Subject: Manoomin Site Specific Sulfate Standard Comment 2023/08/30
From: "john.coleman" <jcoleman@glifwc.org>
Date: 8/30/2023, 10:33 AM
To: "Cole, William (MPCA)" <william.cole@state.mn.us>
CC: Jonathan Gilbert <jgilbert@glifwc.org>, Ann McCammon_Soltis <amsoltis@glifwc.org>, Nancy Schuldt <NancySchuldt@FDLREZ.COM>, Margaret Watkins <mwatkins@grandportage.com>, Esteban Chiriboga <esteban@glifwc.org>

Emailed and submitted via MPCA web site.

Three items I wanted to follow up on from our previous conversations:

1) Seasonal limits based on the period that rice is sensitive may be inappropriate because the total annual sulfate load may be more important because of accumulation of sulfate in sediment pore water and the conversion of sulfate to sulfides.

2) Any site specific standard for sulfate in wild rice waters must take into account seasonal variation in sulfate levels due to dilution, or lack thereof, from precipitation. In particular, winter concentrations will be much higher because of the lack of precipitation input in waterbodies.
Our study of water character leaving the Minntac tailings basin (attached) highlights this seasonal variation despite an approximately constant concentration of sulfate from the basin. While that study was based on 4 years of continuous water quality data, attached is an updated figure of seasonal sulfate levels using 6 years of data. Both data sets show peaks in sulfate levels in late summer and mid-winter.
Unfortunately, the winter drought is often accompanied by little good data on contaminant concentrations and stream flow. For example the July 2022 application for a site specific SO4 standard downstreaam of the UTAC tailings basin by Barr Engineering reported water SO4 levels sampled in October and November only. Based on our work in the Sand River, October and November samples are very unlikely to demonstrate the full range of likely SO4 concentrations.
Both establishment and monitoring of a site specific sulfate standard must take into account the several fold seasonal differences in water chemistry and in particular require adequate information and monitoring during the winter months.

3) After reading over the 2022 application for a site specific standard at UTAC, it is clear that the methodology using the 2017 MPCA equations may be abused to obtain a high site specific standard. Of particular concern was the derivation of a 370 ug/L protective sulfide level as described in that application's Appendix A. Options for use, or misuse, of the equations previously proposed by MPCA should be considered with caution given their complexity and the opportunity to implement them in unintended ways.

Thank you for considering these comments and attached materials.
weweni izhichigen,
john coleman

John Coleman, Environmental Section Leader
Madison Office of the Great Lakes Indian Fish & Wildlife Commission
550 Babcock Drive, Room B102
Madison, WI 53706
608-263-2873(w) or 715-209-1616(c)
jcoleman@glifwc.org

Attachments:

Minntac_SandyR_Tech-Memo_fnl.pdf	926 KB
SANDL04_2023-06-08_SO4_week-box.pdf	15.7 KB

GREAT LAKES INDIAN FISH & WILDLIFE COMMISSION
P.O. Box 9 • Odanah, WI 54861 • 715-682-6619 • FAX 715-682-9294
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<u>Via Electronic Mail</u>

February 10, 2022

Technical Memorandum

To: Nancy Schuldt, Water Projects Coordinator, Fond du Lac Environmental Program

From: John Coleman, GLIFWC Environmental Section Leader

Re: Hourly Conductivity and Sulfate in the Sand River entering the Twin Lakes from the Minntac tailings basin, 2017 - 2021.

The purpose of this memorandum is to describe data collected by GLIFWC staff over a four year period that shows, on an hourly basis, the levels of Specific Conductance and Sulfate in the segment of the Sand River that flows from the Minntac tailing basin to the Twin Lakes.

Methods

From 2017 through 2021 water quality monitoring was conducted in the Sand River in the 1 mile segment of river between Admiral Lake and the Twin Lakes. The Sand River has its origin at the toe of the Minntac tailings basin, flows approximately 1/4 mile into the south-west side of Admiral Lake and from there flows approximately 1 mile to the Twin Lakes (Figure 1). Prior to basin construction the river arose in farm lands which are now covered with tailings. This report will focus on monitoring by GLIFWC in the 1 mile segment of river. Comparisons will be made to additional data collected by the 1854 Treaty Authority.

Analysis will focus on two sampling locations:

- SandL04: on the Sand River, 1/4 mile upstream of the Twin Lakes
- Twin 1 / SW-005: discharge point of Sand River to the Twin Lakes

Figure 1: Sample sites on Sand River between the Minntac tailings basin and the Twin Lakes (Sandy and Little Sandy Lake).

