Previous studies have documented water quality patterns in the Sand River on the east side of the tailings. This includes a study of the Sandy Lake and Little Sandy Lake (Vogt 2015) that found high levels of alkalinity, specific conductance, Total Dissolved Solids (TDS), sulfate, and chloride in those lakes downstream of the tailings.

Relatively limited data exist for surface water quality on the west side of the Minntac tailings. Kelly *et al*. (2014) measured anions at one site on the Dark River in 2012, and limited additional historical data exist for certain sites further downstream (MWH 2004, MPCA 2016a, STORET and NWIS data through Water Quality Portal 2017).

We sought to fill an information gap on water quality on the west side of the Minntac tailings in the watershed of the Little Fork, Sturgeon, and Dark Rivers. In particular, we sought to identify contaminants and their concentrations, and determine the downstream spatial extent of contamination.

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 metal(loid)s, 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 in 2015 and 2016. In 2016, we also sampled at three sites for alkalinity, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), and metals and other 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 the "dirty hand." In August 2015, we only sampled for anions and collected a blank sample for 5% of samples. During sampling in Minnesota in 2016, we collected field sequential replicates for 14% of metal(loid), alkalinity, and TDS/TSS samples, and collected blank and field sequential replicates for 7% of anion samples. We filtered anion samples using syringes and 25 mm diameter, 0.45 µm polysulfone cartridge filters (Pall Acrodisc 4585) within 11 hours of sample collection. We analyzed those samples by ion chromatography within 9 days after sample collection. We did not filter the metal(loid) samples.

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)	Incuctively-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^-**
2016	0.0089[1]	0.0092	0.032[2]	0.0056[1]	0.0055
2015	0.020[2]	0.011[3]	0.030[3]	0.0016	0.0045

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

The Wisconsin State Laboratory of Hygiene analyzed our 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. Limits of detection were less than 0.1 µg/l for all the trace elements, and less than 1 ng/l for most of the trace elements (Appendix F). We used total concentrations of Ca and Mg to calculate total hardness in each sample.

Additional Quality Assurance and Quality Control (QAQC)

We also verified that field and sample laboratory measurements for pH and specific conductance, for sampling events with both field and laboratory measurements, differed by less than 10%. TDS and TSS samples at three fully-sampled sites (SC209, SC078, and SC077B) exceeded the 7 day holding time for the method, so we 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. We excluded TDS measures (SC209) that were lower than the minimum estimates.

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 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 (0.3m resolution) at a spatial resolution of 1:5000 or finer. We conducted a non-parametric local regression (LOESS) analysis for characteristics with adequate sampling (specific conductance and chloride) 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) concentrations at three sites progressively downstream of the tailings to identify similarities in patterns of concentrations that might be indicative of similar sources as well. Finally, we compared our downstream data with limited available data on the SD001 western discharge from the tailings from regulatory documents including Discharge Monitoring Reports and permitting documents.

(2) To compare sites downstream of the tailings with reference sites, we assessed the range of values at different sites and conducted three analyses to statistically compare sites. We used a Principal Components Analysis (PCA) and a clustering analysis, using Ward's hierarchical accumulative method with squared Euclidian distances, 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 PCA and cluster analyses. Finally, we tested for differences between downstream and reference sites for characteristics with adequate sampling 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), and also limited data from regulatory documents and other studies.

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

Study sites were located downstream of the Minntac tailings in the watersheds of the Little Fork, Sturgeon, and Dark Rivers (Figs. 1-2). We also studied a few reference sites that were in those watersheds but not downstream of the Minntac tailings (Figs. 1-2). We recorded field measurements at all sites visited, but only sampled for anions at selected sites in 2015 and 2016, and only sampled for metals and other trace elements in 2016 at three sites (Figs. 1-2). In addition to the tailings basin, the landscape surrounding the river included primarily wetlands, lakes, forests, and roads (Figs. 1-2, Appendix B). The Dark River flows through the listed wild rice waters of Dark Lake (Fig. 1).

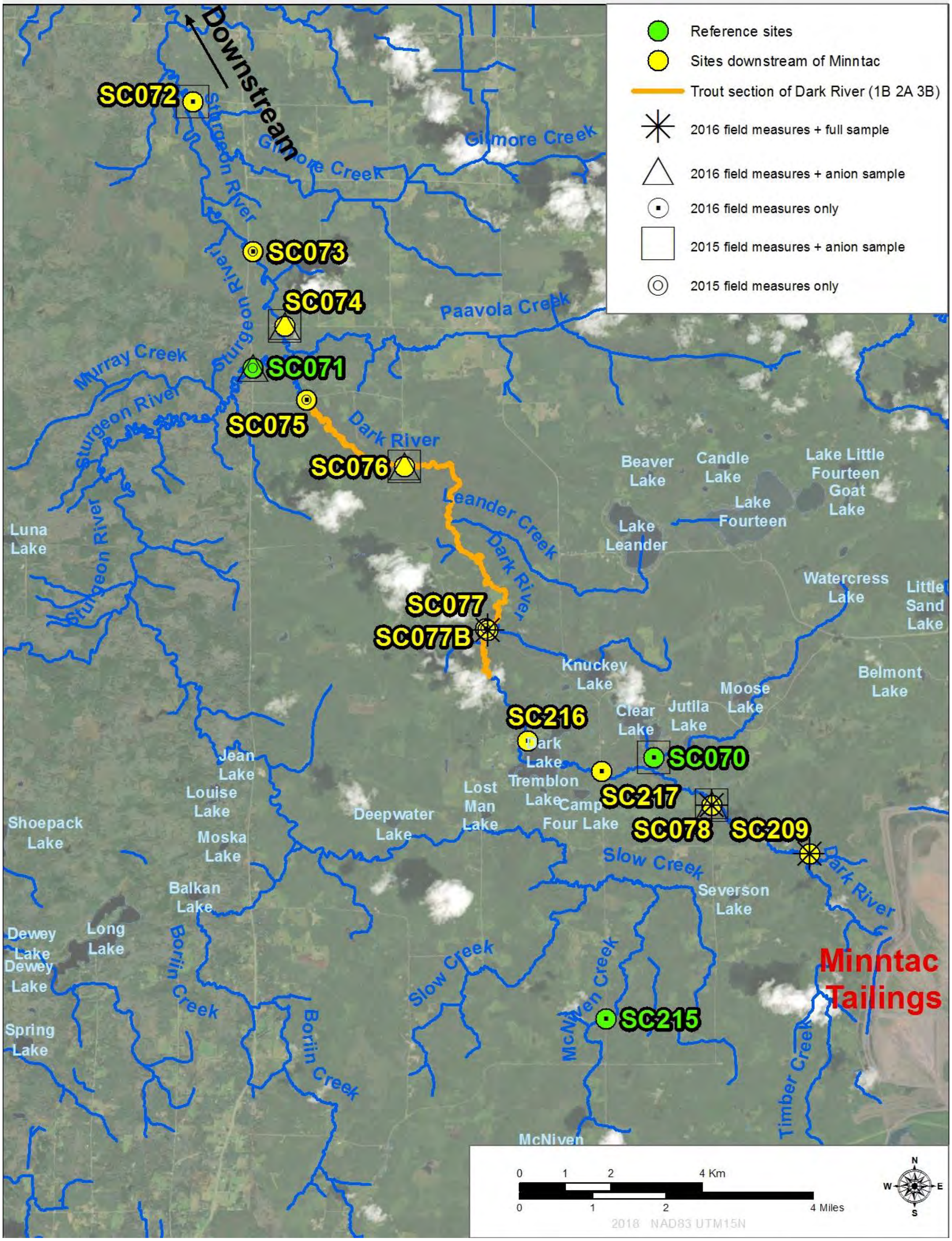


Fig. 1. Map of sampling sites in the upper reaches of the watersheds of the Dark River and Sturgeon River from 2015 and 2016.

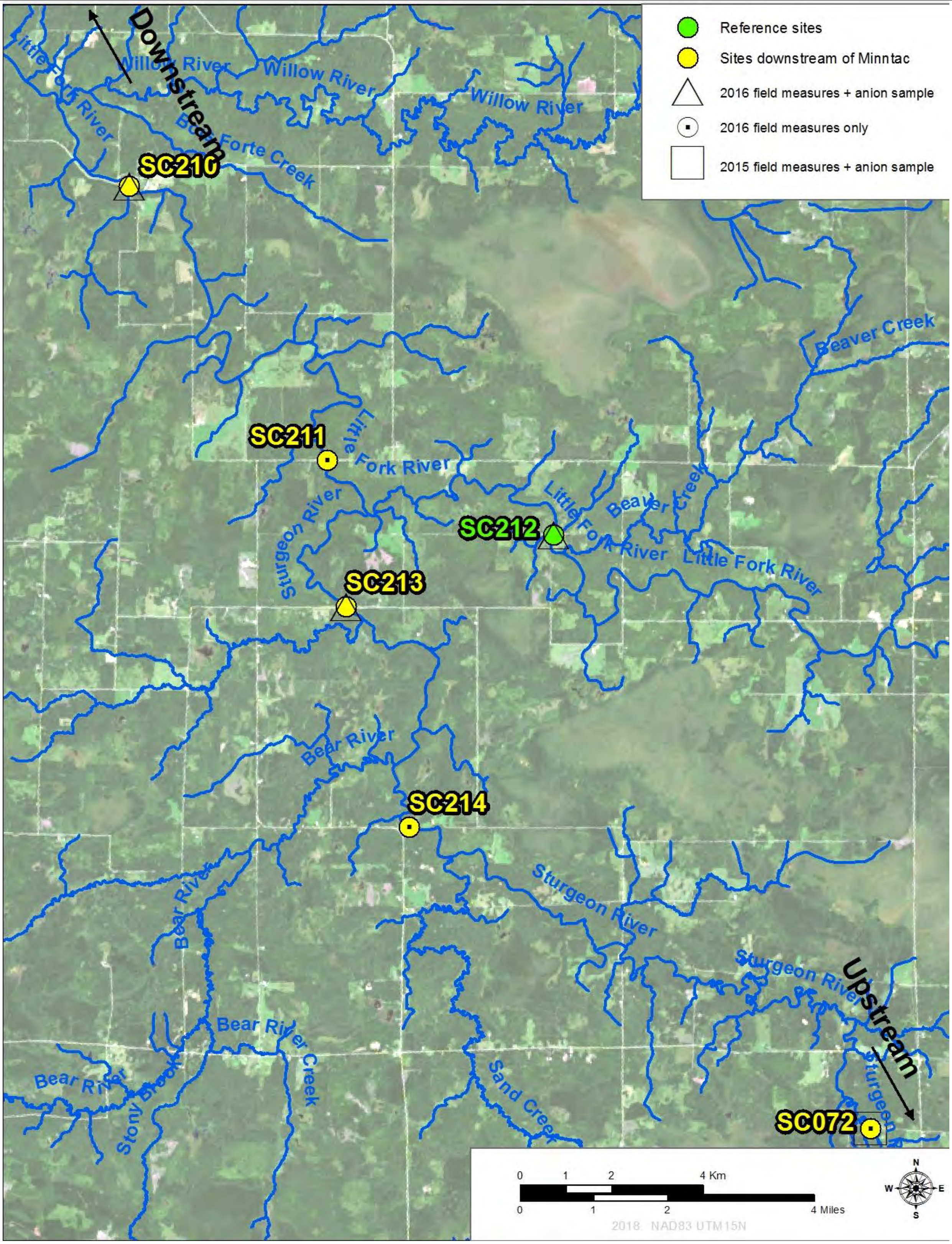


Fig. 2. Map of sampling sites in the downstream reaches of the watersheds of the Dark River and Sturgeon River in 2015 and 2016.

3. RESULTS

(A) Downstream trends, exceedances, and comparison with discharge data

Downstream trends – general water quality characteristics

Most of the measures of general water quality were higher nearest the tailings and decreased at sites further downstream. Specific conductance, TDS, alkalinity, and hardness all demonstrated such a pattern (Figs. 3, 4; Tables 3-4). Specific conductance in 2016 declined over the shortest river distance in the reach between the headwaters and Dark Lake (SC078-SC216), and from upstream to downstream of the confluence with the Sturgeon River (SC075-SC074; Fig. 3; Table 3). LOESS analysis of 2016 data also indicated a consistent decreasing trend in specific conductance downstream (Fig. 3). **Specific conductance** exceeded the state criterion of 1000 µS/cm at the two sites nearest the tailings in 2016 and continued to exceed the criterion even further downstream in the trout reach in 2015 (Fig. 3, Table 3). **TDS** also exceeded the state criterion at SC078, and **hardness** exceeded the applicable state criterion at all three measured headwaters sites (Fig. 4; Table 4). Dissolved oxygen (DO) and pH demonstrated less consistent trends. DO was lowest nearest the tailings, but was also lower downstream of the confluence with the Sturgeon River than upstream of that confluence (Fig. 5; Table 3). The lowest **DO** value at SC209 was below the state minimum criterion, as was the reference site (SC070) in the wetland stream from Clear Lake in 2015 (Fig. 5; Table 3). In both 2015 and 2016, pH was highest in the upper part of the trout reach in the Dark River at SC077/SC077B and was gradually lower than that upstream and downstream of that point (Fig. 6; Table 3).

Downstream trends – major anions

Similar to most of the general water quality characteristics, concentrations of most measured major anions were highest nearest the tailings and decreased at sites further downstream. In 2016, chloride, sulfate, and bromide followed that pattern, although bromide was highest at the site that was the second closest to the tailings, SC078 (Figs. 7-9; Table 3). LOESS analysis also indicated a consistent decreasing trend in chloride concentrations downstream for 2016 (Fig. 8). The greatest declines over the shortest river distance for anions also occurred mostly over the same reaches as for specific conductance in 2016 (Figs. 7-9; Table 3). **Sulfate** exceeded the trout stream reach criterion of 250 mg/l in the trout section of the Dark River in 2015 (Fig. 7; Table 3). Sulfate also exceeded the criterion for wild rice waters at all sites downstream of the tailings, including the measured sites upstream and downstream of the wild rice waters of Dark Lake (Fig. 7; Table 3). The downstream pattern for fluoride concentrations differed from the pattern of the other anions. Although it steadily decreased downstream of SC078 in 2015, fluoride concentrations in the main channel in 2016 exhibited peaks at SC078 and SC074 (Fig. 10, Table 3). The highest fluoride concentration in 2016 overall was at the Sturgeon River reference site of SC071, which is downstream of Hibbing Taconite (Fig. 10, Table 3). That site was also just upstream of the spike in main channel fluoride concentration at SC074 (Fig. 10, Table 3). **Fluoride** did not exceed the state criteria at any of the sites, but exceeded the Canadian criterion of 0.12 µg/l at all sites downstream of Minntac and at the Sturgeon River SC071 site (Fig. 10, Table 3). Fluoride was below 0.12 µg/l at the other measured reference sites (Fig. 10, Table 3). Although nitrate samples exceeded holding times, concentrations were highest in the downstream sections of the Sturgeon River and Little Fork Rivers, both at the reference sites and in the reaches downstream of Minntac (Appendix D). The greatest increase in nitrate occurred between SC077B and SC074 (Appendix D).

Examination of ratios of anions, and anions with specific conductance, indicated that ratios differed in whether or not they distinguished reference sites from sites downstream of Minntac, and how stable they were downstream of the tailings basin. Only the ratios of sulfate to specific conductance and sulfate to chloride had ranges of values that did not overlap between reference sites and sites downstream of tailings (Appendix A). The ratio of chloride to bromide did not overlap between most reference sites and downstream sites, but the ratio at SC071 did overlap with downstream sites (Appendix A). The sulfate ratios and the ratio of bromide to specific conductance decreased downstream of the tailings (Appendix A). The ratios that appeared most stable as one measures from upstream to downstream sites were chloride to specific conductance, and, at least in the reaches upstream and downstream of the Sturgeon River confluence at SC071, fluoride to specific conductance and chloride to fluoride (Appendix A).

Downstream trends – trace elements

The measurements for several metals and other trace elements at three sites indicated that concentrations were highest nearest the tailings and decreased at successive downstream sites. These metals and trace elements included the major elements sodium, magnesium, potassium, and calcium (Fig. 4); the minor elements boron and strontium (Fig. 11); and the trace elements lithium, selenium, rubidium, barium, and uranium (Fig. 12; Table 4). Molybdenum, rhodium, and cesium also demonstrated that pattern, though their concentrations were all < 1 µg/l (Appendix D). Unlike all those elements, iron increased downstream of tailings, particularly between SC078 and SC077B (Fig. 11; Table 4). Similarly, aluminum concentrations increased steadily downstream of the Minntac tailings (Fig. 12). Manganese concentrations decreased between SC209 and SC078, but increased between SC078 and SC077B (Fig. 11; Table 4). Phosphorus demonstrated the inverse pattern of manganese, as it increased between SC209 and SC078, but decreased between SC078 and SC077B (Fig. 12; Table 4). Nonetheless, the highest concentrations for both manganese and phosphorus occurred in one of the two sites nearest the tailings (SC209 or SC078; Figs. 11-12).

Several of the trace element measurements exceeded criteria or guidelines. **Iron** and **manganese** exceeded trout stream criteria at SC077B, and manganese was greater than the EPA human health guideline at the other two sites upstream (Fig. 11; Table 4). **Phosphorus** concentrations at the upstream sites were greater than the 30 µg/l state criterion for lakes in that region, and the concentration at SC077B was greater than the state class 2A trout lake criterion of 20 µg/l (Fig. 12; Table 4). Finally, **selenium** concentrations were within 6% of the state criterion of 5 µg/l at SC209, and exceeded the 2016 EPA streams and rivers criterion of 3.1 µg/l at SC209 and SC078 (Fig. 12; Table 4).

Certain metal constituent ratios were, compared to changes in anion ratios, relatively stable between the three sites. Those included sulfate to calcium, potassium to potassium plus sodium, and magnesium to sodium (Appendix A).

Table 3. Measurements of anion concentrations and other general regulated water quality characteristics relative to state and other criteria at sites in the Dark River downstream of the Minntac tailings. Measurements in **<u>bold and underlined</u>** exceeded apparently applicable Minnesota criteria, and measurements that are only **bold** exceeded other listed criteria or guidelines. Within a given year, sites are listed from upstream to downstream sites, with some reference sites (R) listed at the end of each year. Sites with an asterisk (*) are sites in the designated trout stream reach of the Dark River. The rice water sulfate criterion may also apply in parts of the Dark River watershed.

		Specific conductance (uS/cm)	Dissolved Oxygen (mg/l)	pH	Fluoride (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
Criterion (non-trout stream, Class 2B, 3C, 4A, 4B, 5, and 6)		1000	5.0	6.5-8.5	(0.12 Canada)	230	10 in rice waters
Criterion (trout stream, Class 1B, 2A, 3B, 4A, 4B, 5, and 6)		1000	7.0	6.5-8.5	2 (0.12 Canada)	100	250 (10 in rice waters)
Date	Site Code						
2015-Aug-24	SC078	**<u>1775</u>**	9.1	8.0	**0.41**	66	630
2015-Aug-24	SC077*	**<u>1266</u>**	9.3	8.4		62	
2015-Aug-24	SC076*	**<u>1028</u>**	9.2	8.2	**0.27**	37	**<u>319</u>**
2015-Aug-24	SC075*	908	9.4	8.2		40	
2015-Aug-24	SC074	502	9.3	8.0	**0.21**	17	127
2015-Aug-24	SC073	514	8.8	8.0		22	
2015-Aug-24	SC072	532	9.0	8.1	**0.19**	17	137
2015-Aug-24	SC070 (R)	100	**<u>4.5</u>**	6.6	0.11	7	1.4
2015-Aug-24	SC071 (R)	139	8.4	7.6		7	
2016-Jul-29	SC209	**<u>1723</u>**	**<u>3.0</u>**	7.6	**0.39**	49	524
2016-Jul-28	SC078	**<u>1490</u>**				41	
2016-Jul-29	SC078	**<u>1545</u>**				47	
2016-Jul-30	SC078	**<u>1568</u>**				47	
2016-Jul-31	SC078	**<u>1585</u>**	5.7	7.7	**0.43**	45	476
2016-Jul-31	SC217	939				31	
2016-Jul-31	SC216	659				21	
2016-Jul-31	SC077B*	624	8.0	7.8	**0.17**	16	150
2016-Jul-30	SC077*	627				17	
2016-Jul-30	SC076*	522	8.0	7.4	**0.15**	14	119
2016-Jul-30	SC075*	493				14	
2016-Jul-30	SC074	258	7.5	7.2	**0.34**	7	34
2016-Jul-30	SC073	257				7	
2016-Jul-30	SC072	251				8	
2016-Jul-30	SC214	232				7	
2016-Jul-30	SC213	214	8.0	7.1	**0.19**	5	20
2016-Jul-30	SC211	147				5	
2016-Jul-30	SC210	150	8.0	7.0	**0.15**	4	10
2016-Jul-31	SC215 (R)	113				4	
2016-Jul-31	SC070 (R)	99				9	
2016-Jul-30	SC071 (R)	170	7.3	7.2	**0.44**	6	5.2
2016-Jul-30	SC212 (R)	90	7.1	**<u>6.4</u>**	0.03	4	0.81

Table 4. Measurements of TDS, hardness, phosphorus, selenium, and select regulated metals relative to state and other criteria at sites in the Dark River downstream of the Minntac tailings. Measurements in **<u>bold and underlined</u>** exceeded apparently applicable Minnesota criteria, and measurements that are only **bold** exceeded other listed criteria or guidelines. Sites are in order from upstream to downstream. The site with an asterisk (*) was in the designated trout stream reach of the Dark River. Concentrations are total, not dissolved concentrations.

		Total Dissolved Solids (mg/l)	Total hardness (mg/l)	Phosphorus (µg/l)	Manganese (µg/l)	Iron (µg/l)	Selenium (µg/l)	Uranium (µg/l)
Criterion (non-trout stream, Class 2B, 3C, 4A, 4B, 5, and 6)		700	500	30 (Northern Lakes)	(50 USEPA human health)	(1000 USEPA)	5 (3.1 USEPA, 1 Canada)	30 (USEPA drinking water), 15 (Canada)
Criterion (trout stream, Class 1B, 2A, 3B, 4A, 4B, 5, and 6)		500	250	20 (2A trout lakes)	50	300	5 (3.1 USEPA, 1 Canada)	30 (USEPA drinking water), 15 (Canada)
Date	Site Code							
2016-Jul-29	SC209		**<u>971</u>**	**67**	**198**	122	**4.7**	1.6
2016-Jul-31	SC078	**<u>1170</u>**	**<u>831</u>**	**85**	**127**	153	**4.1**	1.4
2016-Jul-31	SC077B*	416	**<u>295</u>**	29	**<u>149</u>**	**<u>927</u>**	**1.7**	0.57

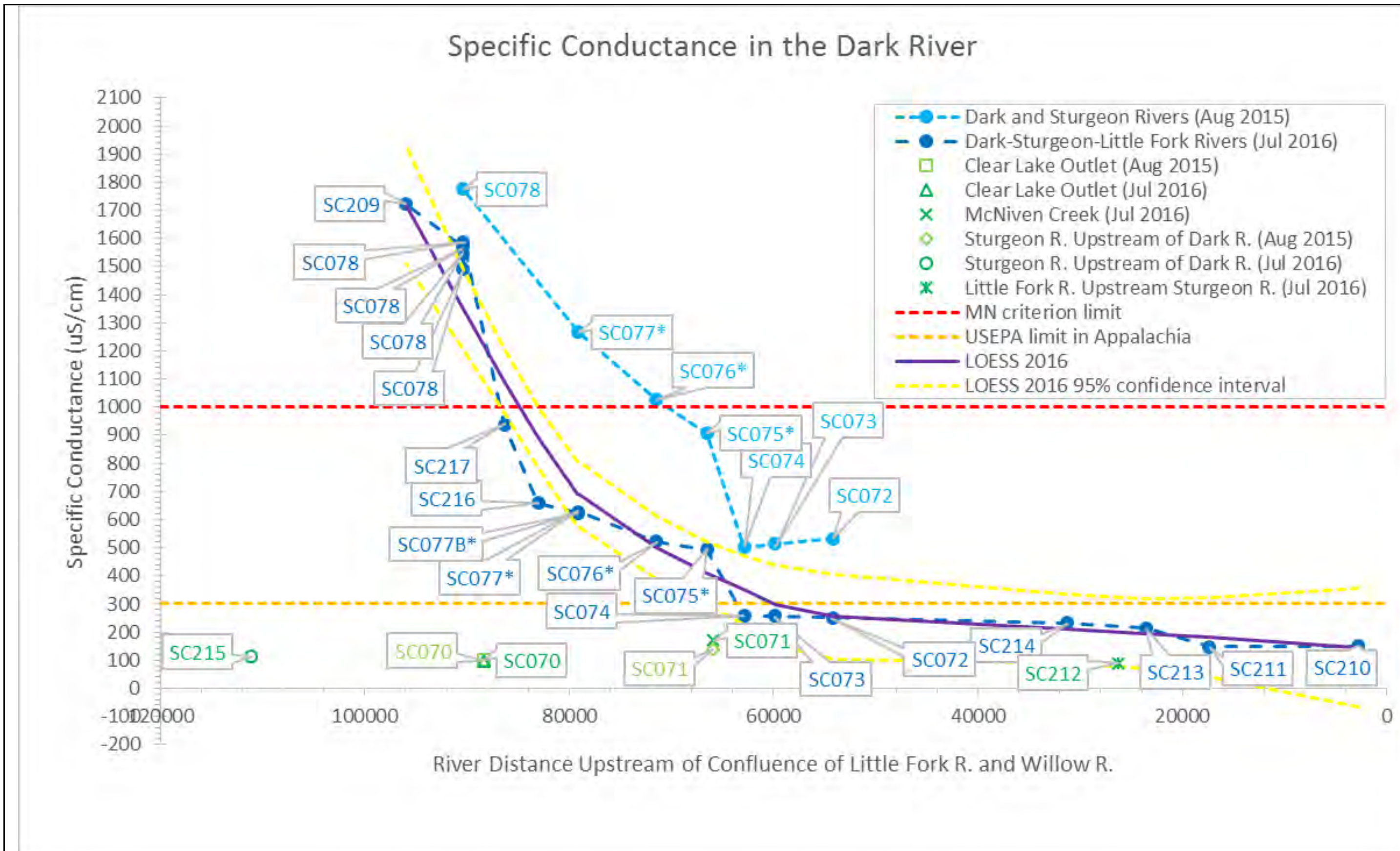


Fig. 3. Specific conductance decreased downstream of the Minntac tailings in the Dark River – Little Fork River systems and remained greater than other tributaries until at least SC213. Specific conductance was lower in July 2016 than in August 2015. Specific conductance exceeded the MN criterion in the headwaters. Site codes with an asterisk represent sites in the designated trout reach of the Dark River. We took several measurements for SC078 between 28 July and 31 July 2016. LOESS analysis indicated that specific conductance decreased with increasing distance downstream of the Minntac tailings in 2016 (smoothing factor was 0.633).

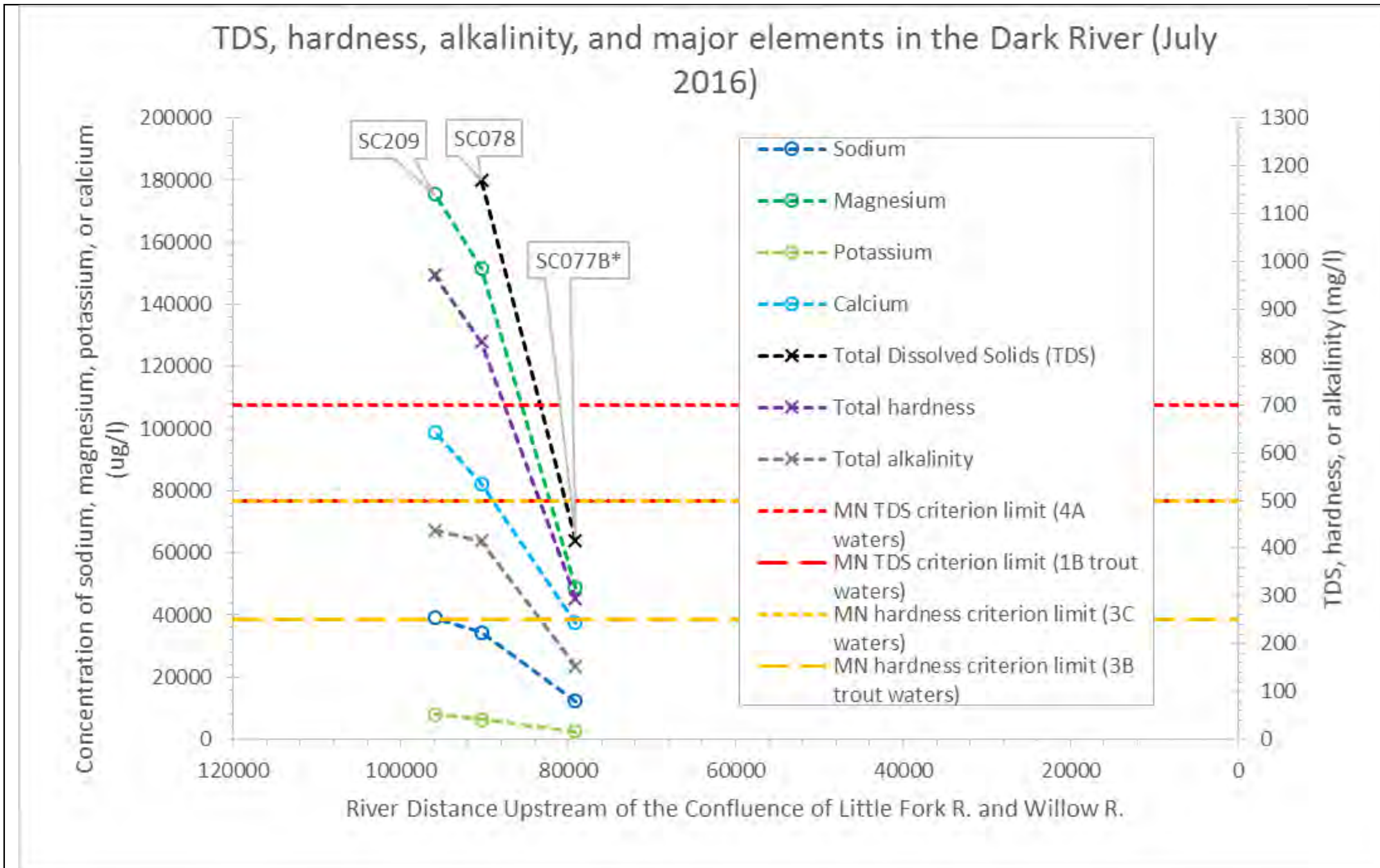


Fig. 4. Total Dissolved Solids (TDS), total hardness, total alkalinity, and concentration of major elements decreased downstream of the Minntac tailings. TDS exceeded the criterion at SC078, and hardness exceeded the applicable criterion at all three sites. The site code with an asterisk (*) represents a site in the designated trout reach of the Dark River.

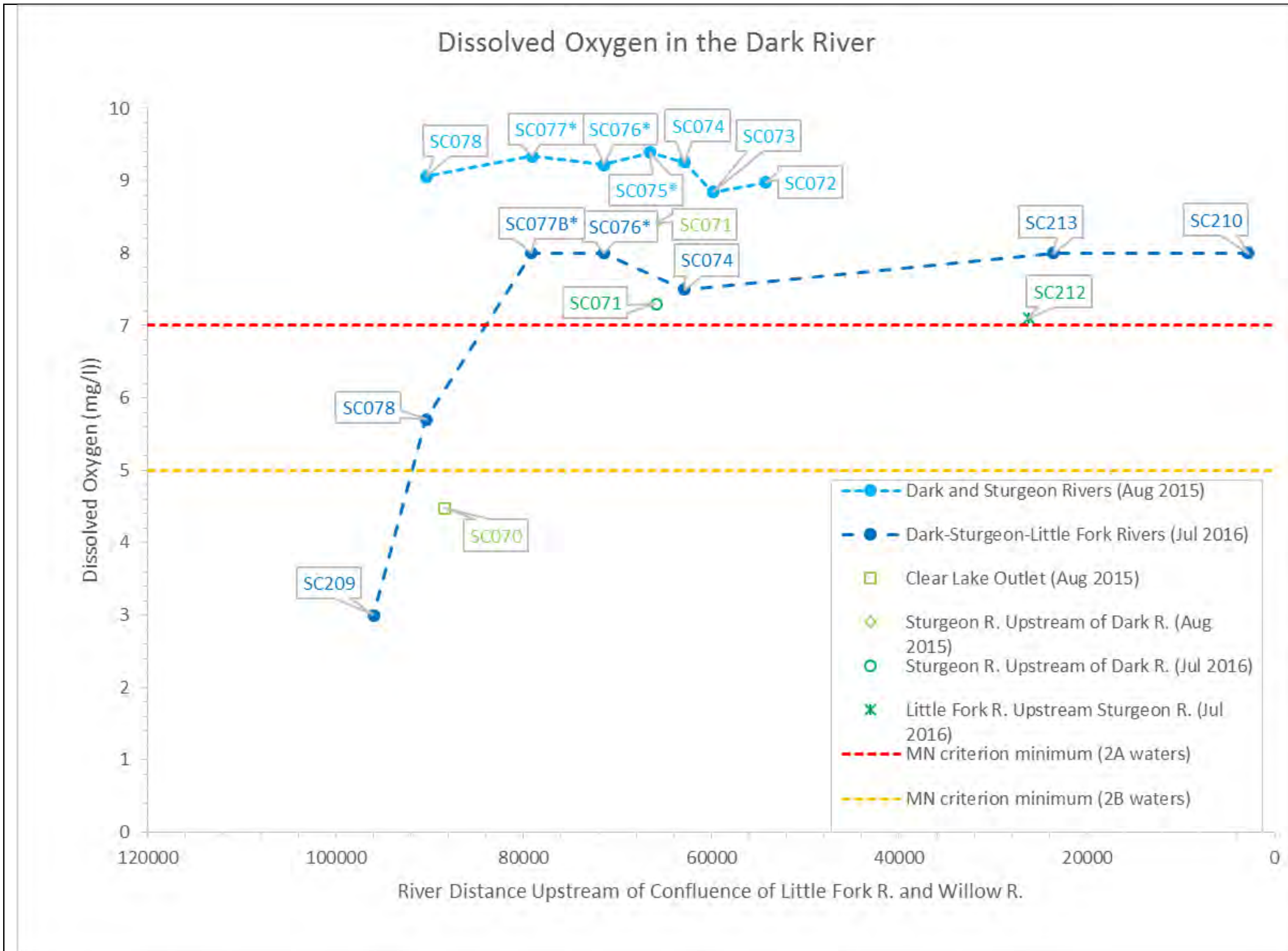


Fig. 5. Dissolved Oxygen (DO) was lowest nearest the Minntac tailings (SC209) in 2016. The Dark River headwaters were below the MN minimum criterion in 2016, as was the stream from Clear Lake. Site codes with an asterisk represent sites in the designated trout reach of the Dark River.

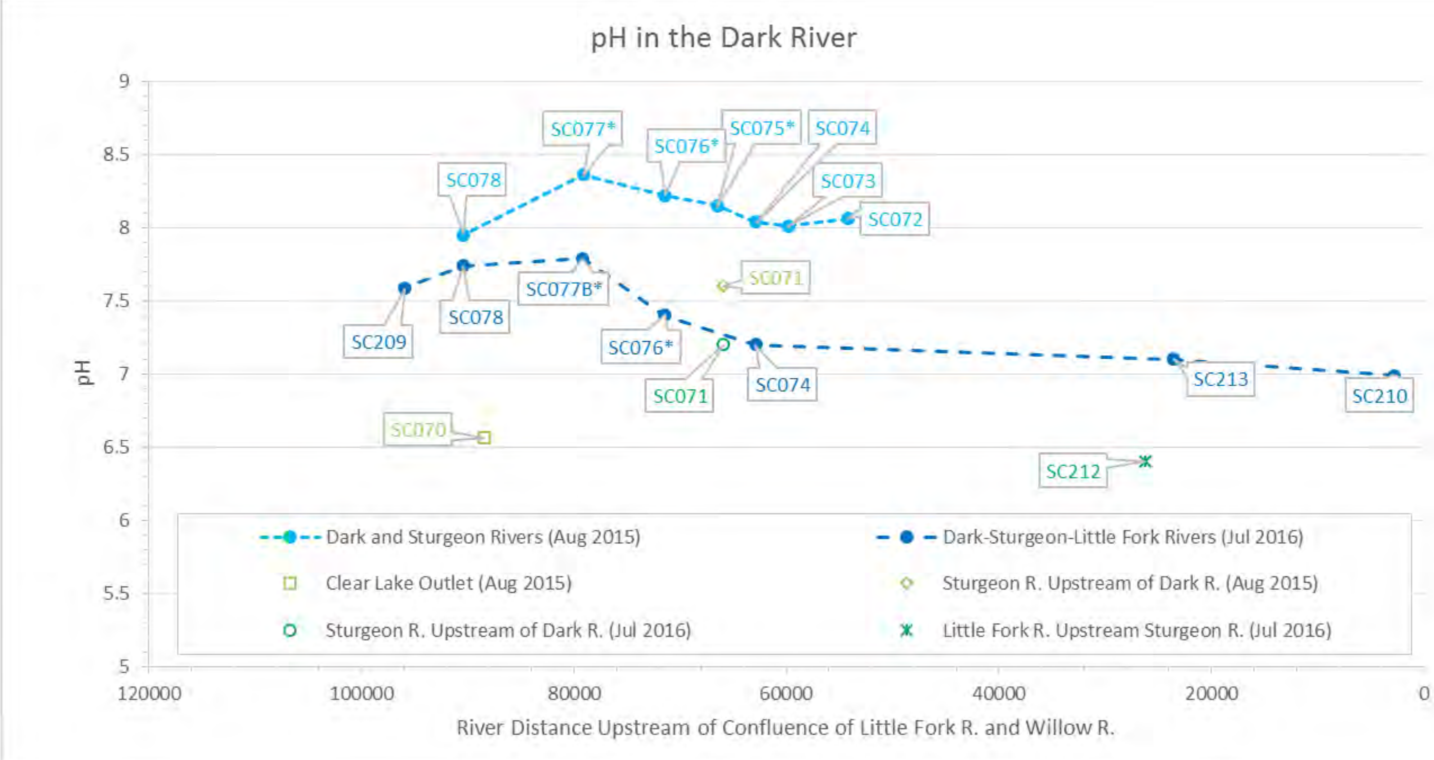


Fig. 6. The pH was highest at a site (SC077/SC077B) downstream of the Dark Lake in 2015 and 2016 sampling. It was also greater in August 2015 than in July 2016. Site codes with an asterisk represent sites in the designated trout reach of the Dark River.

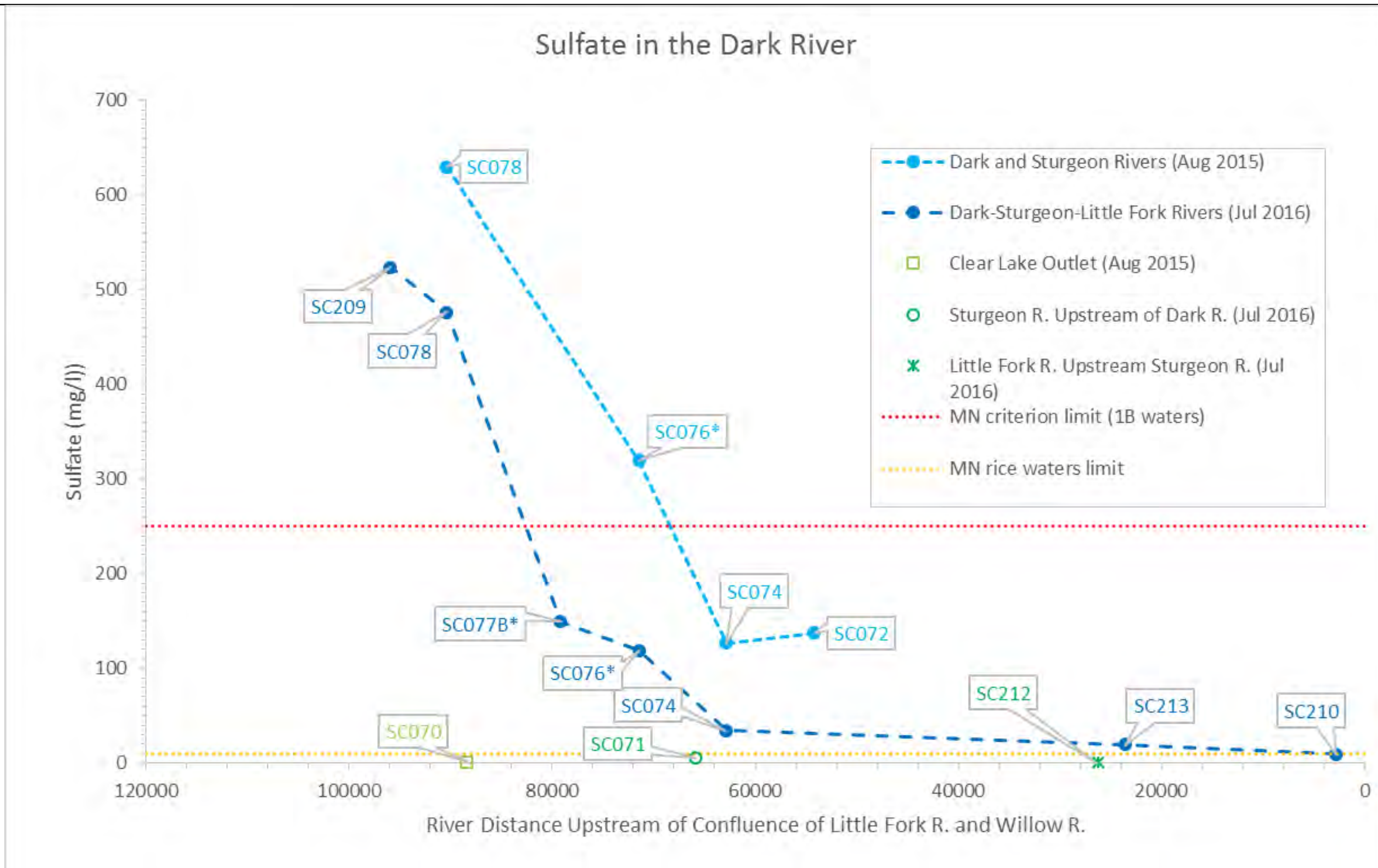


Fig. 7. Sulfate was greatest nearest the Minntac tailings and greater in August 2015 than in July 2016. Site codes with an asterisk represent sites in the designated trout reach of the Dark River.

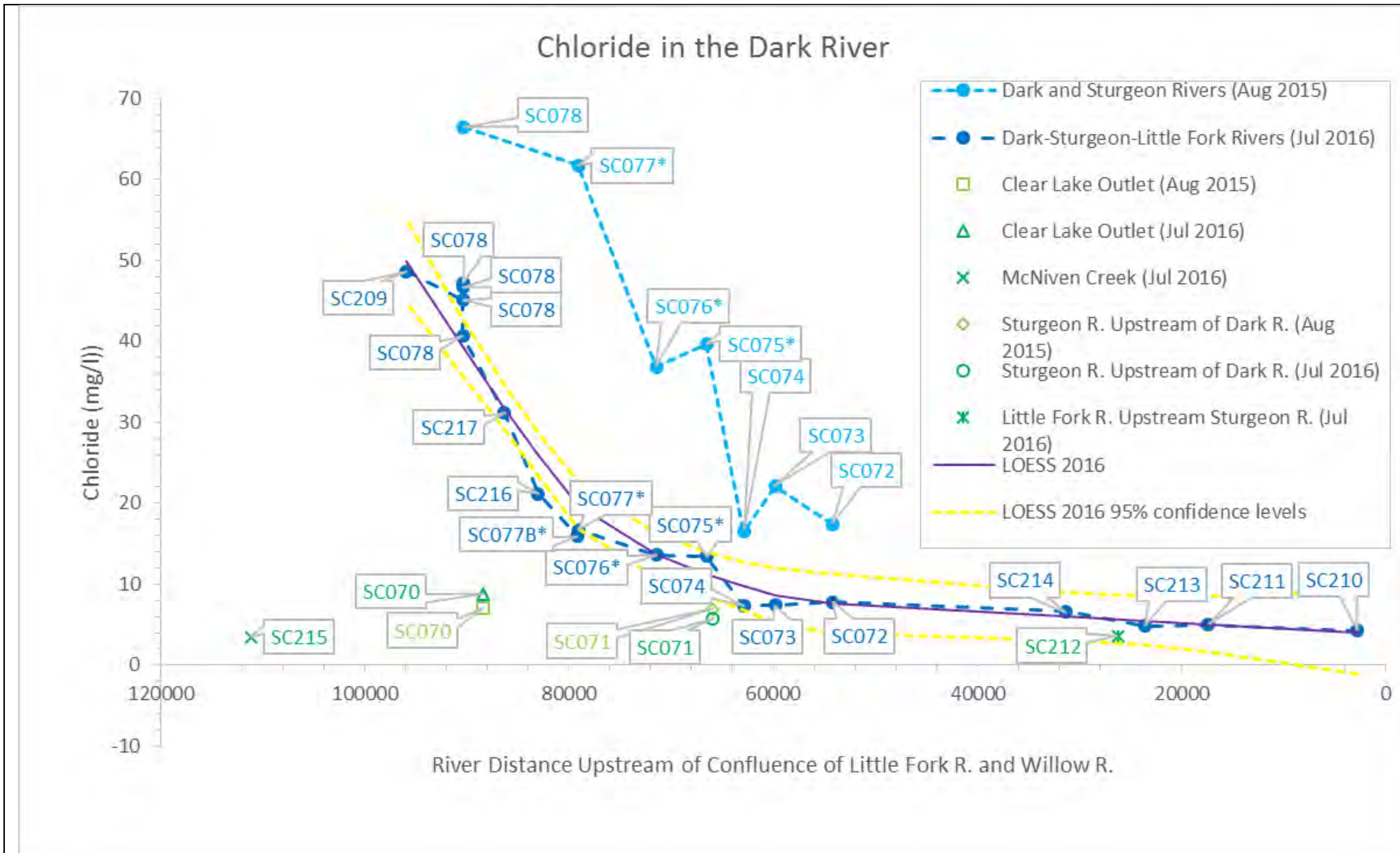


Fig. 8. Chloride concentrations were greatest nearest the Minntac tailings and decreased downstream. Site codes with an asterisk (*) represent sites in the designated trout reach of the Dark River. We took several measurements for SC078 between 28 July and 31 July 2016. LOESS analysis indicated that the chloride concentration decreased with increasing distance downstream of the Minntac tailings in 2016 (smoothing factor was 0.633).