Sampling & Logging methods:

Monitoring was conducted by 3 methods:

- In-stream data logger
- Grab samples
- YSI meter readings

In-stream data logger: An in-stream data logger (Onset U24-001) was placed in the Sand River at location SandL04 in 2017. The logger was tethered to the river bottom and held approximately 1 foot off the bottom by foam flotation material. That logger was programmed to record water temperature and water conductivity every 30 minutes in 2017 & 2018 and every hour in 2019-2021. These readings are nominal referred to as "hourly readings" in this report. The data logger was downloaded one or two times per year during site visits to collect water grab samples.

Grab samples: Water grab samples were collected by GLIFWC at SandL04 once or twice per year from 2017 through 2021. Since 2010 the 1854 Treaty Authority has collected water grab samples at location Twin 1 three to six times per year between late May and late October. That site is approximately 1/4 mile downstream of GLIFWC's site SandL04. Full results of the 1854 Treaty Authority sampling can be found in its annual reports referenced in the citations section. In this memo only the Specific Conductance (water conductivity @ 25 deg.C) and Sulfate results of these water samples will be discussed.

YSI meter readings: Meter reading of specific conductance (Sp.C) were recorded with a YSI ProPlus or ProDSS at SandL04 by GLIFWC staff during site visits to collect grab samples.

Results

In-stream logger records of specific conductance and temperature:

Between August 9, 2017 and July 7, 2021 47,478 date and time stamped records of temperature and conductivity were recorded and downloaded. The water conductivity records were converted to Sp.C using the co-recorded temperature readings. We used the default conversion formula that is used for YSI meters:

Specific Conductance (uS/cm) = Conductivity/(1+(0.019*(degreesC-25)))

This made the logger readings of Sp.C directly comparable to the readings taken with the YSI meter during site visits.

The 47,478 readings of Sp.C had a median of 1,516 uS/cm (mean=1,437) and a maximum of 2,519 uS/cm with the highest readings occurring in mid-winter (Figure 2). To validate the logger readings, Sp.C measurements taken with the YSI meter during site visits were co-plotted with the logger readings (Figure 2, red X's). 1854 Treaty Authority Sp.C data collected at Twin 1 was also co-plotted with the logger readings (Figure 2, red circles). Both auxiliary data sets align well with the in-stream logger records of Sp.C.