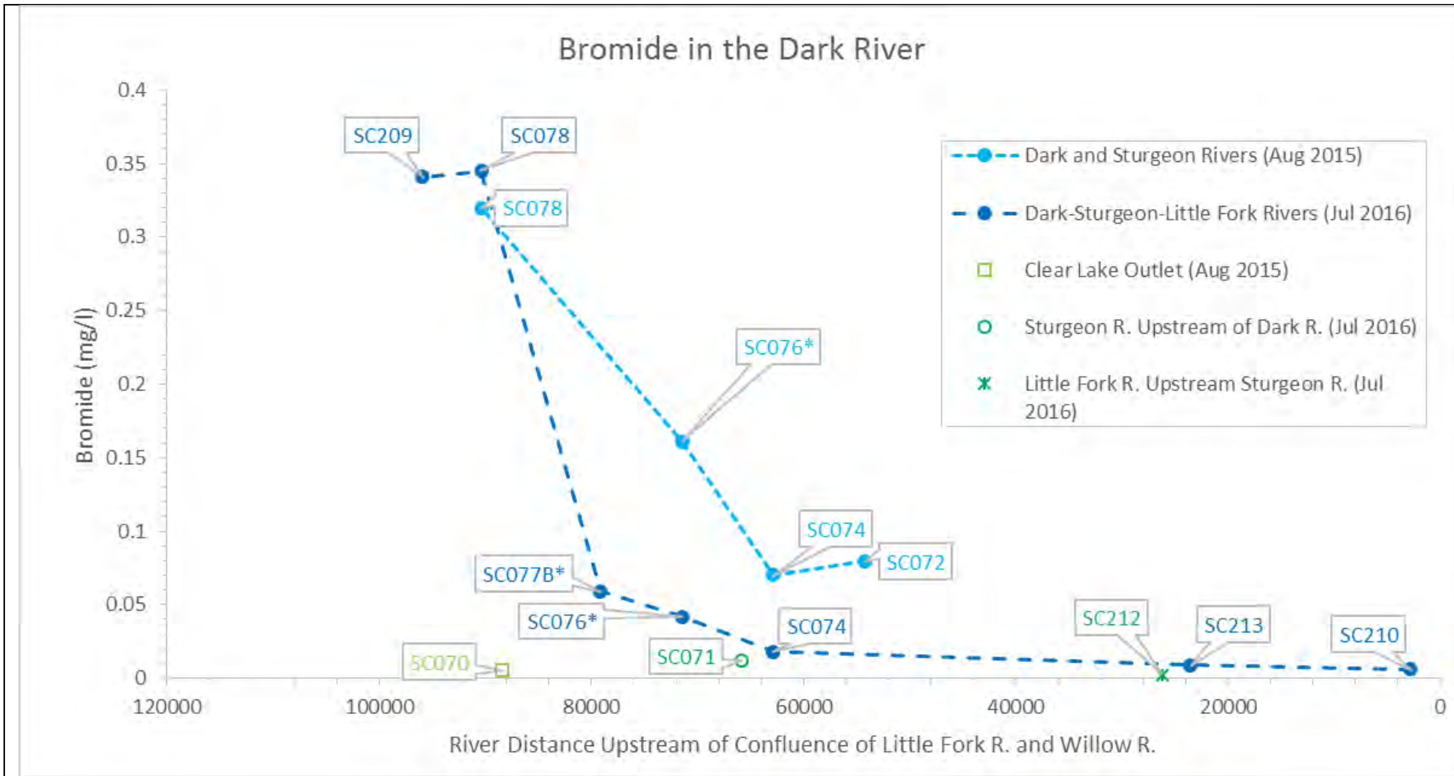


Fig. 9. Bromide was greatest at the two sites nearest the Minntac tailings. Site codes with an asterisk (*) represent sites in the designated trout reach of the Dark River. Measurements at SC070 and SC212 were plotted at half of the Minimum Reporting Limit.

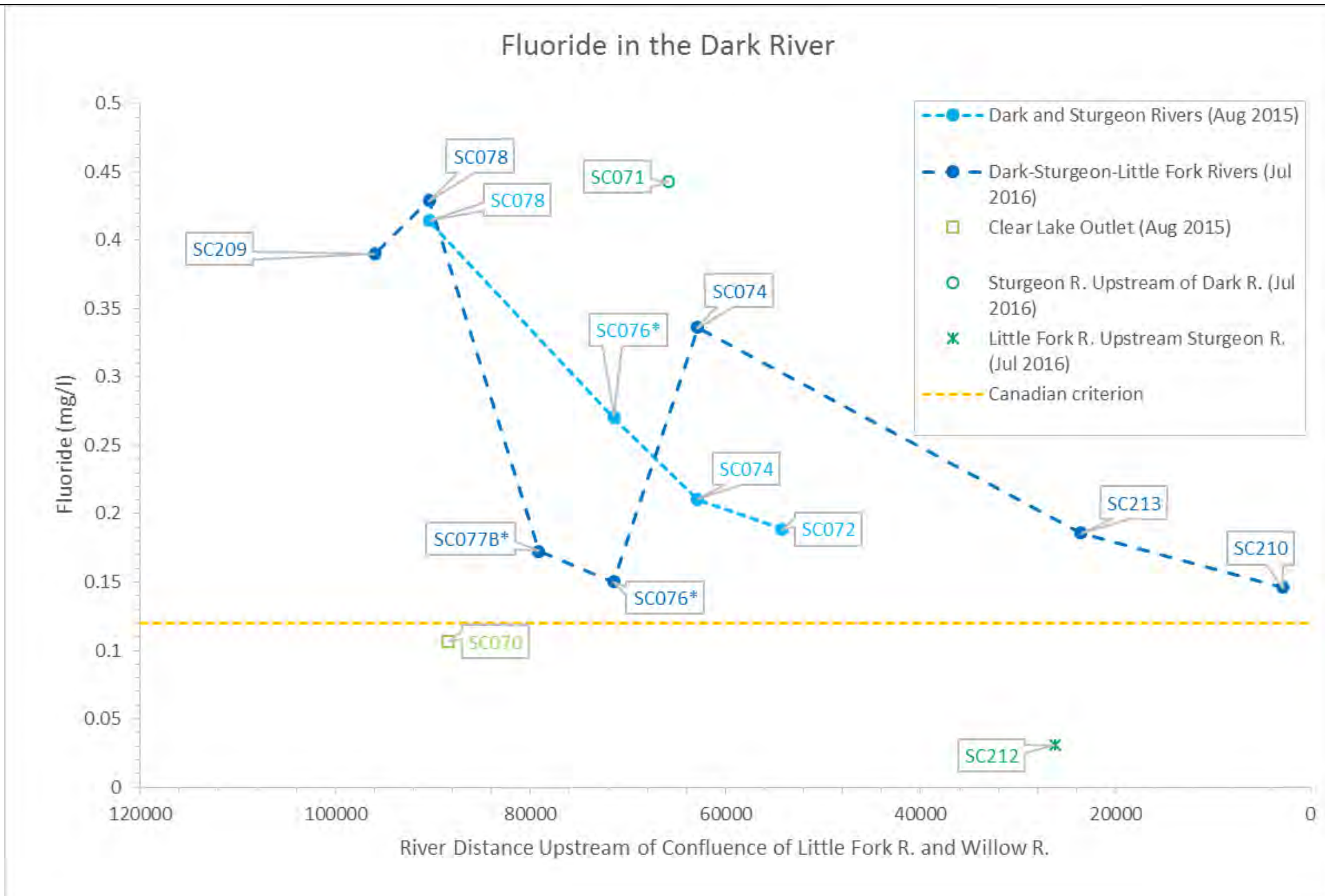


Fig. 10. Fluoride in the Dark River watershed was highest at the two sites nearest the Minntac tailings, but in 2016 was highest in the Sturgeon River upstream of its confluence with the Dark River. Fluoride also was high again downstream of that confluence. Measurements for all but two reference sites were greater than the Canadian fluoride guideline. Site codes with an asterisk (*) represent sites in the designated trout reach of the Dark River.

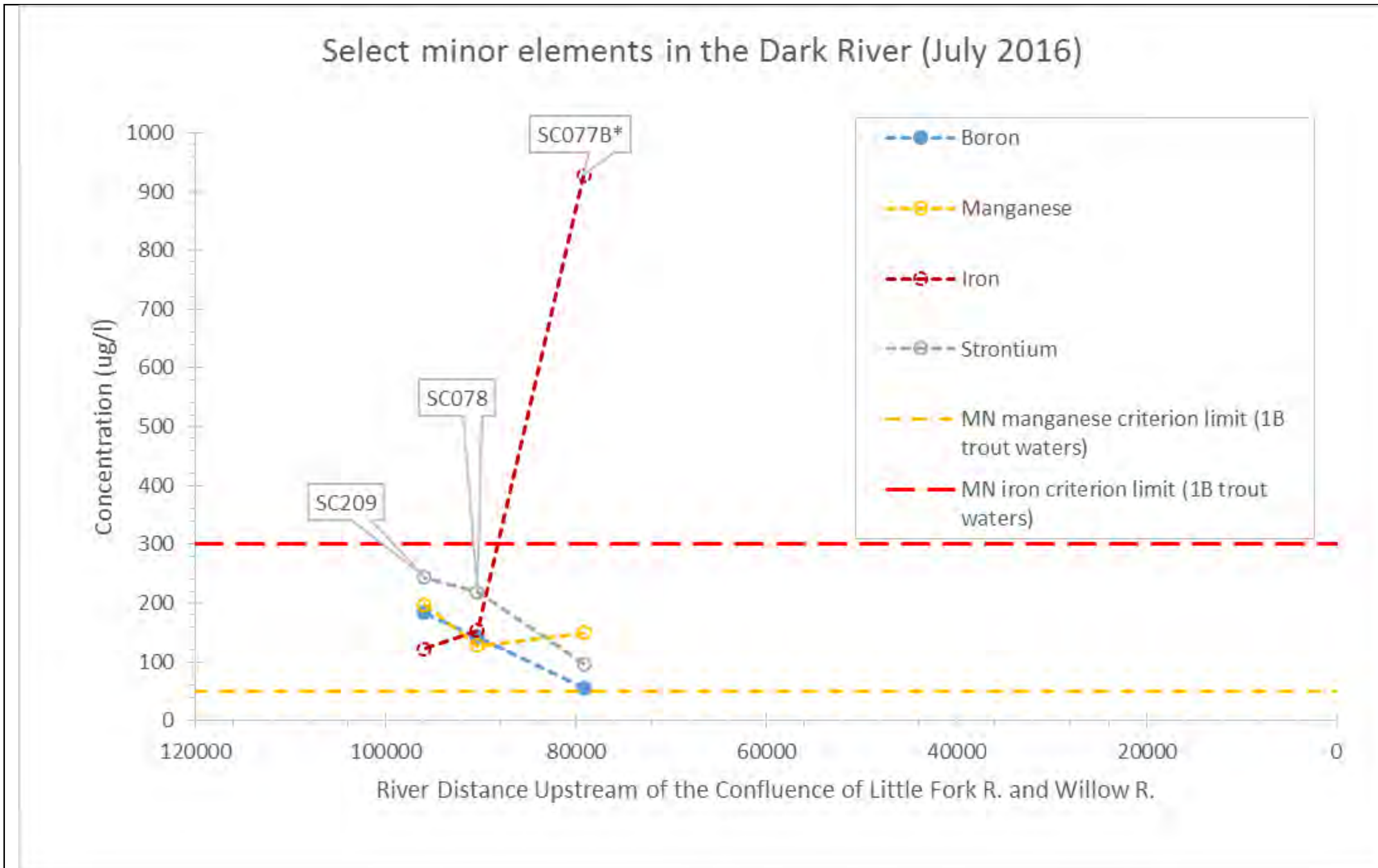


Fig. 11. Concentrations of boron and strontium decreased downstream of the Minntac tailings, but concentrations of manganese and iron decreased (SC209 to SC078) then increased downstream of Dark Lake (SC077B). The site code with an asterisk (*) represents a site in the designated trout reach of the Dark River.

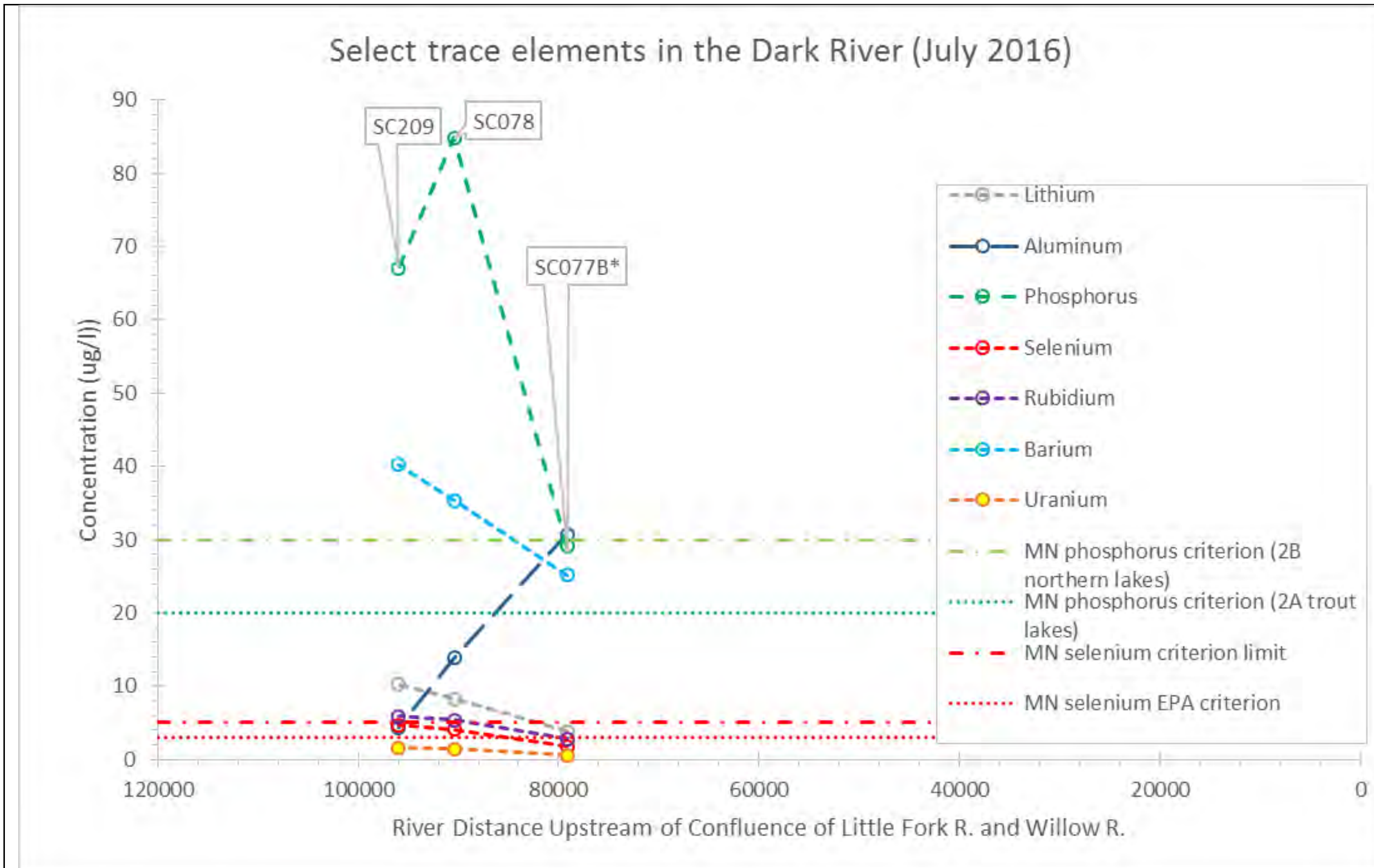


Fig. 12. Concentrations of lithium, selenium, rubidium, barium, and uranium decreased progressively downstream of the Minntac tailings. Aluminum, however, increased downstream, and phosphorus increased then decreased downstream of Dark Lake. Upstream phosphorus exceeded lake phosphorus criterion, and upstream selenium concentrations exceeded the EPA criterion. The site code with an asterisk (*) represents a site in the designated trout reach of the Dark River.

REE Analysis

Comparison of REE concentrations between three Dark River samples and other samples we collected in Minnesota indicated that the Dark River sites closest to the tailings were relatively low in lanthanum but relatively high in europium (Fig. 13). The Dark River site downstream of Dark Lake demonstrated a REE pattern similar to the Dunka River and Dunka Pit outfall stream (Fig. 13).

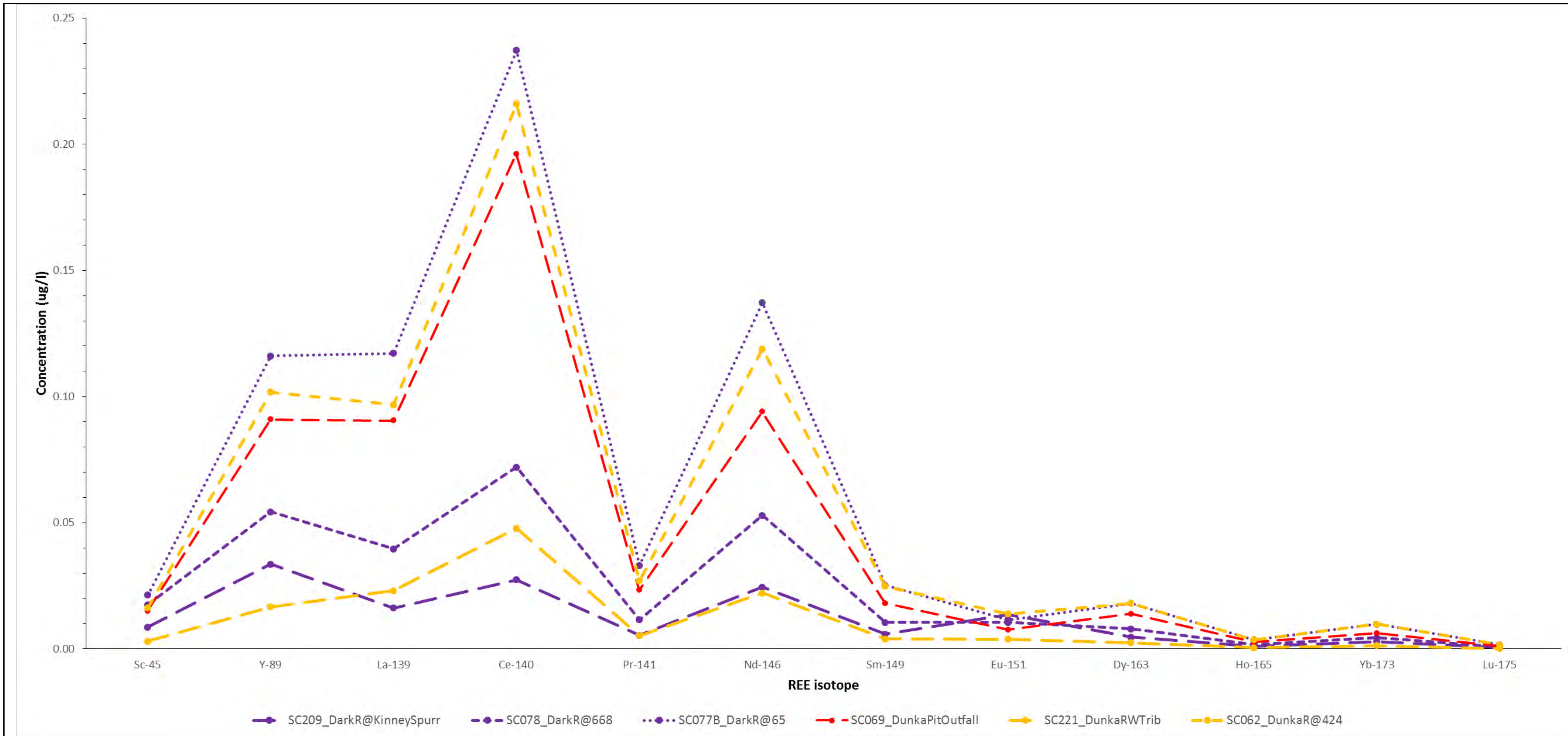


Fig. 13. Comparison of Rare Earth Element (REE) concentrations at sampled sites in Minnesota indicated that the sites nearest the tailings in the Dark River (SC209, SC078) were relatively low in lanthanum (La-139) and the nearest site (SC209) was relatively high in europium (Eu-151). The pattern of REE in the downstream Dark River site (SC077B) was similar to the pattern from the Dunka River (SC062) and the Dunka Pit outfall stream (SC069) near Babbitt, MN.

Comparison with measurements from tailings discharge

Monthly Discharge Monitoring Report (DMR) data indicated that the tailings discharge on the western side of the Minntac tailings (SD001) in recent years demonstrated high specific conductance and sulfate concentrations (Fig. 14), a ratio of sulfate to specific conductance of 0.34-0.45 $mg*l^{-1}*cm*\mu S^{-1}$ (Fig. 15), and a pH usually of 6.8-7.4 (Fig. 16). The discharge has also contained up to 5 mg/l of total recoverable oil and grease, with recent years having higher concentrations (Fig. 17). Total organic amines were reported as "0" between 1999 and 2006, but detection limits were not listed. Specific conductance and sulfate DMR data were monthly maxima, and pH were daily minima and maxima rather than individual measurements.

The range of DMR specific conductance, sulfate, sulfate:specific conductance, and pH measurements were higher than or bracketed the measurements we observed at our study sites closest to the tailings. Specific conductance and sulfate concentrations were at their highest in our measurements at SC209 and those values were within 50% of the DMR monthly maximum measurement values (Figs. 3, 6, 7; Table 3; Appendix A). The DMR values for the ratio of sulfate to specific conductance bracketed the SC078 value for 2015 and our 2016 measurement was within 11 % of that range as well (Fig. 15; Appendix A). Similarly, the pH at SC209 was within 3% of the DMR values (Figs. 6, 16; Table 3).

Information on additional discharge characteristics at SD001 was included in the 2004 Minntac Water Inventory Reduction Draft Environmental Impact Statement (MWH 2004), the Minntac tailings 2011 NPDES/SDS permit application (Liesch Associates 2011), and the 2016 NPDES/SDS permit renewal fact sheet (MPCA 2016a). Although it was unclear in the latter two documents what year samples were collected, data indicated that the tailings and/or tailings discharge at SD001 was high in specific conductance, alkalinity, hardness, and concentrations of TDS, bicarbonate, fluoride, chloride, sulfate, bromide, boron, calcium, magnesium, potassium, sodium, manganese, and selenium. The discharge was also moderately high in oil and grease, nitrate+nitrite, phosphorus, arsenic, iron, cobalt, copper, zinc, molybdenum, cadmium, barium, mercury, and thallium.