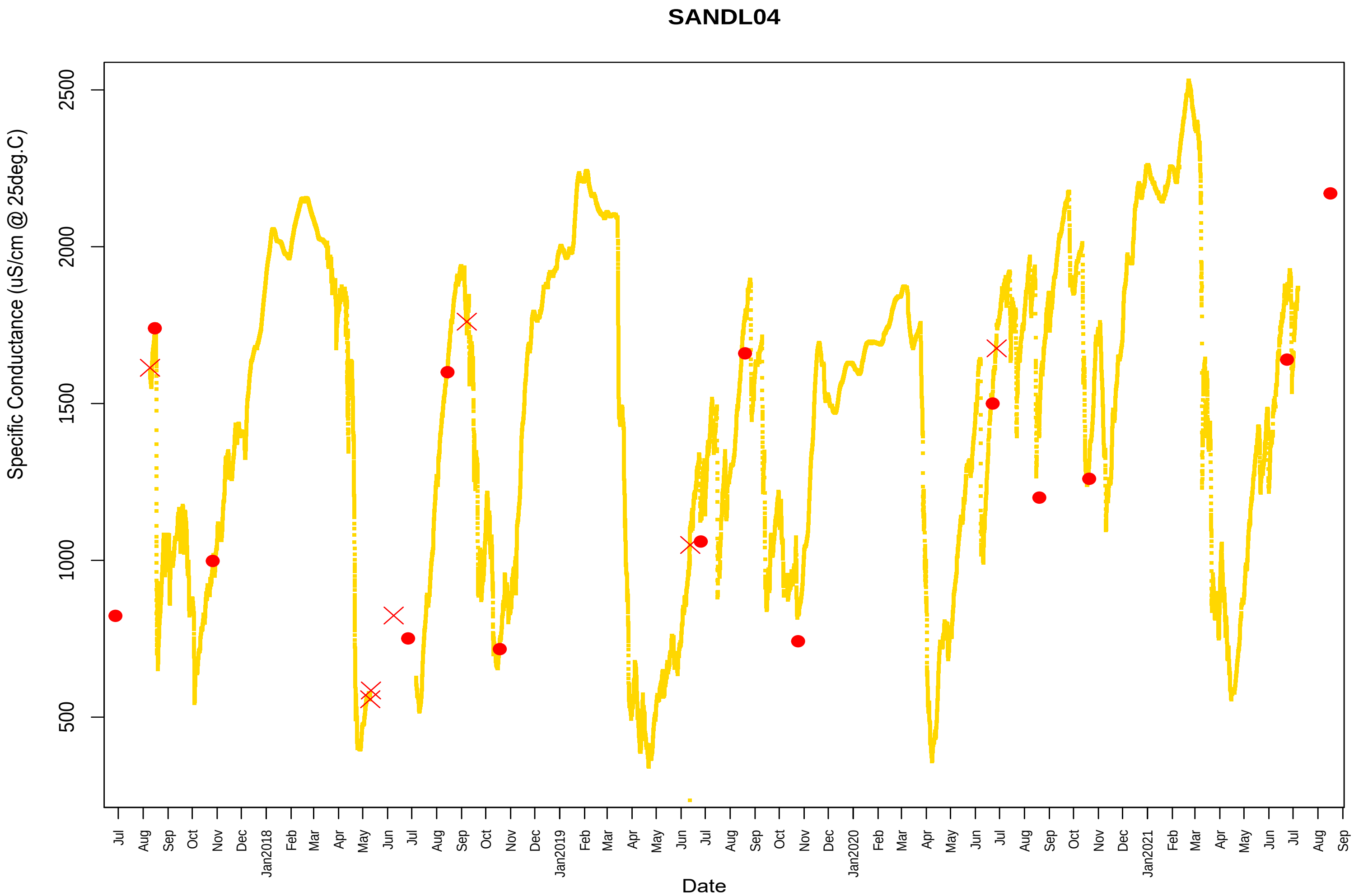


Figure 2: Specific conductance (uS/cm, conductivity at 25 deg.C) in the Sand River at SandL04. Yellow points = U25-001 in-stream logger records; Red X's = specific conductance readings with a YSI meter during GLIFWC site visits; Red circles = specific conductance results from 1854 Treaty Authority grab samples.

Seasonal Patterns in Temperature and Specific Conductance:

Temperature of the Sand River followed an expected pattern of near freezing in winter, gradual warming in the spring, median highs of almost 25 deg.C in mid summer and gradual cooling in fall (Figure 3). The lowest weekly median temperatures were from mid-November to mid-March. Water temperatures were least variable during the winter weeks.

Specific conductance (uS/cm) showed a pattern of high values in winter and during dry spells in summer (Figure 4). Weekly median values were lowest (approximately 500 uS/cm) during snow/ice melt in the the first week of April and highest (approximately 2,150 uS/cm) in the mid-winter weeks of February. Mid-summer high specific conductance was punctuated by drops in specific conductance resulting from large precipitation events introducing low conductivity water into the hydrologic system.