Of those reported characteristics that we also measured (all but bicarbonate, oil and grease, nitrate+nitrite, and mercury), most were highest in our measurements at one or both of the sites closest to the tailings (SC209 and SC078). Those characteristics included specific conductance, TDS, alkalinity, and hardness, and concentrations of fluoride, chloride, sulfate, bromide, boron, calcium, magnesium, phosphorus, potassium, sodium, manganese, selenium, molybdenum, and barium (Figs. 3-4, 7-12; Tables 3-4). Phosphorus and selenium were greater in our measurements (67 μg/l for P, 4.7 μg/l for Se) than in the mean historical discharge measurements (P of 10-100 μg/l, mean of 40 μg/l, in Liesch Associates 2011; P of 2 and 11 μg/l in MPCA 2016a; Se of 3.5 and 3.7 μg/l in MPCA 2016a, and 3.00 μg/l, which may have been the detection limit, in Liesch Associates 2011). We did not detect downstream decreasing trends for the discharge constituents cadmium, arsenic, iron, cobalt, copper, zinc, or thallium (Appendix D).

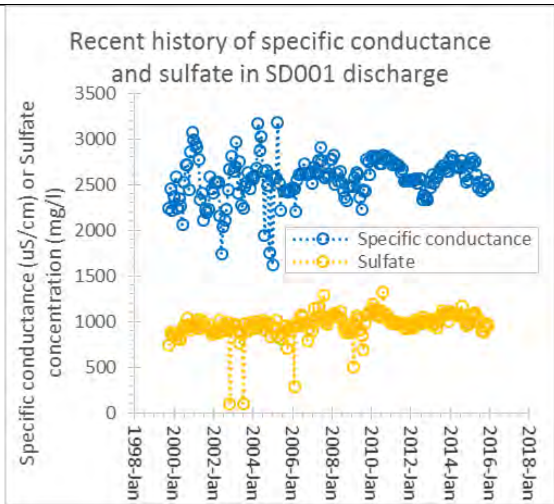


Fig. 14. Specific conductance and sulfate concentrations, as monthly maximums, have remained high in the western tailings discharge since at least 1999, according to monthly Discharge Monitoring Report data.

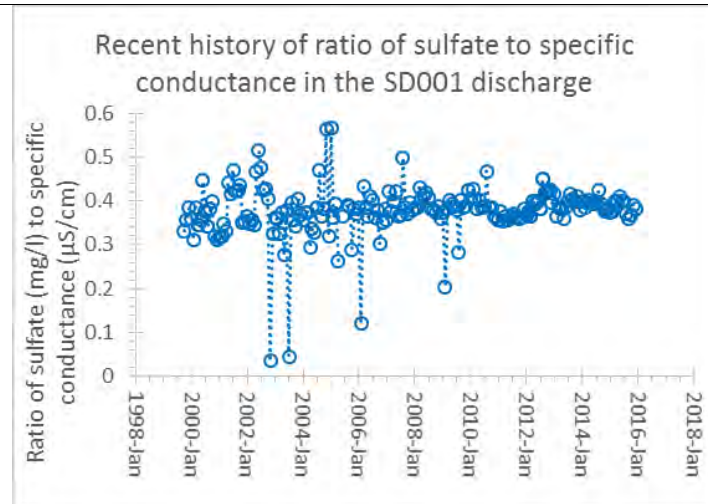


Fig. 15. The ratio of sulfate to specific conductance, as monthly maximums, has remained in the 0.34-0.45 range in the Minntac SD001 discharge since 2011, according to Discharge Monitoring Report data.

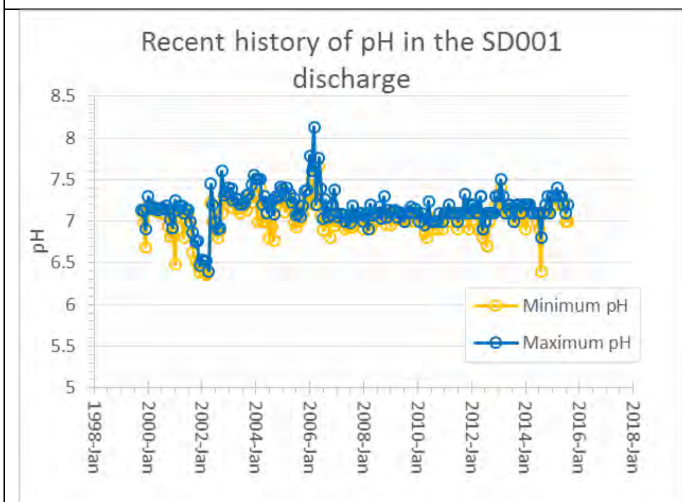


Fig. 16. Most minimum and maximum pH measurements reported in Discharge Monitoring Reports in the discharge at SD001 have been between 6.8 and 7.4 for 2007-2015. Some measurements were below the state criterion of 6.5.

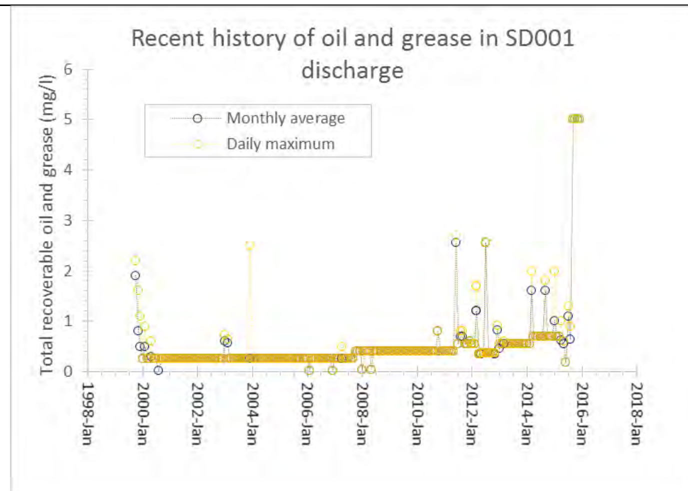


Fig. 17. Total recoverable oil and grease appeared to increase since approximately 2011, according to data from monthly Discharge Monitoring Reports. Low levels mostly represent half of the apparent detection limit, as those measurements were qualified as "< x."

(B) Comparison of downstream sites with reference sites

Range of measurements of characteristics

Comparison of the range of measurements at reference sites with the range of measurements at sites downstream of the Minntac tailings indicated that several field characteristics and anion concentrations were greater at the sites downstream of tailings than at almost all the reference sites. Sulfate was greater at sites downstream of tailings than at all reference sites (Fig. 7; Table 3). Specific conductance, fluoride, and bromide were greater at sites downstream of tailings than at all reference sites except at the Sturgeon River reference site (SC071; Figs. 3, 9-10; Table 3). For each of those measurements, the Sturgeon River reference site (SC071), which is downstream of Hibbing Taconite, had a higher measurement than at least one of the sites further downstream of the Minntac tailings (Figs. 3, 9-10; Table 3). For chloride, the range of reference site measurements overlapped with the low measurements (< 10 mg/l) in the Sturgeon and Little Fork Rivers (Fig. 8; Table 3). DO, ORP, and pH overlapped between downstream sites and references sites (Figs. 5-6; Table 3; Appendix D). We did not measure metals and trace elements at reference sites.

Kruskal-Wallis tests

Comparison of 15 sites downstream of tailings with 4 sites not downstream of Minntac tailings for 2016 using the Kruskal-Wallis test indicated that those groups of sites differed for specific conductance, chloride, and the ratio of chloride to specific conductance (Table 6). The reference sites were lower in specific conductance and chloride than were the sites downstream of Minntac, but had higher ratios of chloride to specific conductance (Figs. 18, 20, 22). When limiting the analysis to only the four most downstream sites in the flow path from the tailings (SC210, SC211, SC213, and SC214) and the four reference sites, specific conductance and chloride did not differ between the two groups ($P > 0.05$), but the ratio of chloride to specific conductance did still differ ($P < 0.043$; Figs. 19, 21, 23; Table 6).

Table 6. Results of Kruskal-Wallis tests indicated that specific conductance, chloride, and the ratio of chloride to specific conductance differed between reference sites and sites downstream of Minntac tailings, but only the ratio was significant when comparing reference sites to the most downstream four sites.

	Comparison of all downstream sites (n=15) with reference sites (n=4)			Comparison of most downstream four sites with reference sites (n=4)		
	Kruskal-Wallis score	*df*	*P* -value	Kruskal-Wallis score	*df*	*P* -value
Specific conductance	7.84	1	0.0051	3.00	1	0.083
Chloride	4.00	1	0.0455	0.08	1	0.773
Chloride : specific conductance	6.76	1	0.0093	4.08	1	0.043

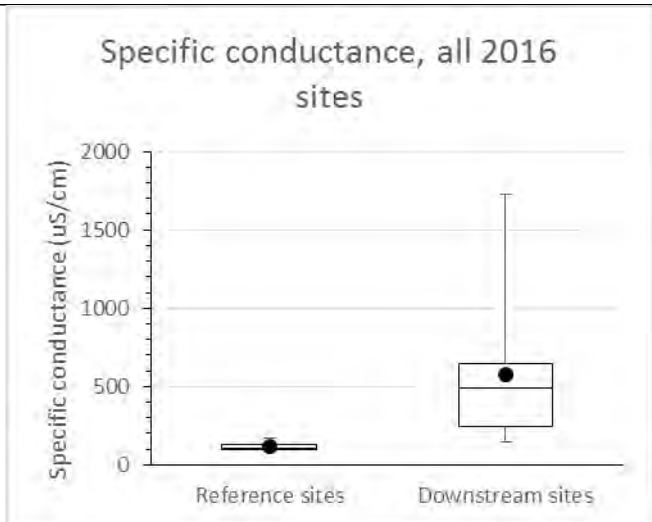
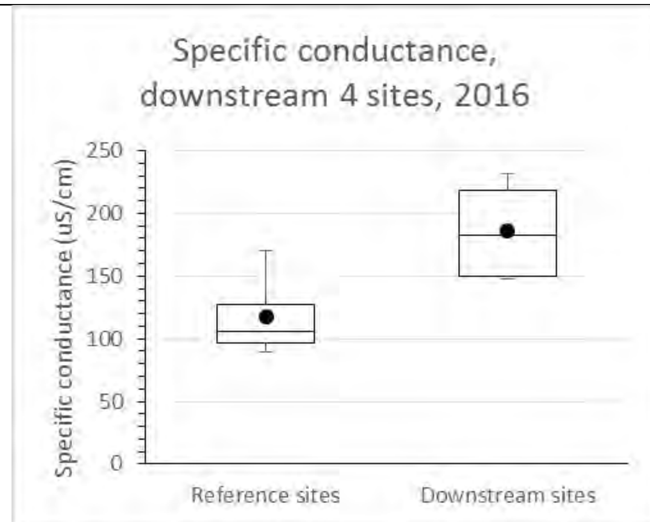
	

Fig. 18. Specific conductance measurements were greater ($P < 0.001$) at sites downstream of the tailings ($n = 15$) than at reference sites ($n = 4$) according to the Kruskal-Wallis test.	Fig. 19. Specific conductance measurements were not greater ($P > 0.05$) at the 4 sites the furthest downstream of the tailings (SC210, SC211, SC213, SC214) than at 4 reference sites according to the Kruskal-Wallis test.

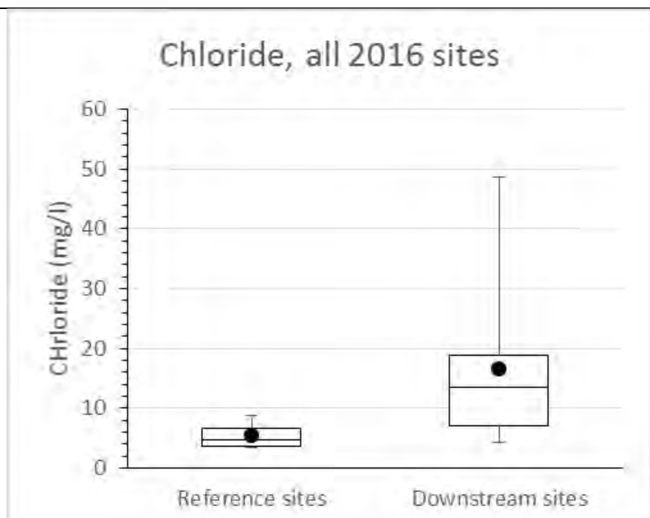
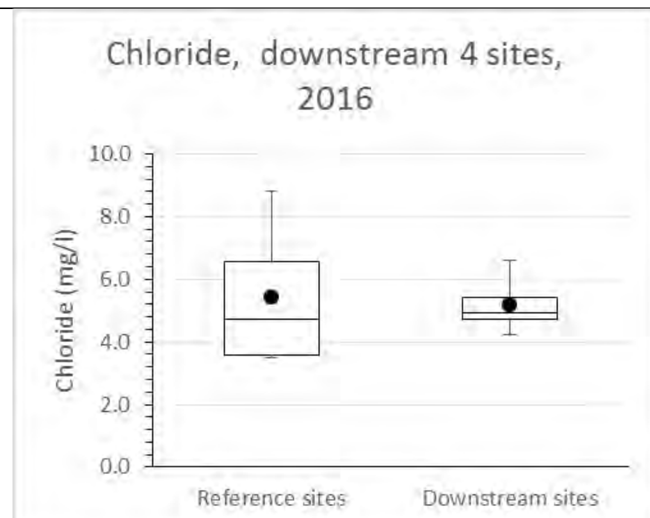
	

Fig. 20. Chloride concentrations were greater ($P < 0.05$) at sites downstream of the tailings ($n = 15$) than at reference sites ($n = 4$) according to the Kruskal-Wallis test.	Fig. 21. Chloride concentrations were not greater ($P > 0.7$) at the 4 sites the furthest downstream of the tailings (SC210, SC211, SC213, SC214) than at 4 reference sites according to the Kruskal-Wallis test.

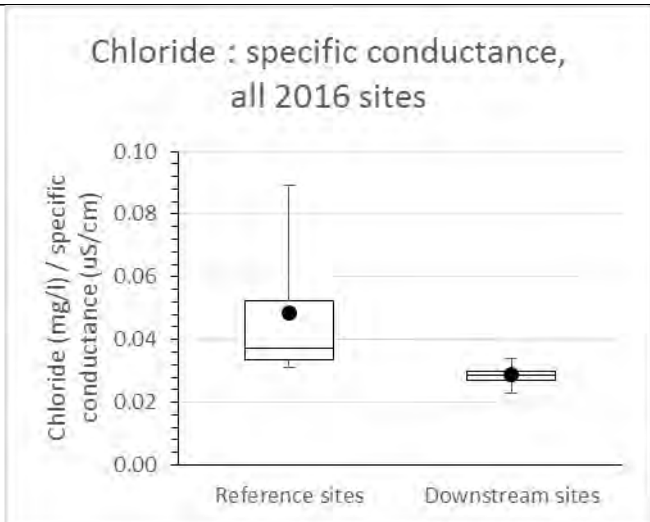
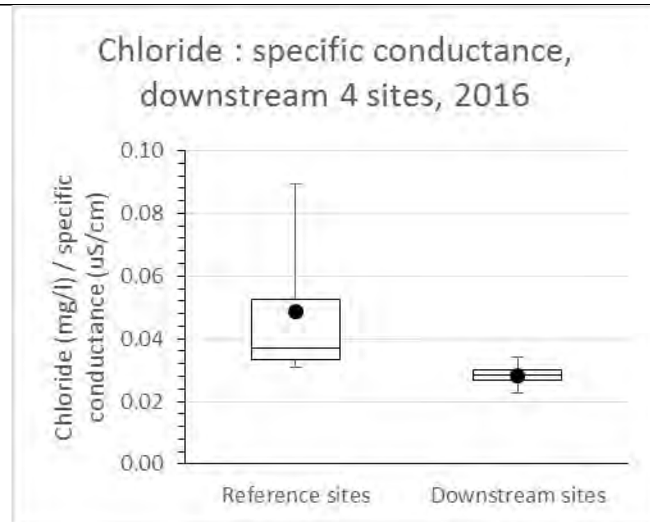
	

Fig. 22. Ratios of chloride concentrations to specific conductance were lower ($P < 0.01$) at sites downstream of the tailings ($n = 15$) than at reference sites ($n = 4$) according to the Kruskal-Wallis test.	Fig. 23. Ratios of chloride concentrations to specific conductance were lower ($P < 0.05$) at the 4 sites the furthest downstream of the tailings (SC210, SC211, SC213, SC214) than at 4 reference sites according to the Kruskal-Wallis test.

Cluster analysis.

The cluster analysis, using ratios of anions to specific conductance, showed that the Sturgeon River reference site clustered with sites downstream of it (Fig. 24). Those downstream sites also had higher fluoride to specific conductance ratios (Appendix A). In a second analysis without the fluoride measurements, all reference sites clustered together (Fig. 25). In the first analysis, the site the further downstream that clustered only with other sites downstream of Minntac was SC072 in August 2015 (Fig. 24). In the second analysis, SC210 was the furthest downstream such site (Fig. 25).

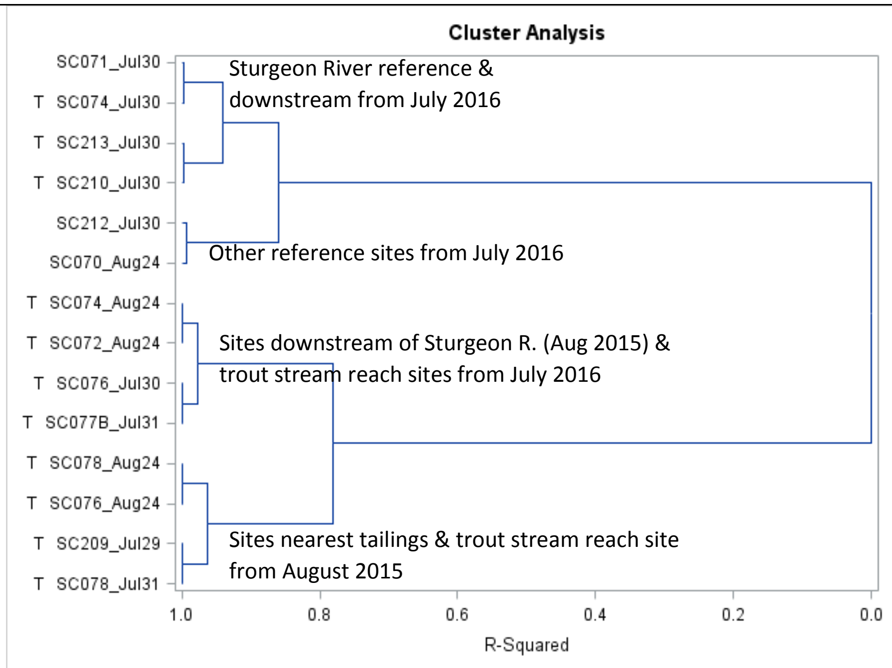


Fig. 24. Cluster analysis of the ratio of anions (fluoride, chloride, sulfate, and bromide) to specific conductance indicated that two of the reference sites (SC212 and SC070) clustered together, but the reference site SC071, which demonstrated high fluoride concentrations, clustered more closely with sites downstream of it that also demonstrated a higher fluoride:specific conductance ratio. The analysis used Ward's method with squared distances. August dates were from 2015 and July dates were from 2016. Sites with a "T" in the label were downstream of tailings.

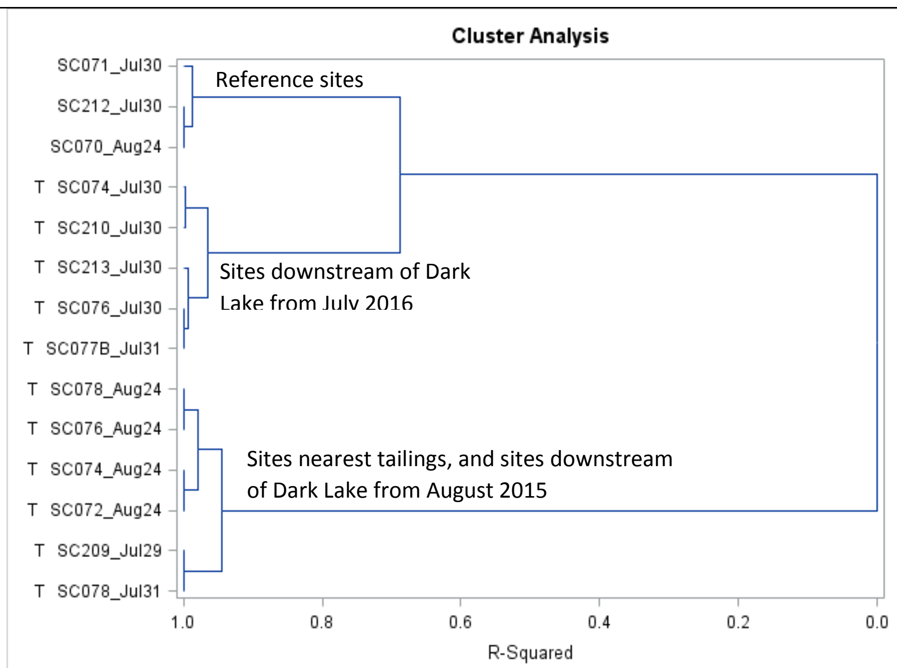
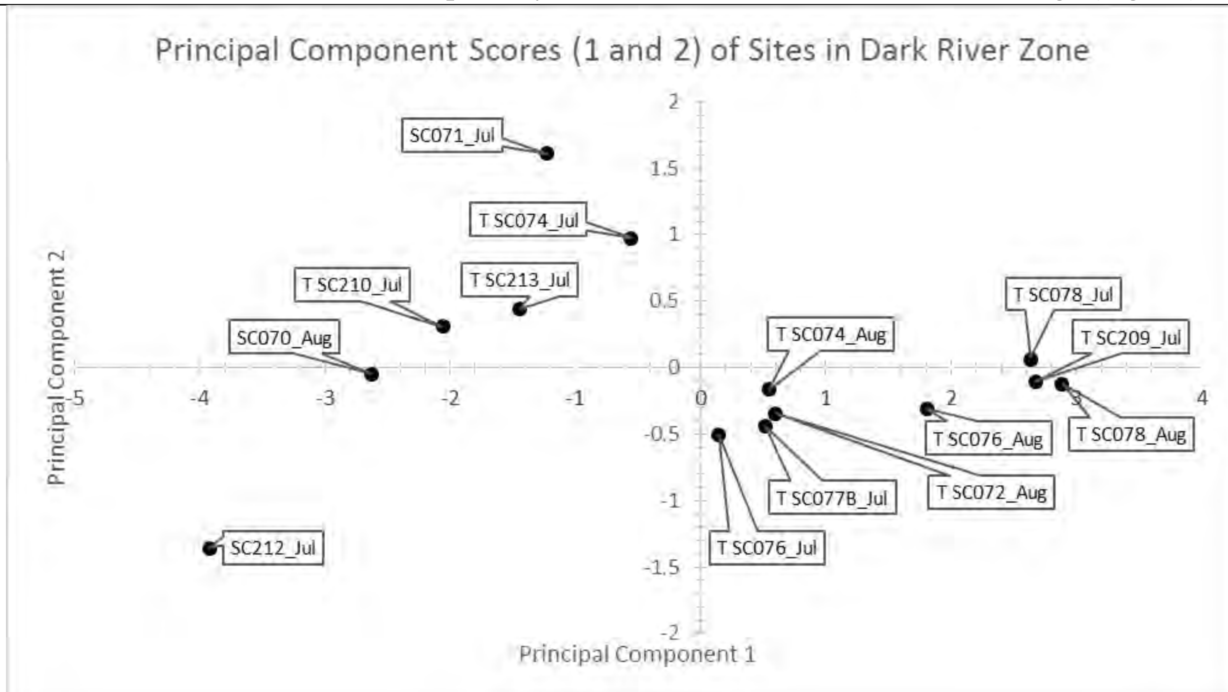


Fig. 25. Cluster analysis of the ratio of anions to specific conductance, but without fluoride, indicated that all three reference sites with anion measurements (SC071, SC212, and SC070) formed a cluster distinct from other sites downstream of Minntac tailings. The analysis used Ward's method with squared distances. August dates were from 2015 and July dates were from 2016. Sites with a "T" in the label were downstream of tailings.