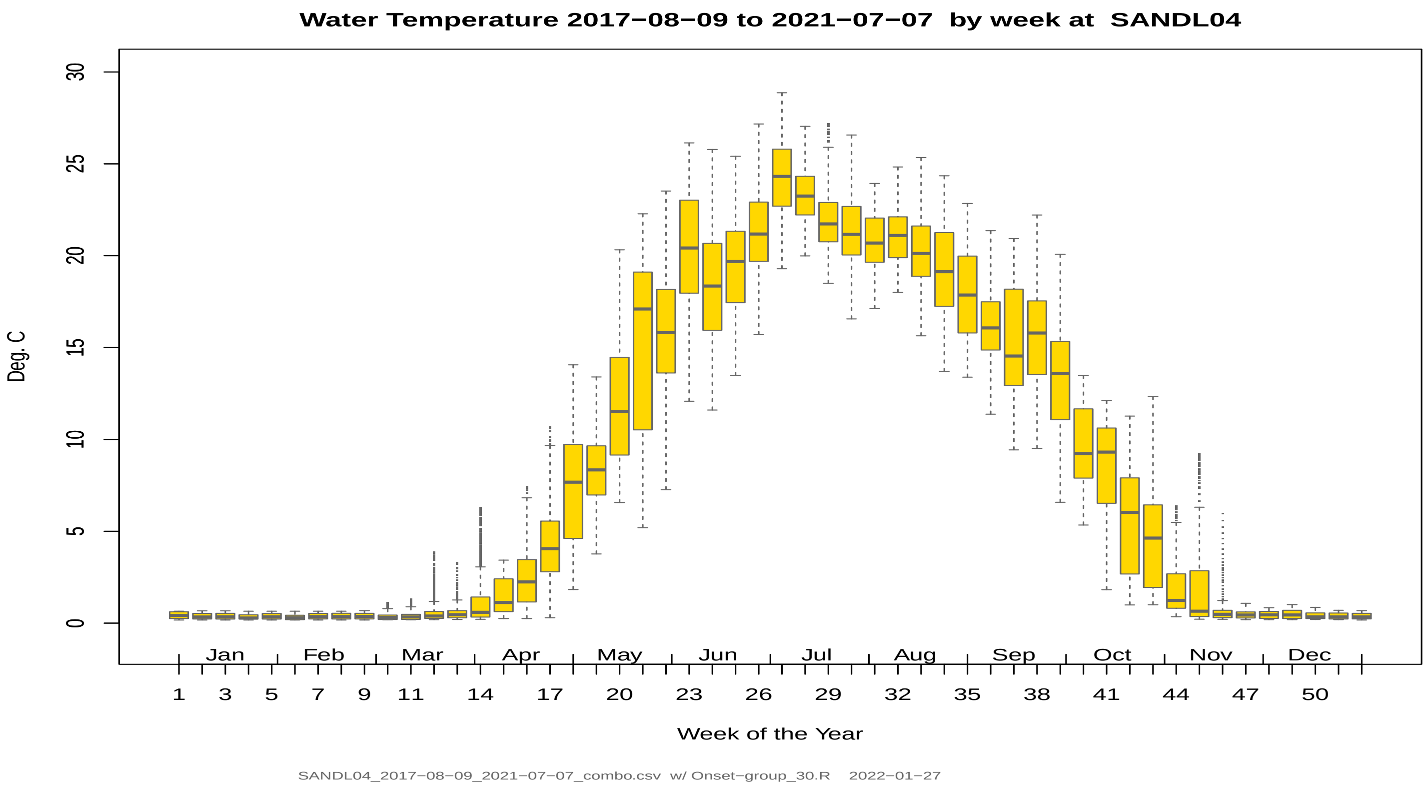


Figure 3: Seasonal temperatures (deg.C) in the Sand River at SandL04 from 2017 through 2021. The 4 year dataset of 47,478 records was broken into a subset for each week of the year and box-plots created for each week. Box-plots show the median and range of temperature for each week of the year. The weekly temperature median and variance were lowest during the winter months.