Principal Components Analysis

PCA results from analysis of specific conductance and major anion data indicated that categories of sites were distinguishable based on PCA scores (Fig. 26; Table 7). Although graphing of the first two components resulted in groups similar to those detected in the cluster analysis, graphing of the first and third components appeared to delineate the reference sites separately from the sites downstream of the tailings (Fig. 26).



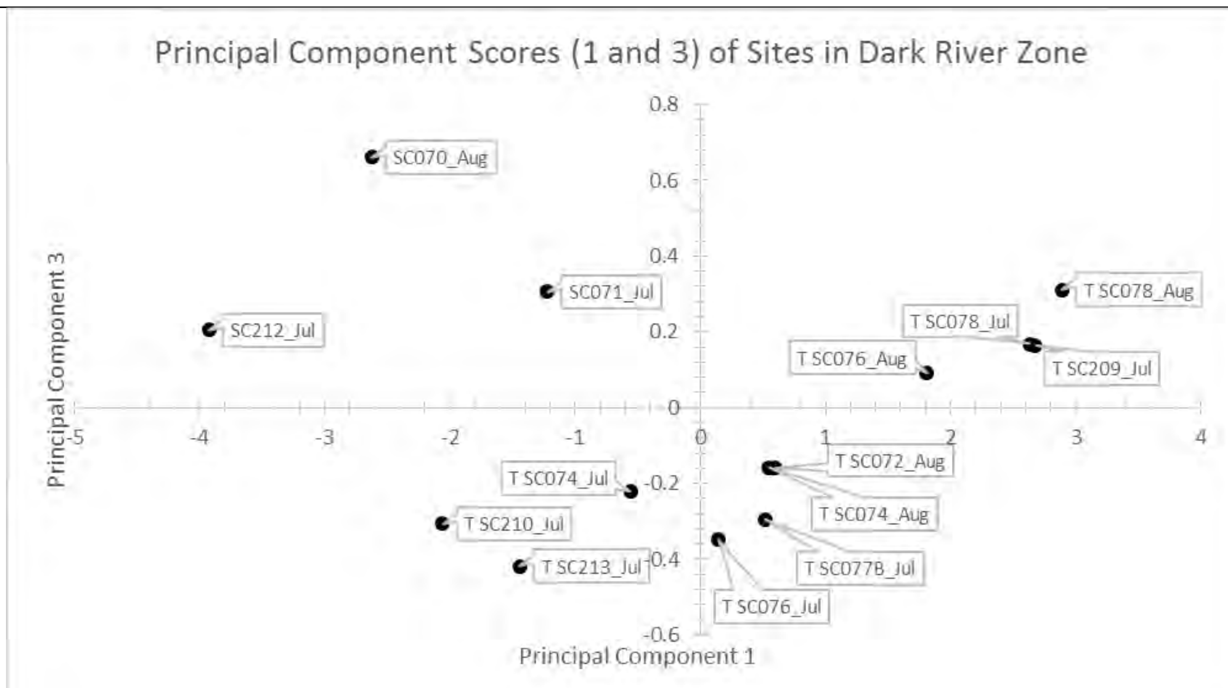


Fig. 26. Results of Principal Components Analysis (PCA) of specific conductance and concentrations of fluoride, chloride, sulfate, and bromide indicated that sites downstream of the Minntac tailings had scores similar to each other but different from sites that were not downstream of those tailings. Certain downstream sites (SC074 in July, SC210, and SC213) were intermediate between tailings-influenced sites and non-influenced sites. Sites with a "T" in the label were downstream of Minntac tailings.

Table 7. Eigenvalues and Eigenvectors for components of PCA of specific conductance and major anions for sites in the watersheds of the Dark, Sturgeon, and Little Fork Rivers. Component 1 represented all factors but fluoride was a greater influence in component 2, and component three consisted primarily of chloride and sulfate.

	Principal Component 1	Principal Component 2	Principal Component 3
Eigenvalue (%)	4.390 (87.8)	0.4925 (9.8)	0.1005 (2.0)
Eigenvectors			
Specific conductance	0.4708	-0.1989	-0.08129
Fluoride	0.3629	0.9243	0.09749
Chloride	0.4574	-0.2737	0.6458
Sulfate	0.4617	-0.1143	-0.7450
Bromide	0.4735	-0.1348	0.1086

(C) Temporal patterns

For sites where we sampled in both 2015 and 2016 for field characteristics and major anion concentrations, measurements and concentrations were lower in July 2016 than in August 2015 except for fluoride and bromide at SC078 (Figs. 3, 7-10). Sulfate measurements, for instance, exceeded 250 mg/l in the trout stream reach in August 2015 but not July 2016 (Fig. 7).

We found limited pre-2015 data from the Water Quality Portal (2017) and regulatory documents and reports (MWH 2004, Kelly *et al*. 2014, Vogt 2015, MPCA 2016a, GLIFWC unpublished data). We used data consisting primarily of field measurements and major ion sample data.

For most sites with no pre-mining data, our measured characteristics fit within the range of values for available historical mining period (post-1960's) data (Appendix B). At sites with older data (pre-mining), on the other hand, characteristics increased over time (Appendix B). At the only site downstream of Minntac tailings with available pre-mining data on the western side of the tailings (SC076), our measurements of specific conductance, pH, and sulfate and chloride concentrations were higher than in 1972 and higher than in pre-mining years (Figs. B-5-B-7). At a site further downstream, SC213, specific conductance, chloride, and sulfate were also higher in recent measurements than in 1972 (Fig. B-12).

We also examined available historical data on ratios of constituents to examine trends and the potential for ratios to serve as tracers of tailings influence, including in the Sand River system. Data were available for reference sites, waters downstream of the tailings to the west (Dark River etc.), waters downstream of the east of the tailings (Sand River, etc.), and from the tailings basin and tailings discharges (MWH 2004, Kelly *et al*. 2014, Vogt 2015, MPCA 2016a, Water Quality Portal 2017, GLIFWC unpublished data). Reference sites clustered separately from upper Dark and/or Sand River and tailings basin and tailings discharge data for ratios of Cl^-:F^-, SO_4^{2-}:Cl^-, SO_4^{2-}:specific conductance, K/(Na + K), and Mg^{2+}:SO_4^{2-} in recent decades (Figs. B-15-B-

19). Sulfate:chloride, K/(Na + K), Mg^{2+}:SO_4^{2-} ratios did not vary as much over time, in the period post-commencement of mining, as did other ratios with available data (Figs. B-16, B-18, B-19). Ratios of chloride:fluoride and sulfate:specific conductance were greater from before to after mining began, while reference site data for those ratios remained less changed (Figs. B-15, B-17).

4. DISCUSSION

Contamination of concern

Analysis of downstream trends, comparisons with tailings discharge data, comparisons with reference sites, and comparison with historical data suggest that the Minntac tailings contaminated the Dark-Sturgeon-Little Fork Rivers with water of high or relatively high specific conductance, TDS, alkalinity, hardness, fluoride, chloride, sulfate, bromide, sodium, magnesium, potassium, calcium, boron, strontium, selenium, rubidium, barium, and uranium. The discharge may also contribute molybdenum, rhodium, and cesium in comparatively low concentrations. Data also suggest that the tailings release manganese and phosphorus, or that the tailings waters cause reactions that release manganese and phosphorus from other sources.

The waters downstream of the tailings appeared to cause exceedances of state criteria for **specific conductance, TDS, hardness, dissolved oxygen, sulfate, and manganese**. In addition, the waters exceeded EPA 2016 criteria for **selenium**, exceeded the state lake criterion for **phosphorus**, and exceeded the Canadian criterion for **fluoride**. Finally, the waters all greatly exceeded sulfate concentrations for wild rice waters, and the Dark River flows through the listed wild rice water of Dark Lake (MPCA 2016b). The known wild rice is in the northern section of that lake, but MPCA data available through STORET/Water Quality Portal indicated high concentrations of sulfate in both sections of the lake (south section sulfate 166 and 396 in May 2010 and 2011, respectively; north section 180 mg/l in June 2011 and 173-176 mg/l in July 2013). Since the Dark River appears to be the only known source of sulfate for Dark Lake, this suggests that the Dark River is contributing to high sulfate concentrations in the wild rice waters of Dark Lake. The MPCA data also indicate that the lake had phosphorus concentrations that exceeded 30 µg/l in August and September 2010 in the south section (2010-2011 range was 7-49 µg/l), and our data suggest that the Dark River contributes to the phosphorus load to that lake.

Potential effects of contaminants

Several of those contaminants that we detected are of particular concern because of their potential effects on aquatic life, wildlife, and humans. Sulfate (and particularly the reduced sulfur form sulfide) are damaging to wild rice (Moyle 1944, 1945, Pastor *et al*. 2017). In addition, sulfate can also 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). Manganese in humans can impair child brain development, and damage kidneys, the urinary tract, and sperm, amongst other effects (ATSDR 2012). Aquatic life toxicity data are limited for manganese, but it is toxic to some fish and invertebrates (Borgmann *et al*. 2005, Harford *et al*. 2015, Kostich *et al*. 2017). 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). Phosphorus can cause the eutrophication of lakes and some rivers (Correll 1998, Hilton *et al*. 2006). Fluoride 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). High specific conductance, TDS, alkalinity, and hardness can also impact aquatic organism communities.

Downstream trends

Our results provide some additional insight on other aspects of contaminant pathways in the Dark River system. The tailings water discharges to the Dark River directly from the base of the tailings dams, but also probably flows into the river from groundwater contaminated by seepage under the tailings (MPCA 2016a). The increase in concentrations between SC209 and SC078 for fluoride, bromide, and phosphorus, as well as the relatively gradual decline in concentrations of other constituents over that reach, may provide evidence of such groundwater discharge flowing into the river in the zone between those two sites. The high concentration of iron further downstream at SC077B could also indicate groundwater seepage effects, but uncertainty on groundwater flows, constituent concentrations in Dark Lake, and potential iron redox reactions make this difficult to interpret. Current understanding of the hydrology in that zone appears inadequate, especially since the 2016 NPDES document (MPCA 2016a) predicted lower concentrations of phosphorus, manganese, and selenium at the upstream end of the trout reach (P of 2.8 μg/l, Mn of 79 μg/l, and Se of 1.5 μg/l) than what we measured ca. 1.8 km downstream of that point at SC077B (P of 29 μg/l, Mn of 149 μg/l, and Se of 1.7 μg/l).

The Minntac tailings appear to not be the only mine tailings influencing the lower reaches of the Sturgeon and Little Fork Rivers. Measurements in the Sturgeon River at SC071 were greater than at other reference sites, particularly for fluoride. This site, however, is downstream of the Hibbing Taconite tailings basin, which discharges tailings water to the Shannon River, which joins the Sturgeon River. That facility is likely to influence characteristics such as specific conductance, bromide, and fluoride that we observed at levels higher than expected. Indeed, DMR data for the Hibbing Taconite facility at SD001 indicated that the facility discharge water was generally lower in specific conductance and concentrations of sulfate than was the Minntac SD001, but was high in fluoride (e.g., 1.7-2.8 mg/l in 2014). This could explain why the fluoride at SC071 was more anomalous than sulfate or specific conductance. This also suggests that the Hibbing Taconite tailings may influence the Shannon River and Sturgeon River all the way downstream to SC071.

Extent of mine influence

The Minntac tailings appear to influence the river far downstream. Examination of temporal trends indicated that measurements of specific conductance, chloride, and sulfate were higher than pre-mining at SC076, approximately 26 km downstream of the tailings. The cluster analysis indicated that sites downstream at least as far as SC072 in August 2015, for the analysis with fluoride, or SC210 for the analysis without fluoride, were distinguishable from reference sites. SC072 is approximately 44 km downstream, and SC210 approximately 95 km downstream of the Minntac tailings. The influence of the high fluoride concentrations at SC071 explains the difference in the two cluster analyses. The ratio of fluoride to specific conductance appears to reflect the influence of waters at SC071, which were probably impacted by the Hibbing Taconite tailings. The downstream pattern for that ratio of fluoride to specific conductance suggests an influence of the SC071 waters on the Sturgeon River downstream of the confluence with the Dark River all the way downstream to SC210. The ratios of sulfate and bromide to specific conductance, on the other hand, appear to reflect the influence of the Minntac tailings only. It is likely that both mine tailings basins are influencing the reaches downstream of the Sturgeon River confluence as far as SC210. The Kruskal-Wallis tests of reference and downstream sites, and the PCA, also indicated that sites downstream as far as SC210 remained distinguishable from reference sites by specific conductance and anion concentrations. These results also suggest that combinations of characteristics including specific conductance, and concentrations of anions and REE (lanthanum and europium for shorter distances) appear useful as tracers for the tailings.

Historical trends

The examination of temporal variation also yielded new information on contamination in the river. Specific conductance, pH, DO, sulfate, and chloride measurements were greater at all sites in August 2015 than they were in July 2016. Hydrological conditions may have differed between the two years or may regularly differ between July and August, but we did not measure flow in August 2015 to compare with. Alternatively, the difference could have resulted from changes in tailings facility management or ore processing, but we do not have any information on such changes. The difference does suggest that concentrations of elements that we did not sample for in 2015, such as manganese and selenium, may be even higher under the conditions of August 2015. The comparisons of older data were most useful at the site with pre-mining data (SC076). The data at that site appear to confirm that the tailings have increased specific conductance, pH, and sulfate and chloride concentrations in the river.

Remaining data gaps

Our study does not represent a complete analysis of the Dark River system, but rather a snapshot identifying contaminants and extent of contamination over a short time period. Additional sampling could allow for more complete assessment of temporal and hydrological variation, groundwater contamination, partitioning of constituents, sediment contaminants, and concentrations of additional constituents (e.g., total and methylmercury, asbestiform mineral fibers, processing chemical degradation products including amines, and gross alpha and beta radioactivity).

Conclusion

Previous public information had not documented the presence of constituents such as selenium, phosphorus, or uranium in the surface waters downstream from the Minntac tailings, or documented the downstream trend in contamination. We reported high concentrations of constituents of concern, including sulfate, selenium, manganese, hardness, specific conductance, and TDS, and determined that the influence of tailings on water quality appeared to extend for 95 km downstream of the tailings.

5. ACKNOWLEDGEMENTS

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APPENDIX A. Downstream ratio trend figures

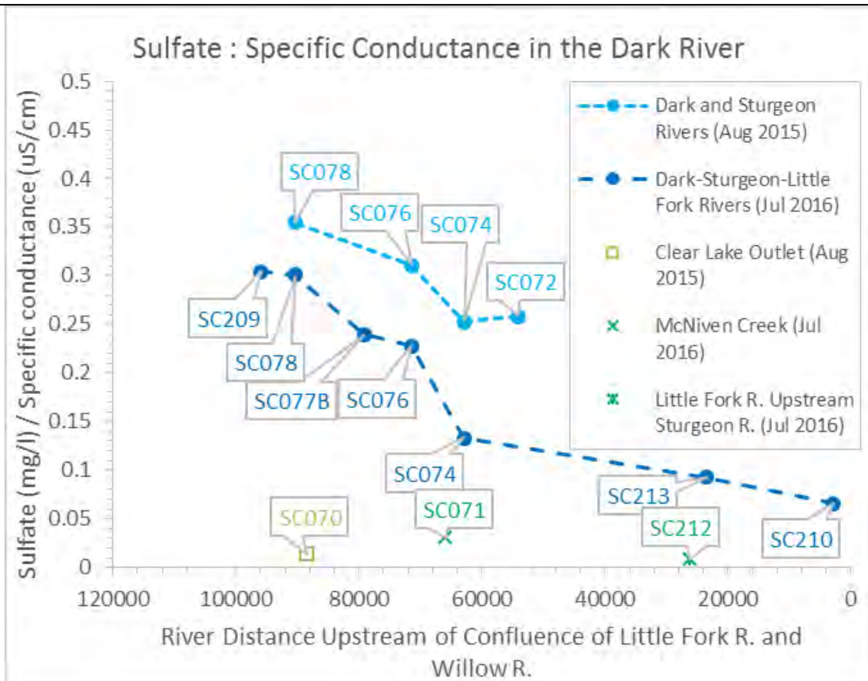

Fig. A-1. The ratio of sulfate to specific conductance decreased downstream of SC209 from 0.3-0.07 $mg*l^{-1}*cm*\mu S^{-1}$ along the main river in 2016. The Sturgeon River waters (SC071) did not appear to input higher sulfate:specific conductance waters to the river.

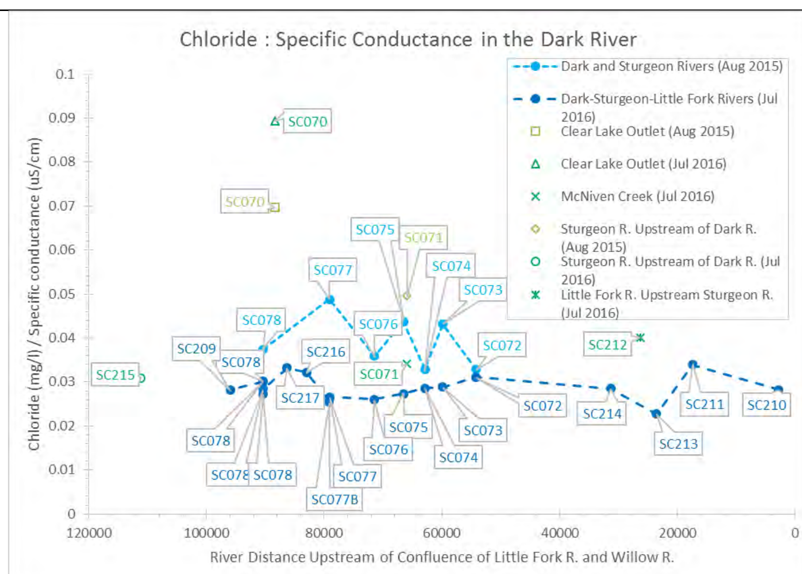

Fig. A-2. The ratio of chloride to specific conductance varied only from 0.02-0.03 $mg*l^{-1}*cm*\mu S^{-1}$ along the main river in 2016. The Sturgeon River waters (SC071) did not alter the trend in the reach with the confluence in 2016.

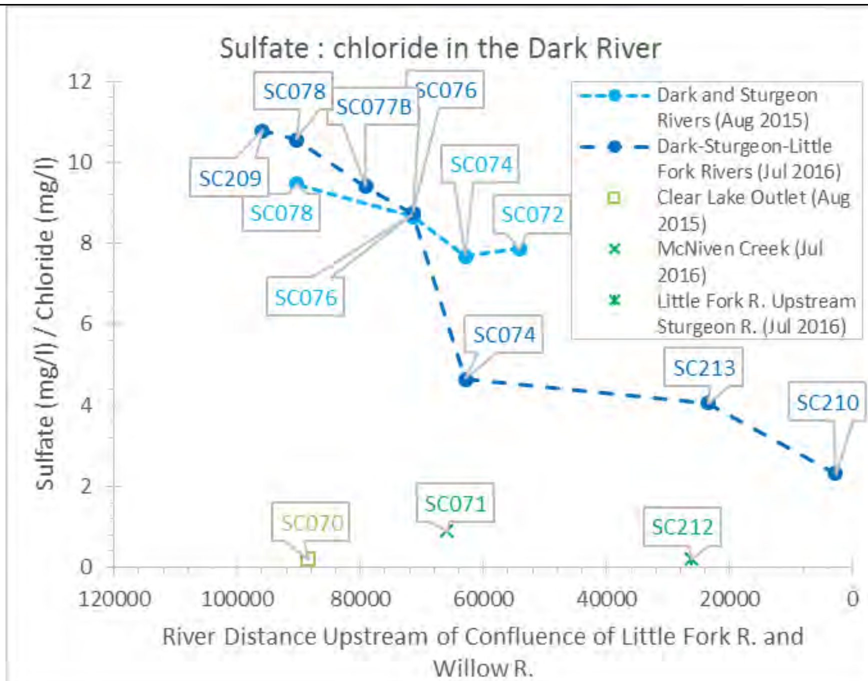

Fig. A-3. The ratio of sulfate to chloride was greater at sites downstream of tailings than at reference sites, and decreased downstream of the tailings.

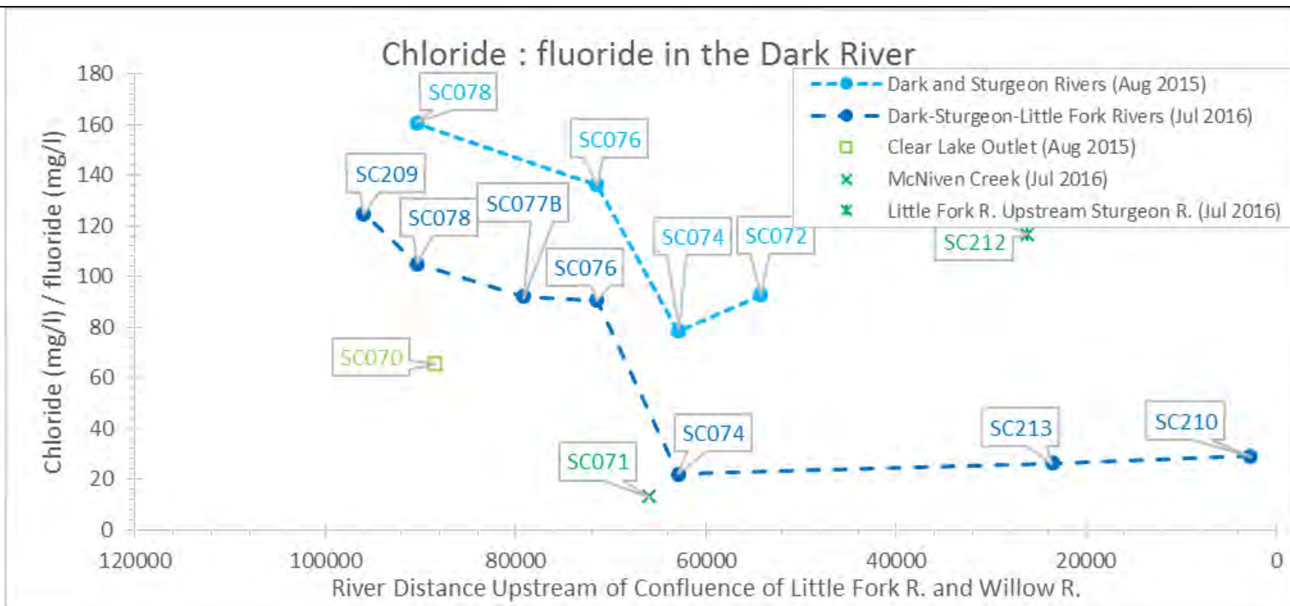

Fig. A-4. The ratio of chloride to fluoride mostly decreased downstream of the tailings until the confluence with the Sturgeon River. Reference sites were within the range of the sites downstream of tailings.