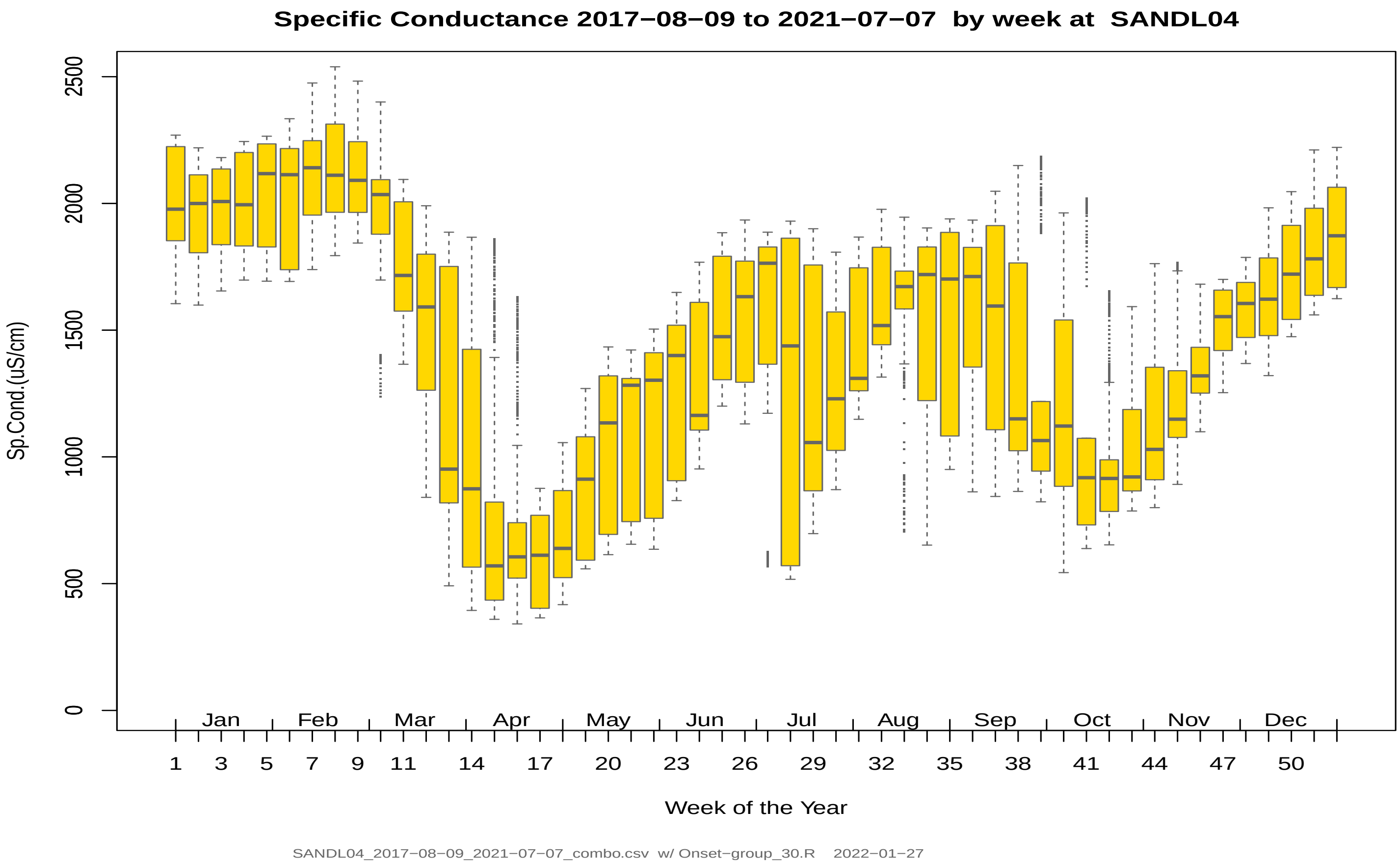


Figure 4: Seasonal specific conductance (conductivity at 25 deg.C, uS/cm) in the Sand River at SandL04 from 2017 through 2021. The 4 year dataset of 47,478 records was broken into a subset for each week of the year and box-plots created for each week. Box-plots show the median and range of specific conductance for each week of the year. The weekly specific conductance median was highest during the mid-winter and summer months.

Relationship between Specific Conductance and Sulfate levels:

The 1854 Treaty Authority data set of Sp.C and SO4 measurements from 2010 to 2021 was used to develop a statistical relationship between those two parameters. A least-squares regression was conducted with the Sp.C and SO4 data as shown in Figure 5. The correlation observed was very strong with an R^2 of 0.913. The equation relating Sp.C and SO4 was: SO4(mg/L) = 0.3716*Sp.C(uS/cm) - 71.00 . USS's consultant conducted a similar analysis of Sp.C vs. SO4 (USS 2021 Section 4.1.3) to develop"a robust correlation between the sulfate concentration and specific conductance". However, USS used data from the Mt. Iron Pit and tailings basin reclaim water, whereas we used data from the Sand River near the site where we then predicted SO4 levels.

With this strong, site-specific relationship between Sp.C and SO4 we were able to predict SO4 levels in the Sand River using the hourly records collected at SandL04. This gave us a near-continuous 4-year record of sulfate levels in the Sand River at SandL04 (Figure 6).

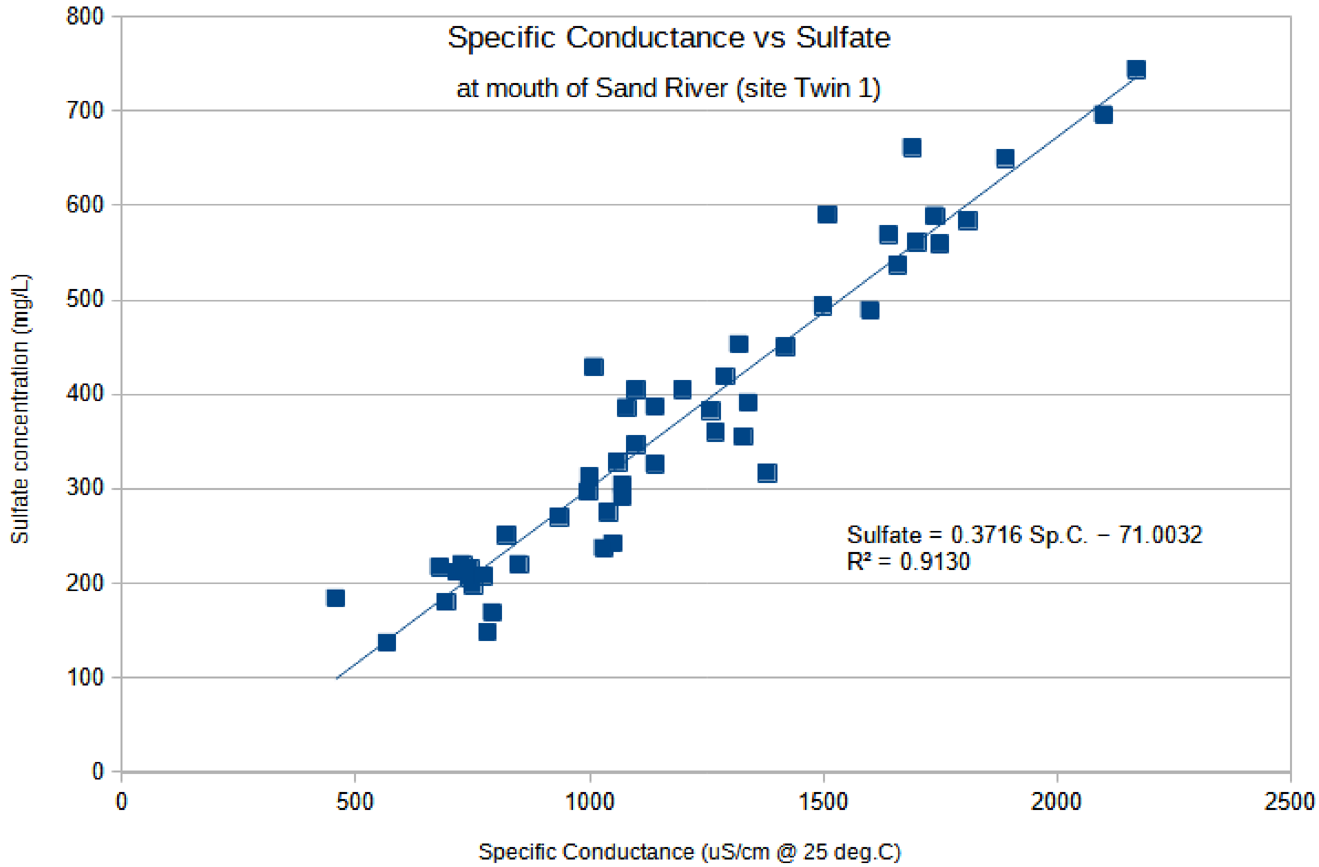


Figure 5: Specific conductance (conductivity @ 25 deg.C, uS/cm) vs. Sulfate concentration (mg/L) in 51 water samples collected by the 1854 Treaty Authority at the mouth of the Sand River (site Twin 1), 2010 through 2021.

Predicted Sulfate Levels:

The 47,478 predicted hourly values for SO4 were the highest in February of 2021 and lowest in April of 2019 (Figure 6). Predicted SO4 had a median of 492 (mean=463) and a maximum level of 865 mg/L over the 4 years. To provide some confidence that the predicted sulfate levels were accurate, we compared logger readings to GLIFWC's YSI readings of Sp.C. We also compared our predicted SO4 levels to GLIFWC's water grab sample results at site SandL04 (Table 1).

On 5 occasions GLIFWC staff collected YSI meter readings and grab samples at SandL04 while the in-stream data logger was running (Table 1). In all cases the in-stream logger readings of specific conductance were close to, but slightly higher (average 2%) than, the readings of the YSI meter. The predicted sulfate levels were also slightly higher (average 5%) than the results of the grab samples.

Table 1: Water sample sulfate, predicted sulfate, meter read Sp.C, and in-stream logger read Sp.C. at site SandL04 on 5 dates.

Date	Time	sample SO4	predicted SO4		YSI meter Sp.C.	Onset logger Sp.C.
2020-06-27	11:05	566	567		1676	1718
2019-06-12	09:00	306	337		1049	1098
2018-09-07	11:10	552	594		1761	1789
2018-05-10	10:05	132	140		557	567
2017-08-09	11:25	517	520		1614	1590

To further corroborate the SO4 predictions, in Figure 6, we plotted the hourly sulfate levels predicted with the contemporaneous 14 sulfate results from grab samples by 1854 Treaty Authority at site Twin 1. The SO4 levels observed in the grab samples from Twin 1 are very similar to the predicted values for site SandL04.