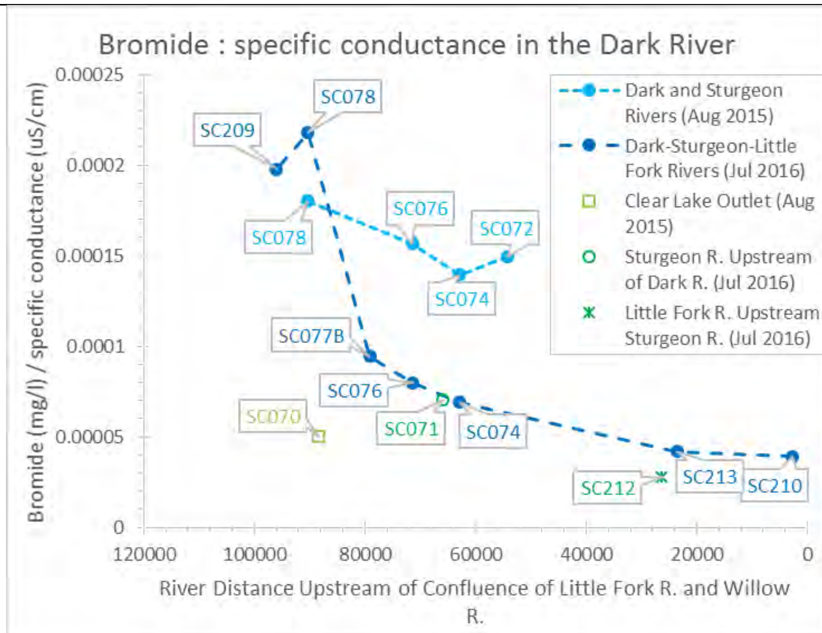

Fig. A-5. The Sturgeon River waters (SC071) did not alter the trend in the 2016 ratios of bromide to specific conductance. Bromide measurements at SC070 and SC212 were below the Minimum Reporting Limit (MRL) and we used half of the MRL for the ratio.

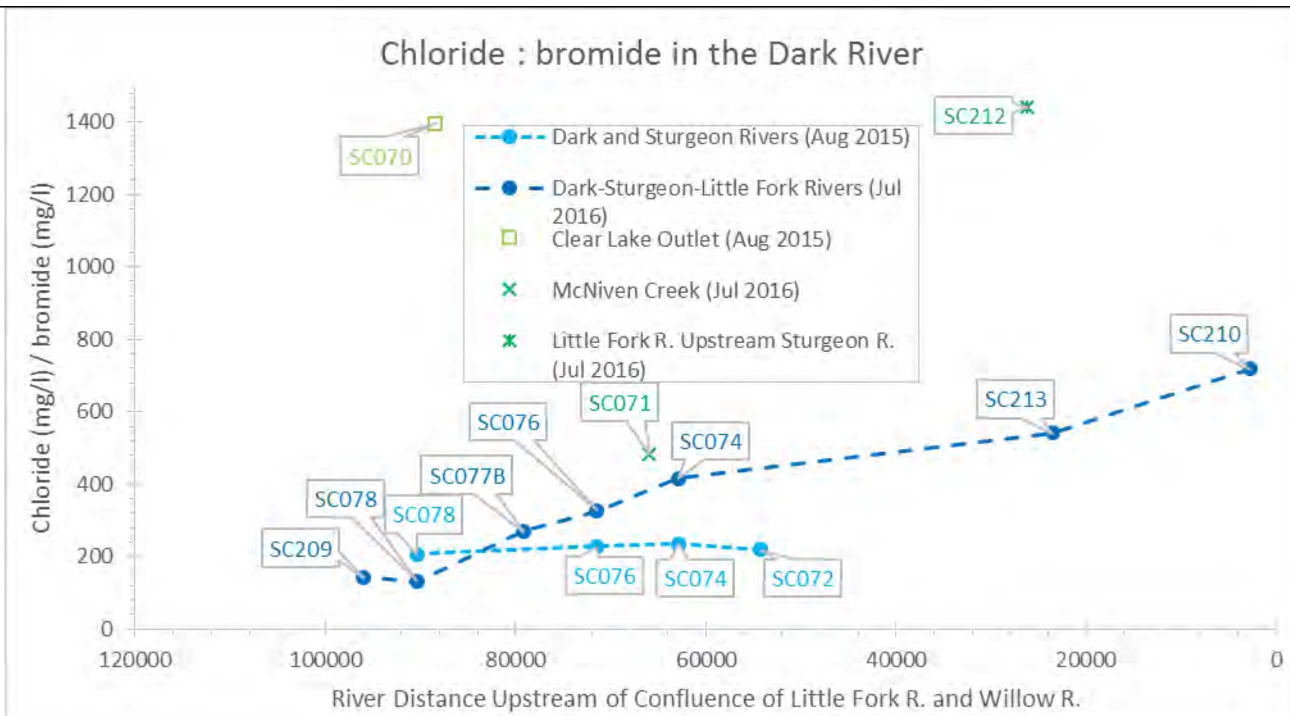

Fig. A-6. The ratio of chloride to bromide increased downstream of tailings in 2016. The site in the Sturgeon River was within the range of the sites downstream of tailings, but other reference sites were not.

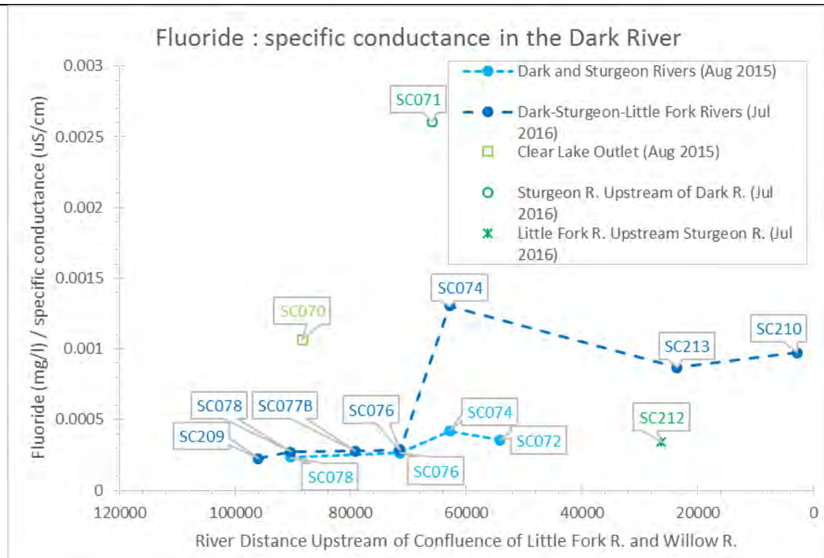

Fig. A-7. The ratio of fluoride to specific conductance increased in the reach (SC076 to SC074) with the confluence of the Dark River with the Sturgeon River, which demonstrated the highest ratio (at SC071).

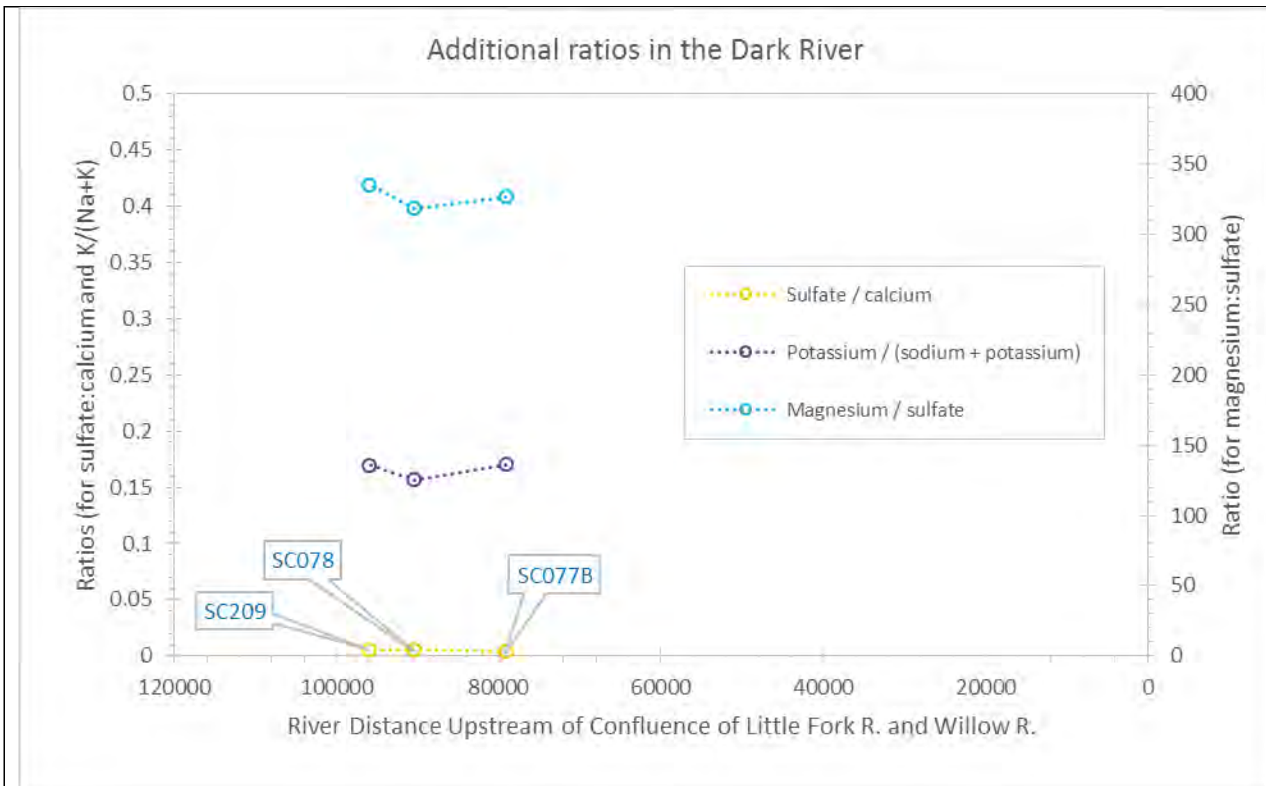

Fig. A-8. Ratios of sulfate : calcium, potassium to potassium plus sodium, and magnesium to sodium differed by less than 31%, 8%, and 5%, respectively, between three sites with data for those constituents.

APPENDIX B. Temporal trends figures

Sites between Minntac tailings and Dark Lake

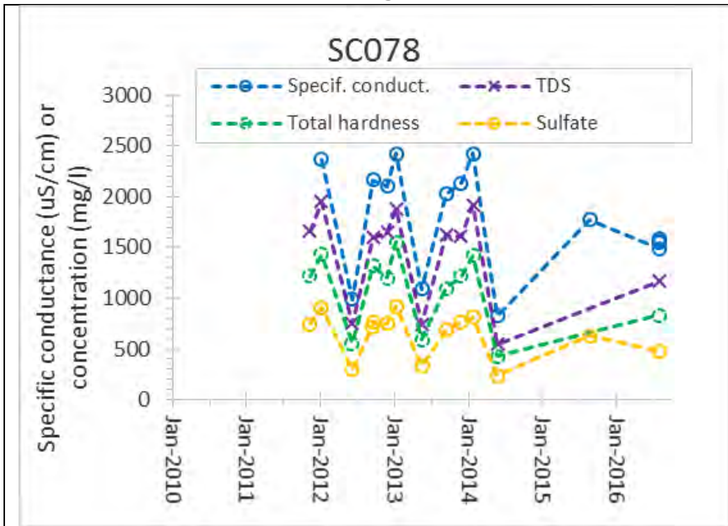

Fig. B-1. Specific conductance, total hardness, total dissolved solids, and sulfate that we measured at site SC078 in 2015 and 2016 were within the range reported in permitting documents (MPCA 2016a) and Kelly *et al*. (2014) for 2011-2014. The state limits at this site were 1000 µS/cm for specific conductance, 700 mg/l for TDS, and 500 mg/l for hardness.

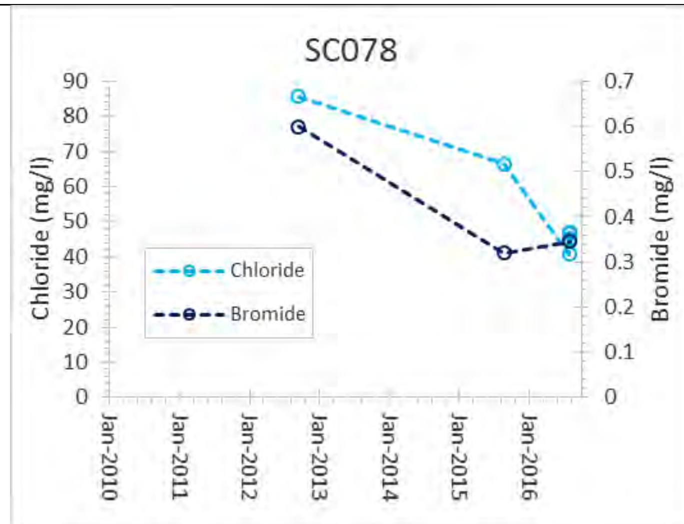

Fig. B-2. Chloride and bromide concentrations were lower in 2015 and 2016 than measurements from September 2012 (Kelly *et al*. 2014) at SC078. The mass ratio of $Cl^-:Br^-$ was 143 in 2012, 208 in August 2015, and 131 in July 2016.

Sites between Dark Lake and confluence with Sturgeon River (designated trout stream)

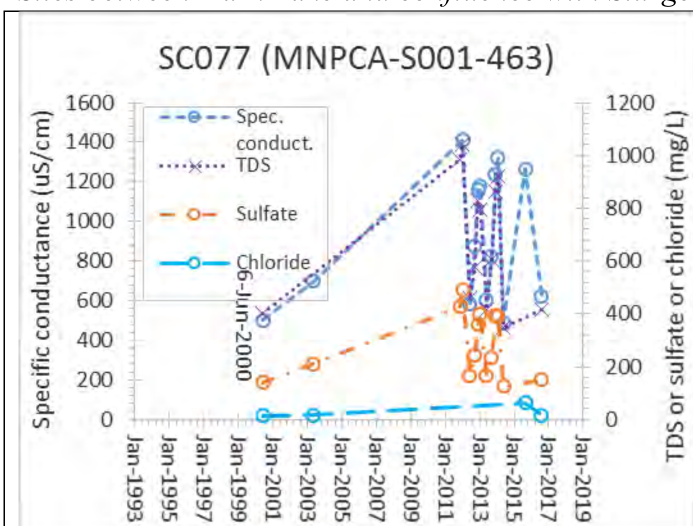

Fig. B-3. At site SC077, our 2015 measurements were within the recent historical range (MPCA 2016a), but our 2016 measurements were lower than many recent measurements of specific conductance, TDS, and sulfate concentration. The state limits at this site were 1000uS/cm for specific conductance, 500 mg/l for TDS, and 250 mg/l for sulfate.

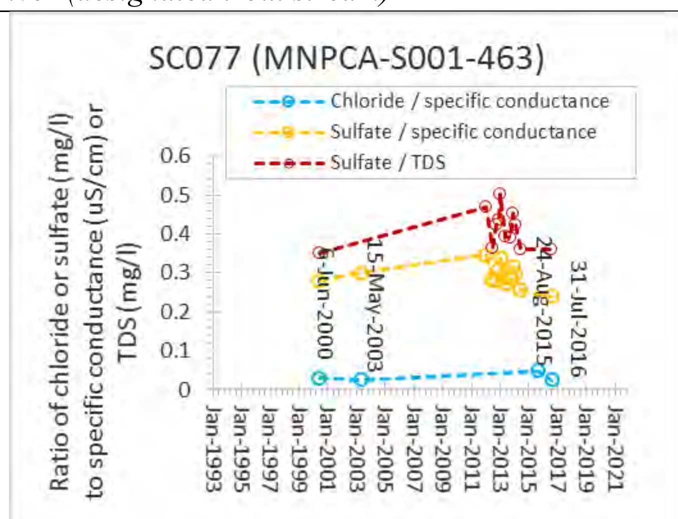

Fig. B-4. For site SC077, 2016 chloride and sulfate measurements were also lower than post-1999 measurements when considered as ratios to TDS or specific conductance, but 2015 chloride was higher.

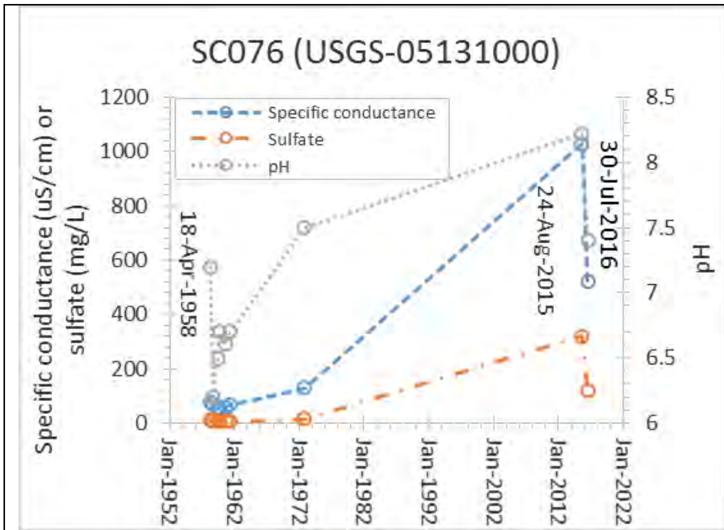

Fig. B-5. Specific conductance, pH, and sulfate concentrations were at their recorded highest in 2015 but lower in 2016 at site SC076. Measurements in both years were higher than pre-mining measurements.

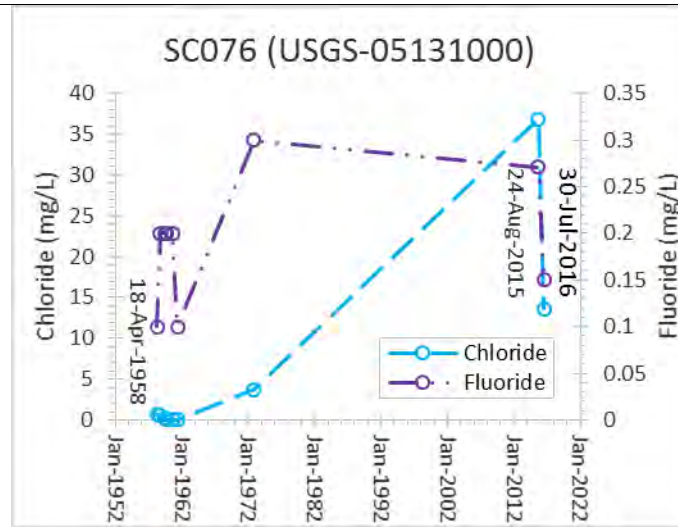

Fig. B-6. Chloride and fluoride concentrations were at or within 10% of their recorded highest in 2015, but lower in 2016 at site SC076. Measurements in both years were higher than pre-mining measurements for chloride.

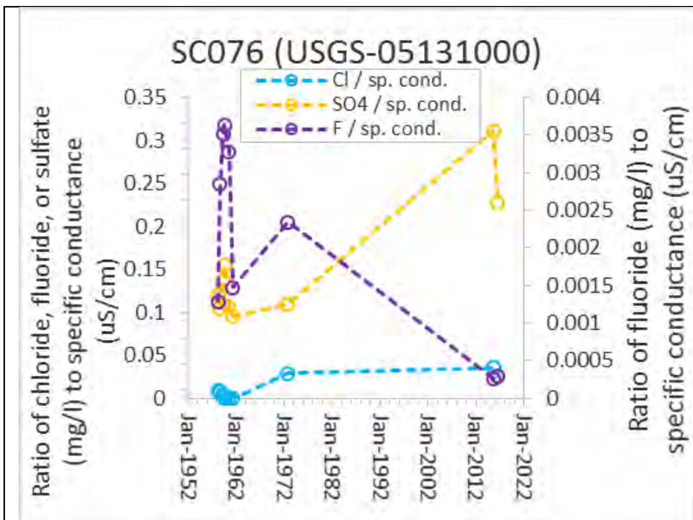

Fig. B-7. For site SC076, 2015 and 2016 chloride and sulfate measurements were also higher than available pre-mining measurements when considered as ratios to specific conductance. Fluoride:specific conductance was lower in 2015 and 2016 than pre-mining.

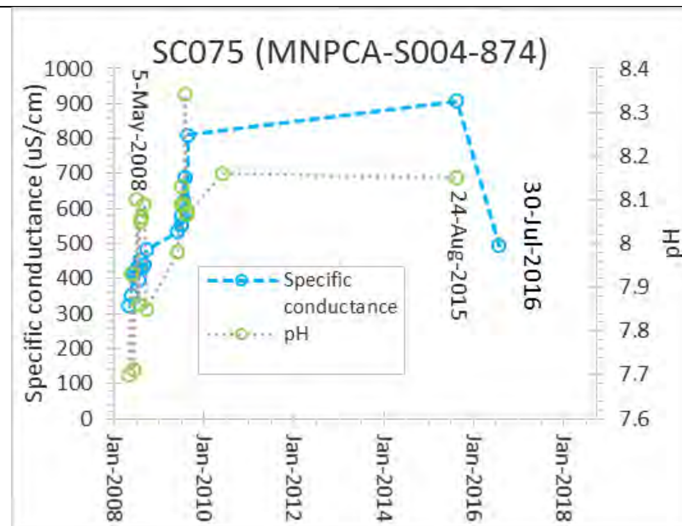

Fig. B-8. Specific conductance measurements were at their recorded highest at SC075 in 2015, and were lower but within the historical (Water Quality Portal 2017) range in 2016. 2015 pH measurements were within the historical range as well.