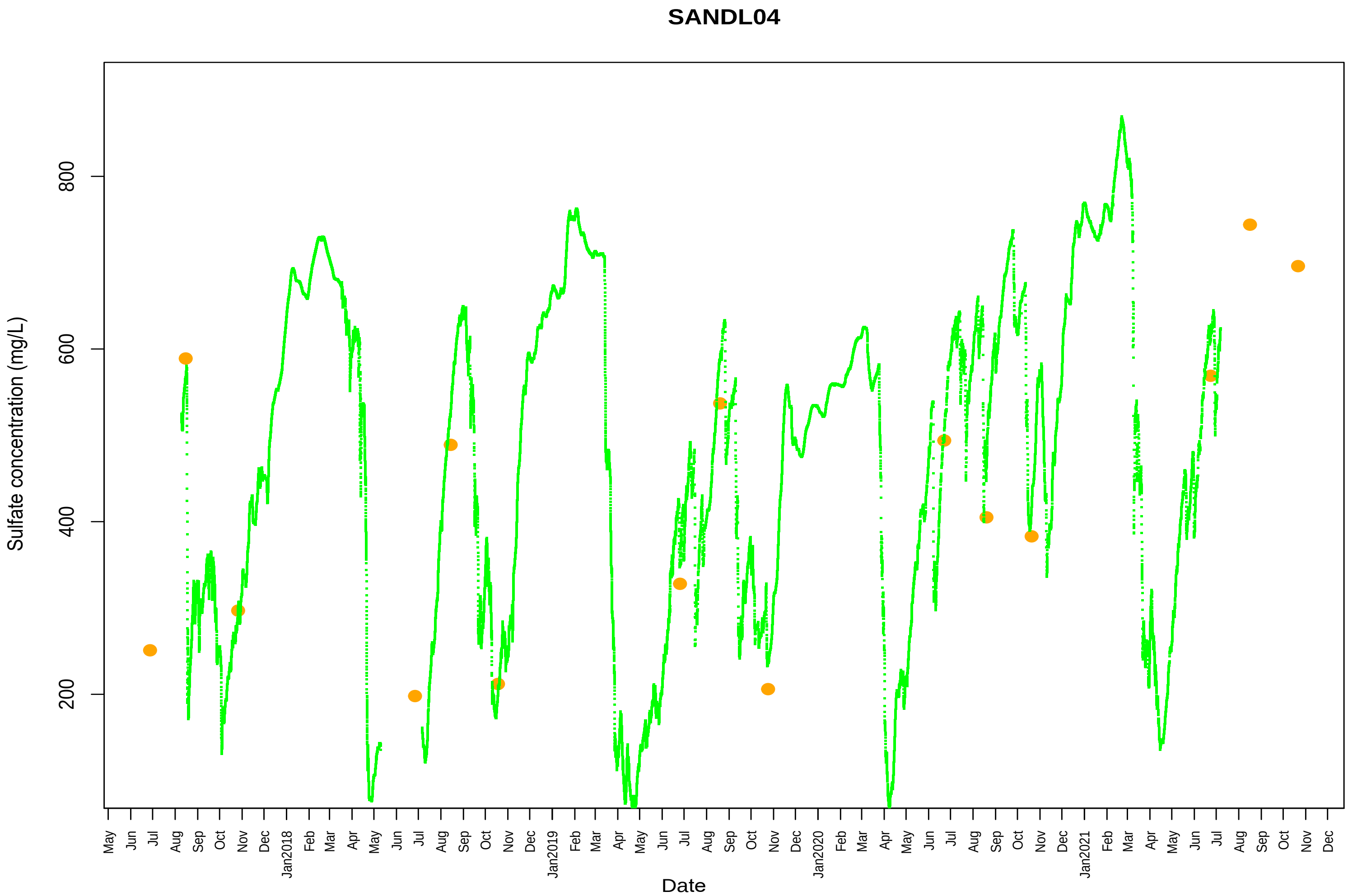


Figure 6: Predicted hourly sulfate concentrations (mg/L) in the Sand River at site SandL04 (green points) and 1854 Treaty Authority sulfate (mg/L) results (orange dots) from samples taken 1/4 mile downstream at the mouth of the Sand River (site Twin 1), 2017 to 2021.

Seasonal pattern of sulfate concentrations:

The annual pattern of SO4 levels by week (Figure 7) parallels that observed for Sp.C. concentrations. Levels were highest in mid-winter with weekly medians around 750 mg/L and lowest in spring with weekly medians around 150 mg/L, when snow and ice melt dilutes concentrations.