Sites in Sturgeon River and in Dark River between Sturgeon River and Little Fork River confluences

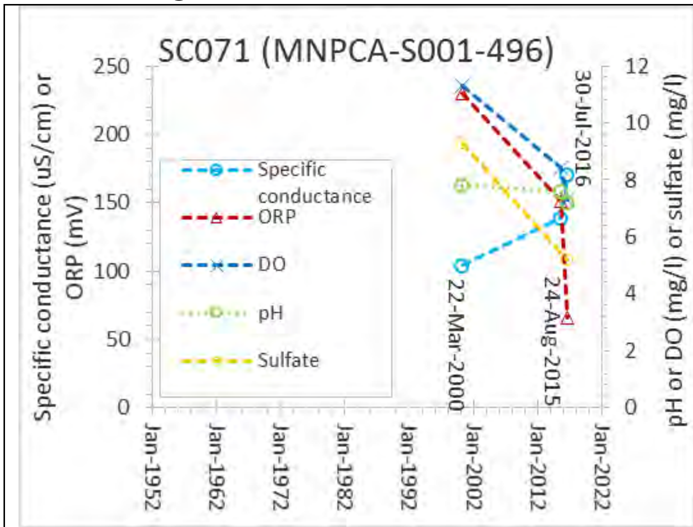

Fig. B-9. At the Sturgeon River site of SC071, not downstream of Minntac, specific conductance was higher in 2015 and 2016 than in 2000 (Water Quality Portal 2017), but dissolved oxygen (DO), oxidation reduction potential (ORP), and sulfate concentrations were lower than in 2000.

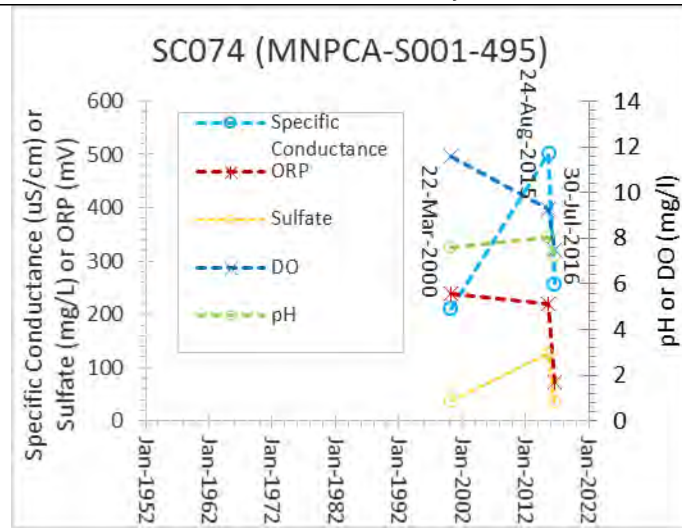

Fig. B-10. Specific conductance and sulfate concentrations were lowest in 2000, high in 2015, and lower in 2016 at site SC074. DO and ORP, however, decreased from 2000-2016.

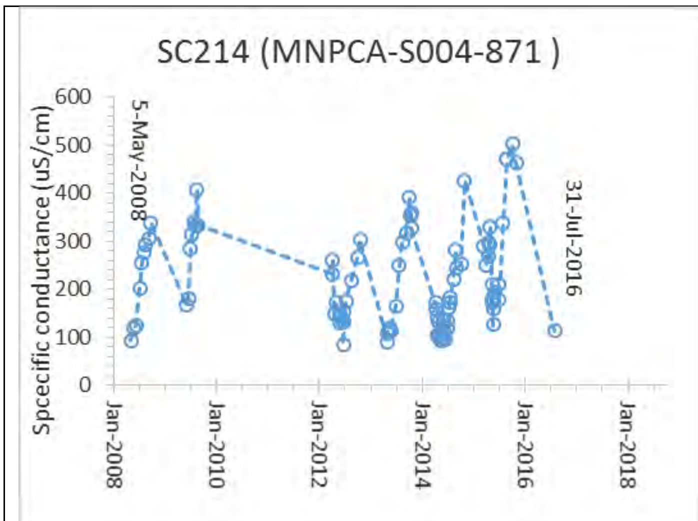

Fig. B-11. Specific conductance in 2016 was within the recent historical range (Water Quality Portal 2017) at site SC214.

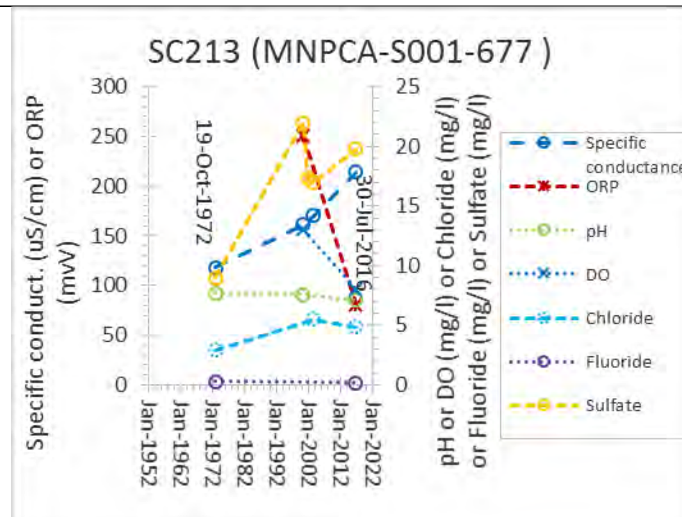

Fig. B-12. Specific conductance increased from 1972 to 2016 for available data (Water Quality Portal 2017) at site SC213. Other characteristics did not demonstrate such a regular trend.

Sites in Little Fork River and in Dark River downstream of confluence with Little Fork River

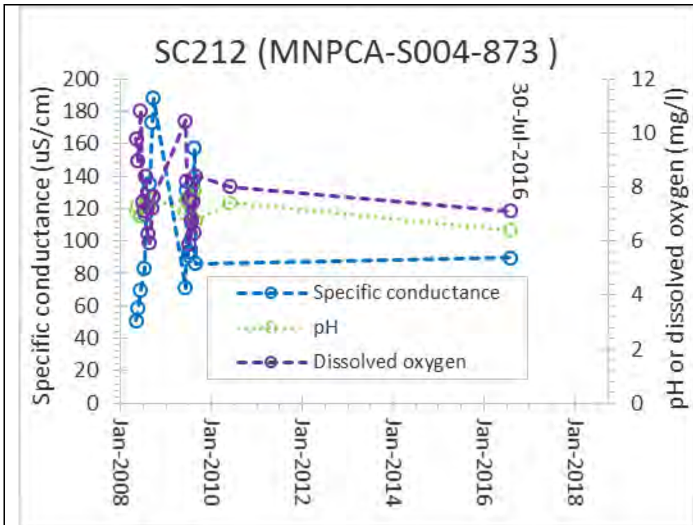

Fig. B-13. At the Little Fork reference site of SC212, 2016 measurements were within or within 10% of the recent historical range (Water Quality Portal 2017) for specific conductance, dissolved oxygen, and pH.

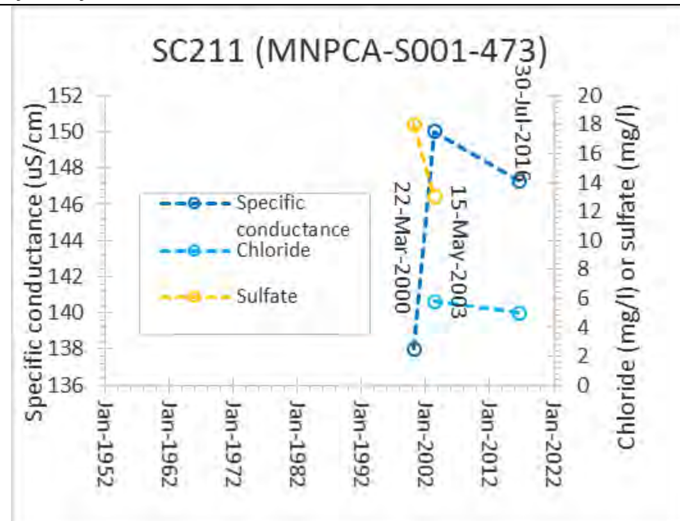

Fig. B-14. 2016 measurements at SC211 were within 15 % of 2003 measurements (Water Quality Portal 2017) for specific conductance and chloride concentration.

Temporal patterns in select mass ratios including reference sites, tailings, and Sand River sites

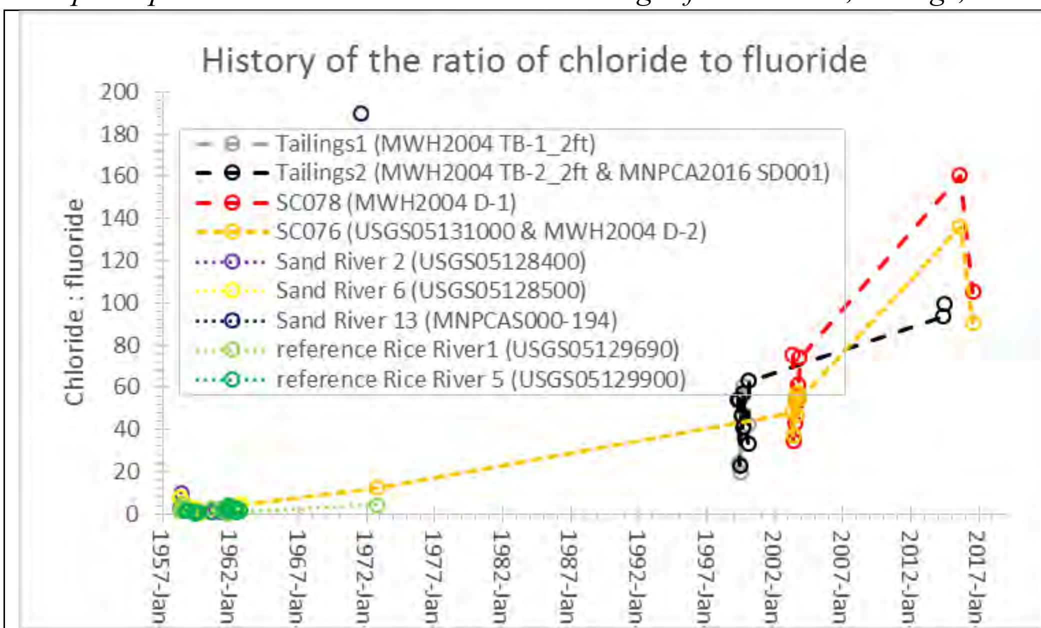

Fig. B-15. The mass ratio of chloride to fluoride was greater in recent decades than in the 1950's to 1972 for SC078 near the tailings or SC076 downstream of Dark Lake. Data for the tailings were greater in 2014 than in 1999-2000.

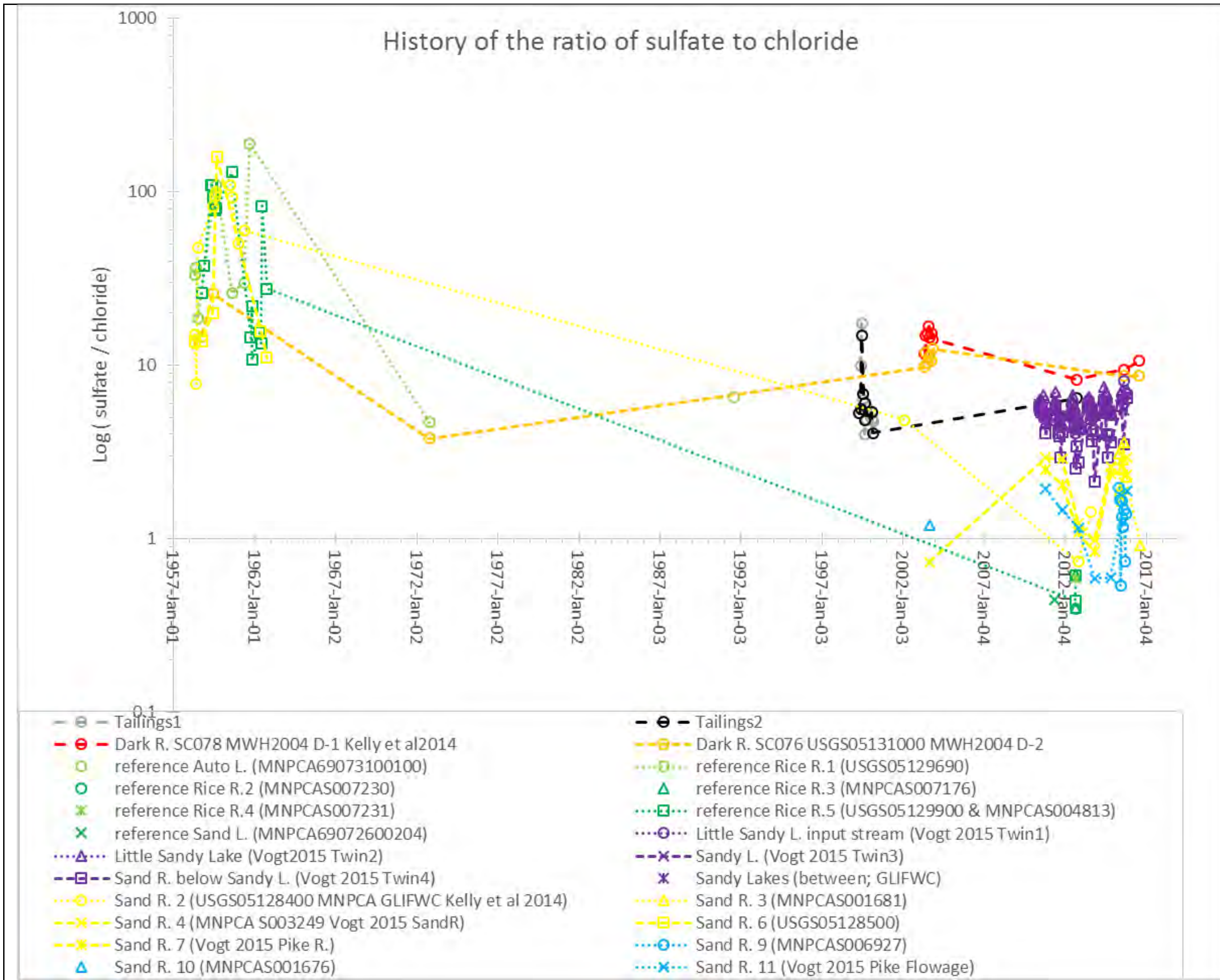

Fig. B-16. The mass ratio of sulfate to chloride (on $\log_{10}$ scale) in recent decades was more similar at SC078 and SC076 in the Dark River to Minntac tailings and data near the tailings in the Sand River system than to reference sites and downstream Sand River sites. The ratio for reference sites, downstream Sand River sites, and SC076 was greater in the 1950’s and 1960’s, but lower in 1972.

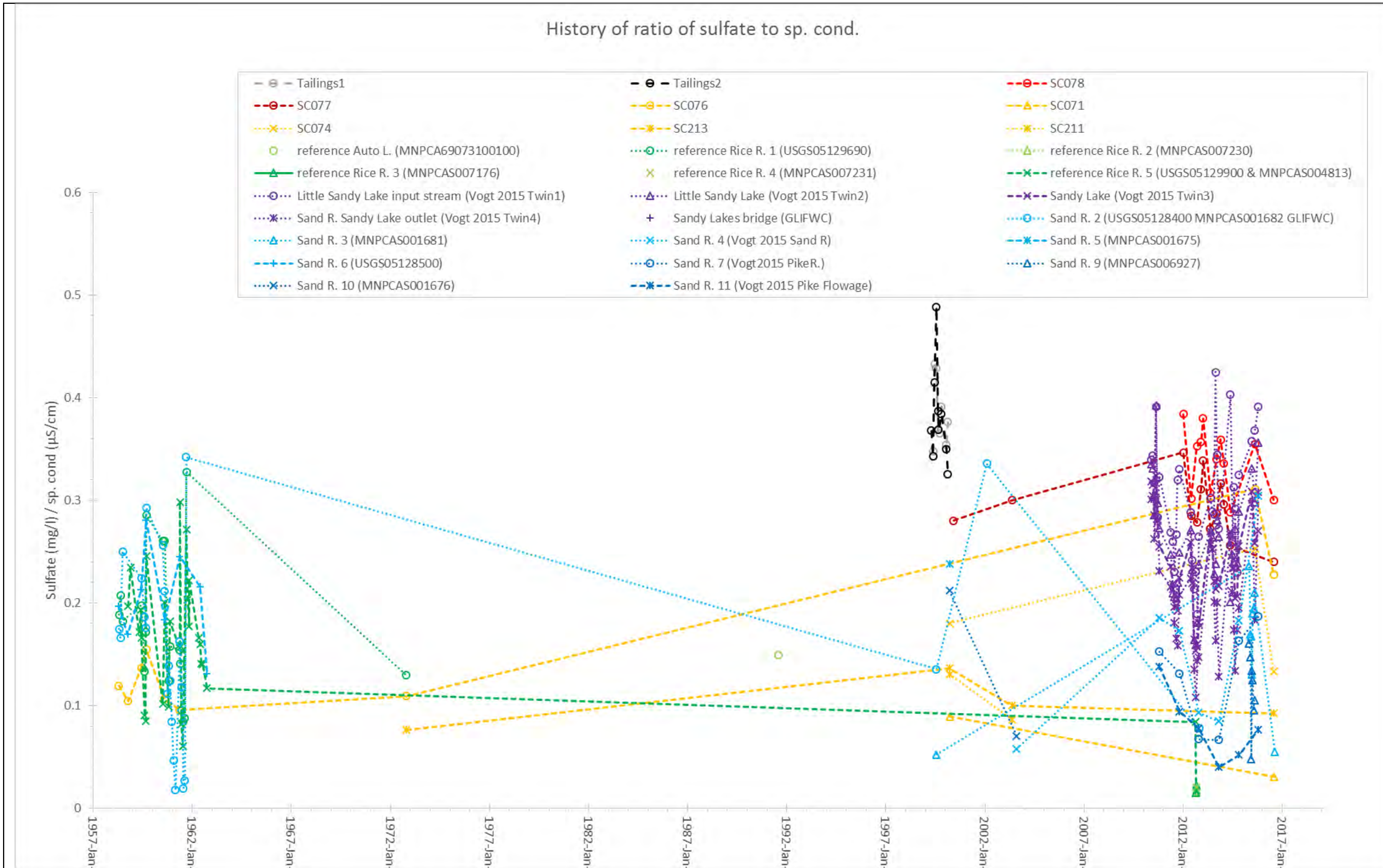

Fig. B-17. The ratio of sulfate to specific conductance in recent decades was more similar at SC078 and SC077 in the Dark River to Minntac tailings and data near the tailings in the Sand River system than to reference sites and downstream Iron River and Sand River sites. The ratio for a reference site was lower in the last decade than in the 1950's to 1960's, but was within the historical range for a Sand River site and was greater for a Dark River site.

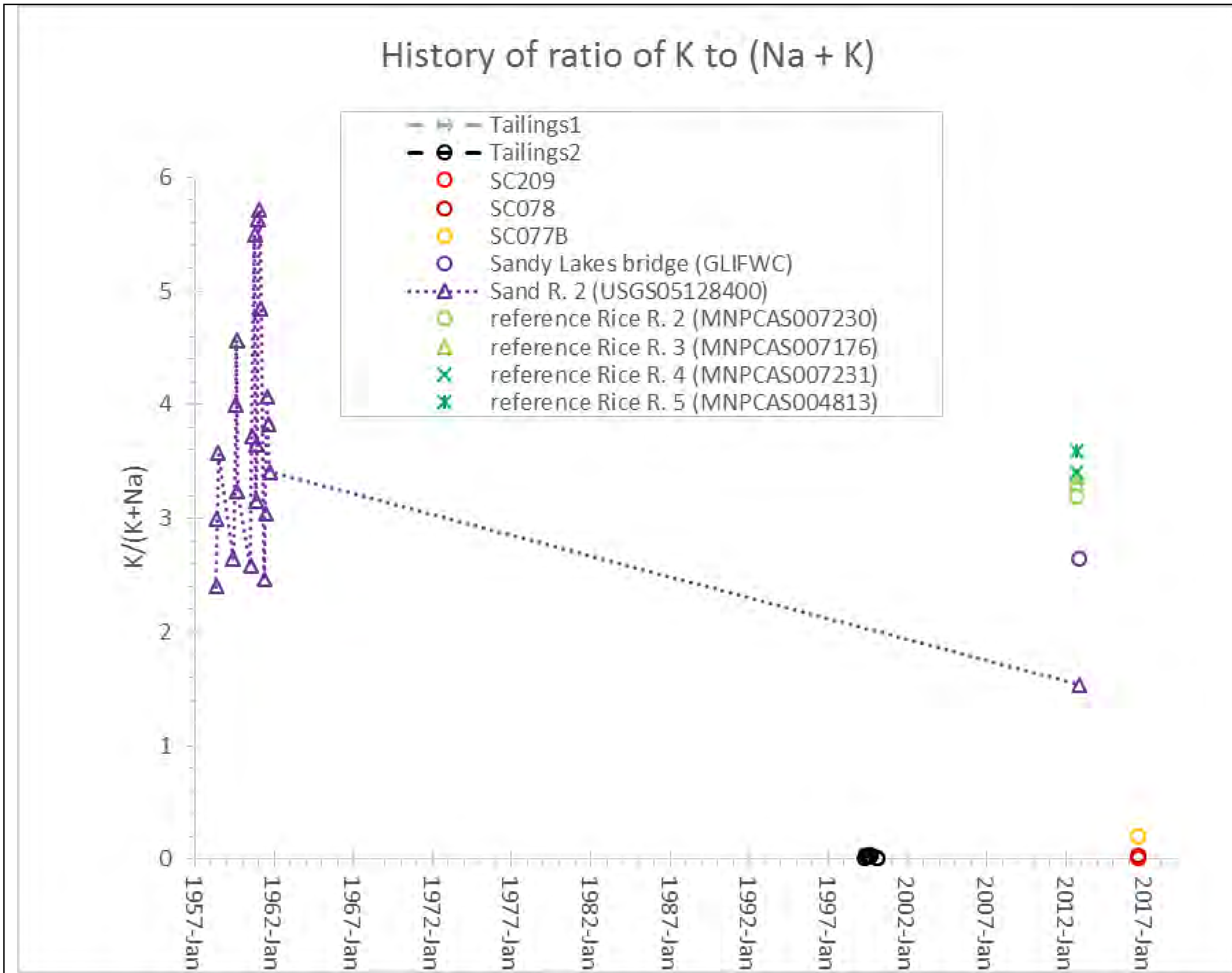

Fig. B-18. The ratio of potassium to the sum of potassium and sodium was comparable between the tailings in 1999-2000 and SC209, SC078, SC077B in 2016. The ratio was much greater at sites in the Sand River system and at reference sites on the Rice River.

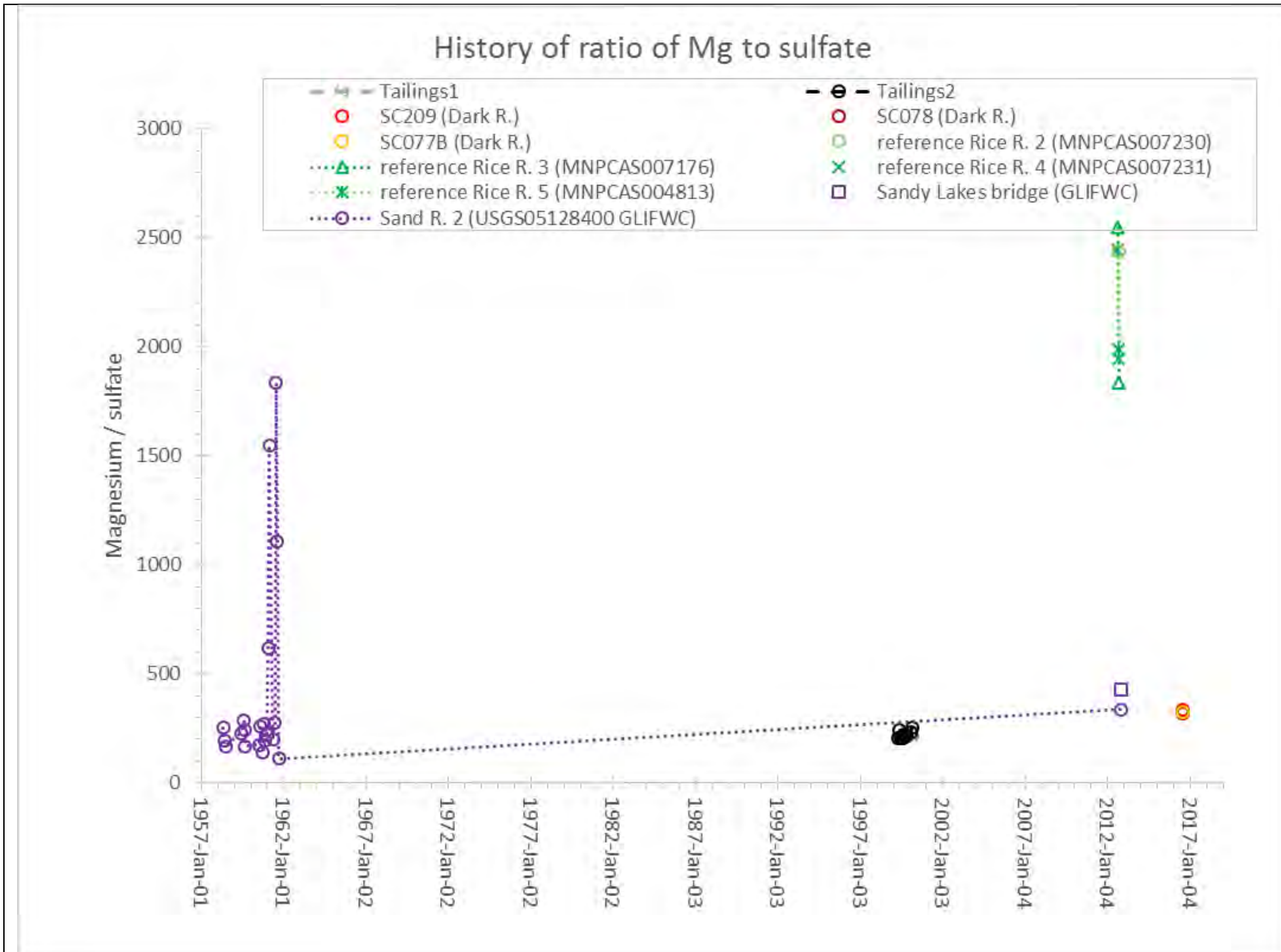

Fig. B-19. The ratio of magnesium to sulfate was greater at reference sites than at tailings, Dark River, and Sand River sites. The ratio at the Sand River site in 2012, however, was within the range of data from the 1950's and 1960's.

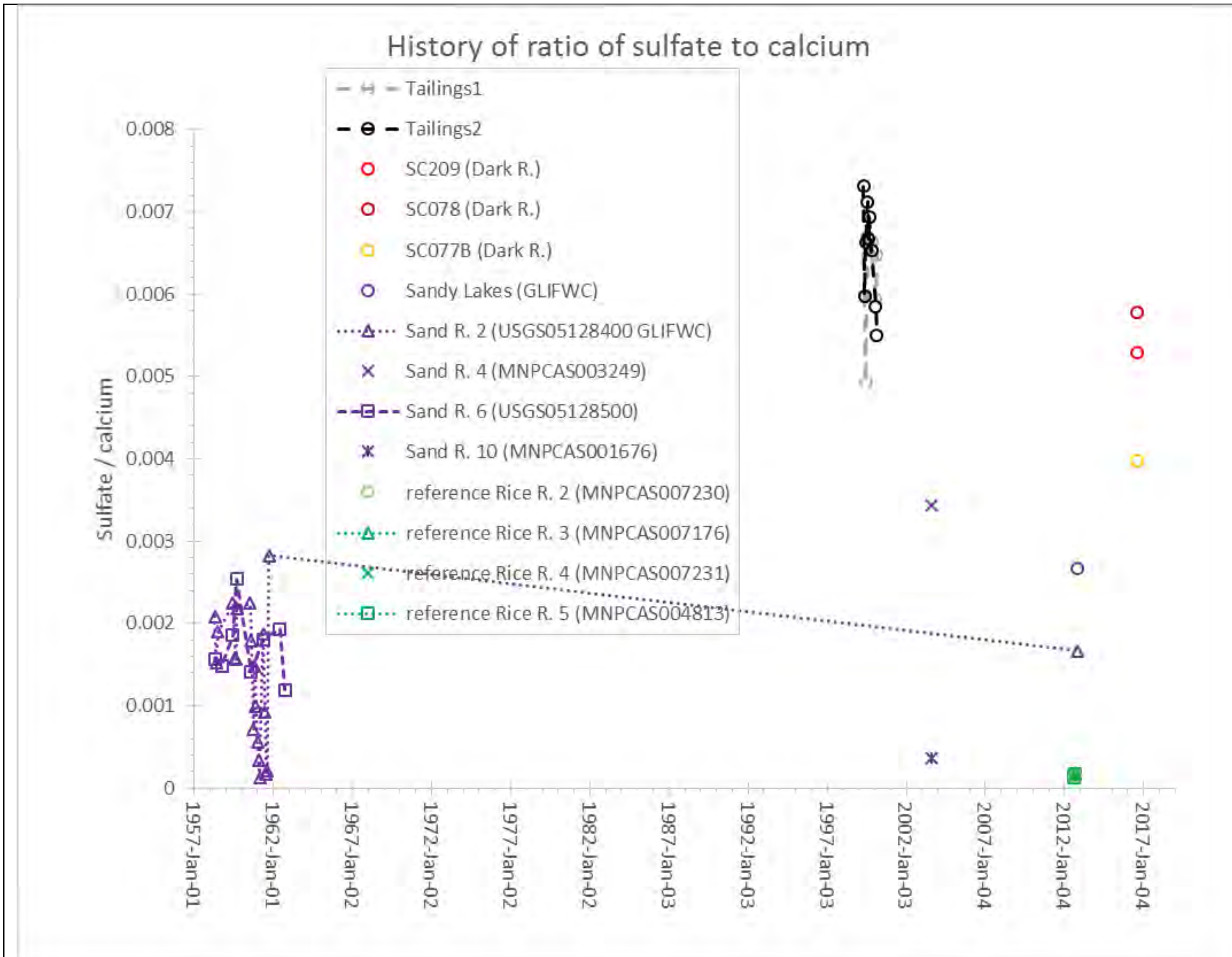

Fig. B-20. The ratio of sulfate to calcium was lower at reference sites than at tailings and Dark River sites in recent decades. The ratio at the Sand River site in 2012, however, was within the range of data from the 1950's and 1960's.

APPENDIX C. Site photos

Fig. C-1. Upstream view of the Dark River at SC209, the closest site to the Minntac tailings, 29 July 2016. Photo by Emma Cassidy.

Fig. C-2. Upstream view of the Dark River at the bridge at SC078, the second closest site to the Minntac tailings, 31 July 2016. Photo by Emma Cassidy.

Fig. C-3. Upstream view of the Dark River at SC217, 31 July 2016. Photo by Emma Cassidy.

Fig. C-4. Upstream view of the Dark River at SC216, 31 July 2016. Photo by Emma Cassidy.

Fig. C-5. Upstream view of the Dark River at SC077B (trout stream reach), 31 July 2016. Photo by Emma Cassidy.

Fig. C-6. Upstream view under bridge of the Dark River at SC076 (trout stream reach), 24 August 2015.

	
Fig. C-7. Upstream view of the Dark River at SC075 (trout stream reach), 24 August 2015.	Fig. C-8. Upstream view of the Sturgeon River at SC074, 30 July 2016. Photo by Emma Cassidy.

	
Fig. C-9. Upstream view of the Sturgeon River at SC073, 30 July 2016. Photo by Emma Cassidy.	Fig. C-10. Upstream view of the Sturgeon River at SC072, 30 July 2016. Photo by Emma Cassidy.

Fig. C-11. Upstream view of the Little Fork River at SC211, 30 July 2016. Photo by Emma Cassidy.

Fig. C-12. Westward view of the Little Fork River at SC210, 30 July 2016. Photo by Emma Cassidy.

Fig. C-13. Upstream view of the Sturgeon River at the reference site SC071, which is downstream of Hibbing Taconite, 24 August 2015.

Fig. C-14. Upstream view of the Little Fork River at the reference site SC212, 30 July 2016. Photo by Emma Cassidy.

APPENDIX D. Data collected in 2015 and 2016.

Date	SiteCode	Time	Temperature (water;°C)	Specific conductance (µS/cm)	DO (mg/l)	DO (%)	pH	ORP (mV)	Turbidity (FNU)	Temperature (air, C)	Flow (cfs)	F^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	Br^- (mg/l)	NO_3^- (mg/l)
2015-Aug-24	SC078	19:34	14.1	1775	9.1	93	8.0	237		10.9		0.41	66.5	629.6	0.320	0.01[a]
2015-Aug-24	SC077*	18:51	15.0	1266	9.3	97	8.4	219		10.1			61.7			
2015-Aug-24	SC076*	17:57	14.3	1028	9.2	94	8.2	218		12.2		0.27	36.9	319.4	0.161	0.01[a]
2015-Aug-24	SC075*	16:59	13.6	908	9.4	95	8.2	214		12.4			39.7			
2015-Aug-24	SC074	16:20	14.4	502	9.3	95	8.0	221		11.5		0.21	16.5	126.8	0.070	0.01[a]
2015-Aug-24	SC073	15:31	14.4	514	8.8	91	8.0	220		10.8			22.1			
2015-Aug-24	SC072	14:34	15.2	532	9.0	94	8.1	231		12.0		0.19	17.5	137.3	0.080	0.01[a]
2015-Aug-24	SC070	12:34	14.0	100	4.5	46	6.6	67		10.8		0.11	7.0	1.4	0.005[a]	0.01[a]
2015-Aug-24	SC071	13:46	14.9	139	8.4	87	7.6	152		12.1			6.9			
2016-Jul-29	SC209	14:27	20.9	1723	3.0	34	7.6	40	0	23.1	4.1	0.39	48.6	523.9	0.341	0.005[a]
2016-Jul-31	SC078	15:17	22.4	1585	5.7	69	7.7	98	0	27.1	3.4	0.43	45.1	476.3	0.345	0.01
2016-Jul-28	SC078	11:30	20.2	1490						21.0			40.7			
2016-Jul-29	SC078	18:37	23.5	1545						24.3			46.7			
2016-Jul-30	SC078	20:03	23.4	1568						21.5			47.2			
2016-Jul-31	SC217	14:22	23.6	939						25.1			31.2			
2016-Jul-31	SC216	13:23	26.7	659						25.8			21.2			
2016-Jul-31	SC077B*	12:47	23.9	624	8.0	99	7.8	115	1.0	26.2	12.5	0.17	15.9	149.6	0.059	0.005[a]
2016-Jul-30	SC077*	19:43	25.9	627						21.4			16.7			
2016-Jul-30	SC076*	19:07	22.9	522	8.0	98	7.4	78		23.7		0.15	13.6	118.8	0.042	0.033
2016-Jul-30	SC075*	18:24	21.8	493						27.8			13.5			
2016-Jul-30	SC074	17:31	23.2	258	7.5	92	7.2	72		29.2		0.34	7.4	34.4	0.018	0.068
2016-Jul-30	SC073	17:04	22.9	257						27.1			7.4			
2016-Jul-30	SC072	16:49	22.5	251						27.8			7.8			
2016-Jul-30	SC214	16:17	23.1	232						28.2			6.6			
2016-Jul-30	SC213	15:37	23.6	214	8.0	98	7.1	81		26.9		0.19	4.9	19.8	0.009	0.068
2016-Jul-30	SC211	14:18	23.6	147						26.3			5.0			
2016-Jul-30	SC210	13:01	23.9	150	8.0	97	7.0	88		25.4		0.15	4.2	9.8	0.006	0.086
2016-Jul-31	SC215	10:46	18.9	113						24.8			3.5			
2016-Jul-31	SC070	11:04	24.5	99						27.1			8.8			
2016-Jul-30	SC071	17:55	23.3	170	7.3	88	7.2	66		28.7		0.44	5.8	5.2	0.012	0.076
2016-Jul-30	SC212	14:56	24.1	90	7.1	88	6.4	108		26.7		0.03	3.6	0.8	0.0025[a]	0.075

* sites in trout stream reach; [a] measurements were below reporting limit, so listed measurements are half of reporting or detection limit;
[b] measurement did not meet QAQC criteria.

Date	2016-Jul-29	2016-Jul-31	2016-Jul-31
SiteCode	SC209	SC078	SC077B*
Time	14:27	15:17	12:47
Total alkalinity (mg/l)	437	415	153
TDS (mg/l)	254[b]	1170	416
TSS (mg/l)	1.0[a]	1.0[a]	1.0[a]
Total hardness as $CaCO_3$	971	831	295
Li7 (µg/l)	10.29	8.25	3.82
Li7 ±	0.43	0.056	0.050
B11 (µg/l)	183	143	55.7
B11 ±	7	3	2
Na23 (µg/l)	39052	34329	12398
Na23 ±	1361	320	279
Mg25 (µg/l)	175666	151769	48846
Mg25 ±	3108	2955	1133
Al27 (µg/l)	4.38	13.9	30.8
Al27 ±	0.1	0.7	1
P31 (µg/l)	67.0	84.8	29.1
P31 ±	2.8	3.7	1.2
S32 (µg/l)	182639	152635	48234
S32 ±	2033	4676	1509
K39 (µg/l)	7989	6387	2539
K39 ±	506	139	41
Ca44 (µg/l)	98923	82332	37562
Ca44 ±	3028	2576	713
Sc45 (µg/l)	0.0086	0.018	0.021
Sc45 ±	0.007	0.007	0.002
Ti49 (µg/l)	0.218	0.381	0.944
Ti49 ±	0.081	0.060	0.101
V51 (µg/l)	0.263	0.509	0.544
V51 ±	0.013	0.021	0.026
Cr52 (µg/l)	0.124	0.171	0.301
Cr52 ±	0.007	0.018	0.018
Mn55 (µg/l)	197.8	127.3	149.1
Mn55 ±	3.7	1.6	2.0
Fe56 (µg/l)	122.2	152.8	927.5
Fe56 ±	2.8	3.2	11.4
Co59 (µg/l)	0.125	0.164	0.302
Co59 ±	0.011	0.010	0.019
Ni60 (µg/l)	0.465	0.322	0.637
Ni60 ±	0.040	0.025	0.059
Cu63 (µg/l)	0.0949	0.0852	0.2026
Cu63 ±	0.009	0.012	0.010
Zn66 (µg/l)	0.100	0.154	0.674
Zn66 ±	0.025	0.064	0.053

Date	2016-Jul-29	2016-Jul-31	2016-Jul-31
SiteCode	SC209	SC078	SC077B*
Time	14:27	15:17	12:47
As75 (µg/l)	0.493	0.537	0.744
As75 ±	0.10	0.035	0.084
Se82 (µg/l)	4.66	4.06	1.74
Se82 ±	0.11	0.048	0.048
Rb85 (µg/l)	5.89	5.39	2.82
Rb85 ±	0.08	0.10	0.03
Sr88 (µg/l)	243.8	218.8	96.9
Sr88 ±	4.5	3.8	0.9
Y89 (µg/l)	0.034	0.054	0.116
Y89 ±	0.001	0.001	0.003
Nb93 (µg/l)	0.0056	0.0075	0.0085
Nb93 ±	0.00055	0.00046	0.00044
Mo95 (µg/l)	0.498	0.370	0.272
Mo95 ±	0.020	0.008	0.010
Rh103 (µg/l)	0.0211	0.0150	0.0065
Rh103 ±	0.0037	0.0006	0.0003
Pd108 (µg/l)	0.0034	0.0043	0.0052
Pd108 ±	0.0007	0.0008	0.0006
Ag109 (µg/l)	0.0007	0.0008	0.0008
Ag109 ±	0.0003	0.0003	0.0002
Cd111 (µg/l)	0.0046	0.0054	0.0047
Cd111 ±	0.0008	0.0018	0.0004
Sn118 (µg/l)	0.011	0.006	0.011
Sn118 ±	0.001	0.000	0.003
Sb121 (µg/l)	0.022	0.023	0.028
Sb121 ±	0.003	0.006	0.006
Cs133 (µg/l)	0.1380	0.1124	0.0389
Cs133 ±	0.0049	0.0028	0.0012
Ba137 (µg/l)	40.2	35.4	25.2
Ba137 ±	1.2	0.5	0.6
La139 (µg/l)	0.0162	0.0397	0.1171
La139 ±	0.0012	0.0004	0.0019
Ce140 (µg/l)	0.0274	0.0721	0.2371
Ce140 ±	0.0010	0.0022	0.0026
Pr141 (µg/l)	0.0053	0.0116	0.0332
Pr141 ±	0.0005	0.0003	0.0003
Nd146 (µg/l)	0.0245	0.0529	0.1372
Nd146 ±	0.0008	0.0021	0.0044
Sm149 (µg/l)	0.0059	0.0105	0.0252
Sm149 ±	0.0011	0.0008	0.0010
Eu151 (µg/l)	0.0136	0.0105	0.0116
Eu151 ±	0.0023	0.0009	0.0007

Date	2016-Jul-29	2016-Jul-31	2016-Jul-31
SiteCode	SC209	SC078	SC077B*
Time	14:27	15:17	12:47
Dy163 (µg/l)	0.0047	0.0080	0.0181
Dy163 ±	0.000358	0.000551	0.0017
Ho165 (µg/l)	0.0011	0.0016	0.0037
Ho165 ±	0.0002	0.0001	0.0003
Yb173 (µg/l)	0.0029	0.0045	0.0099
Yb173 ±	0.0003	0.0006	0.0004
Lu175 (µg/l)	0.0005	0.0008	0.0017
Lu175 ±	0.0002	0.0001	0.0001
W184 (µg/l)	0.004	0.002	0.003
W184 ±	0.001	0.001	0.001
Pt195 (µg/l)	0.0002	0.0005	0.0007
Pt195 ±	0.0001	0.0001	0.0002
Tl205 (µg/l)	0.0012	0.0016	0.0033
Tl205 ±	0.0003	0.0002	0.0003
PbSum (µg/l)	0.001	0.007	0.048
Pb_ ±	0.000	0.001	0.001
Th232 (µg/l)	0.0041	0.0092	0.0204
Th232 ±	0.0003	0.0004	0.0012
U238 (µg/l)	1.614	1.408	0.571
U238 ±	0.057	0.010	0.013

APPENDIX E. Site locations

SC code	Location name	Location description	Latitude (°,WGS84)	Longitude (°,WGS84)	GPS precision (m)
SC070	Clear Lake Outlet at Williams Rd.	ca 20m upstream of culvert in 2015 and upstream side of culvert in 2016	47.63303	-92.74863	5
SC071	Sturgeon River at State Highway 73	ca 10m upstream of bridge	47.71014	-92.86524	5
SC072	Sturgeon River at Anton Rd. (Co.Hwy. 492)	ca 15m upstream of bridge	47.76271	-92.88265	6
SC073	Sturgeon River at boat landing near State Highway 73	ca 100m upstream of bridge	47.73311	-92.86530	4
SC074	Sturgeon River at Goodell Rd. (Co. Hwy. 652)	ca 8m upstream of bridge	47.71830	-92.85602	5
SC075	Dark River at Graham Rd. (Co. Hwy. 688)	ca 100m upstream of bridge and ca 10m downhill from road	47.70373	-92.84954	6
SC076	Dark River at Carpenter Rd. (Co. Hwy. 481)	ca 5m downstream of bridge	47.69062	-92.82108	6
SC077	Dark River at Osborn Rd. (Co. Hwy. 65)	upstream side of bridge	47.65858	-92.79744	5
SC077B	Dark River at Osborn Rd. (County Highway 65)	adjacent to road and ca 100m upstream of SC077	47.65828	-92.79693	3
SC078	Dark River at Sherwood Anderson Rd. (Co. Rd. 668)	ca 8m downstream of bridge in 2015 and ca 1m upstream side of bridge	47.62362	-92.73183	4
SC209	Dark River at Kinney Spurr Trail (County Road 7941)	downstream side of bridge	47.61389	-92.70331	3
SC210	Little Fork River at Samuelson Park picnic area	ca 15m from NE side of river	47.94846	-93.09951	3
SC211	Little Fork River at County Hwy 114	ca 20m upstream of bridge	47.89445	-93.04147	3
SC212	Little Fork River at W Riek Road	ca 2m upstream of bridge	47.87984	-92.97517	3
SC213	Sturgeon River at State Highway 1 near Celina	ca 10m downstream of bridge	47.86565	-93.03588	3
SC214	Sturgeon River at Lind Road (County Highway 107)	downstream side of bridge	47.82221	-93.01745	3
SC215	McNiven Creek at Smith Road (County Highway 25)	upstream side of culvert bridge	47.58155	-92.76285	3
SC216	Dark River at N Dark Lake Road (County Road 663)	adjacent to road	47.63641	-92.78532	3
SC217	Dark River at County Highway 25	ca 8m upstream of bridge	47.63034	-92.76381	3

Appendix F. Method details

Limits of detection (LOD) for SF-ICP-MS analysis at Wisconsin State Laboratory of Hygiene

Element and isotope (Low Resolution, Medium Resolution, or High Resolution)	LOD (ng/l)		Element and isotope (Low Resolution, Medium Resolution, or High Resolution)	LOD (ng/l)
Li7(LR)	3.3		Mo95(LR)	2.2
B11(LR)	45		Rh103(LR)	0.73
Na23(MR)	780		Pd108(LR)	0.15
Mg25(MR)	460		Ag109(LR)	0.18
Al27(MR)	35		Cd111(LR)	0.14
Si28(HR)	12,500		Sn118(MR)	2.2
P31(MR)	50		Sb121(MR)	0.45
S32(MR)	970		Cs133(LR)	0.55
K39(HR)	220		Ba137(MR)	3.5
Ca44(MR)	740		La139(LR)	0.012
Sc45(MR)	2.2		Ce140(LR)	0.18
Ti49(MR)	3.5		Pr141(LR)	0.025
V51(MR)	0.45		Nd146(LR)	0.11
Cr52(MR)	2.1		Sm149(LR)	0.085
Mn55(MR)	12		Eu151(LR)	0.22
Fe56(MR)	22		Dy163(LR)	0.14
Co59(MR)	0.25		Ho165(LR)	0.011
Ni60(MR)	1.9		Yb173(LR)	0.35
Cu63(MR)	1.4		Lu175(LR)	0.012
Zn66(MR)	17		W184(LR)	0.32
As75(HR)	4.5		Pt195(LR)	0.12
Se82(LR)	30		Tl205(LR)	0.095
Rb85(LR)	2.5		Pb(sum)	0.35
Sr88(MR)	85		Th232(LR)	0.081
Y89(LR)	0.35		U238(LR)	1.1
Nb93(LR)	0.28			