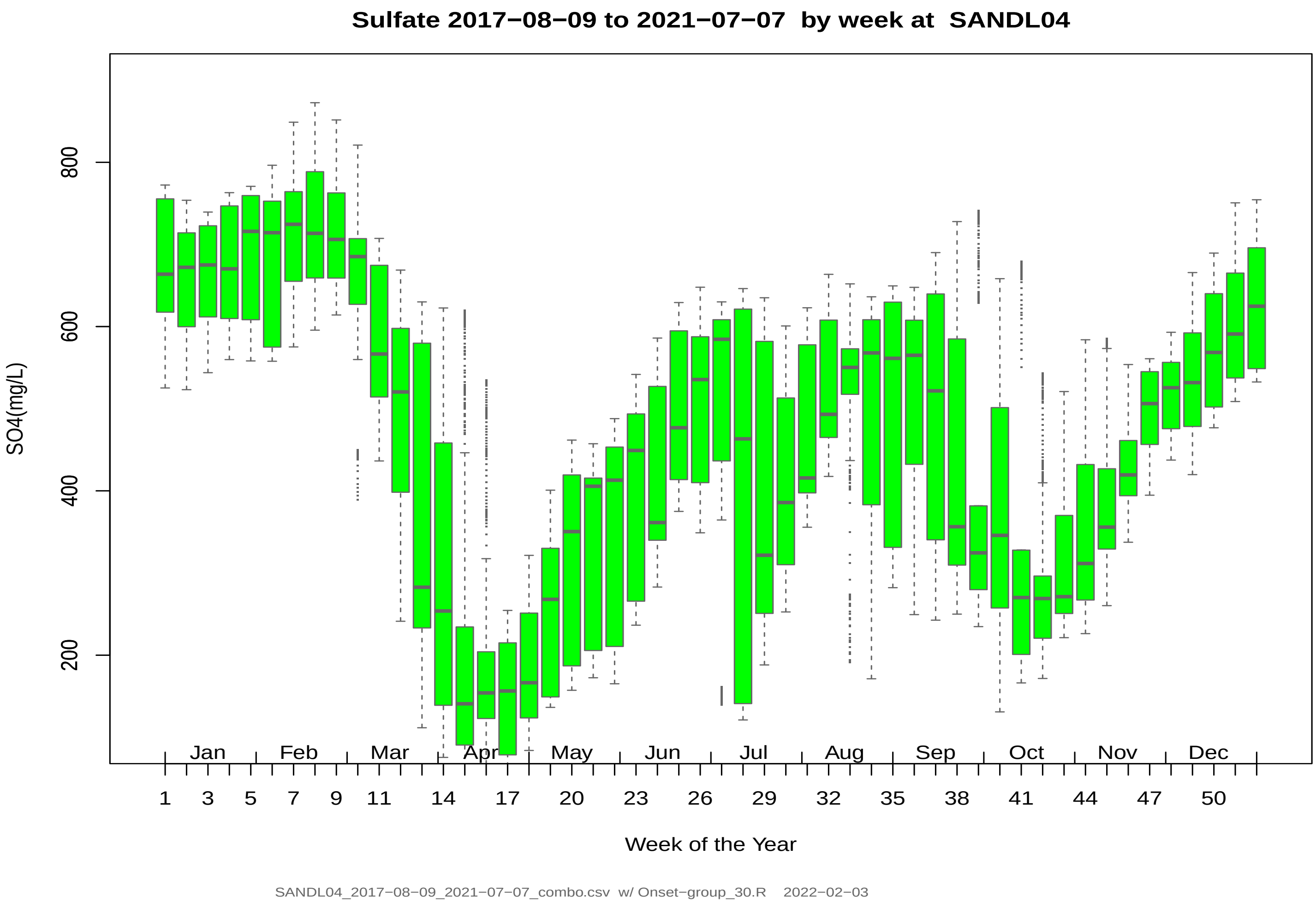


Figure 7: Predicted weekly sulfate concentrations (mg/L) in the Sand River at SandL04 from 2017 through 2021. The 4 year dataset of 47,478 records was broken into a subset for each week of the year and box-plots created for each week. Box-plots show the median and range of sulfate concentration for each week of the year.

Conclusions

Near-continuous logging of specific conductance in the Sand River at the site SandL04, a quarter mile upstream from the Twin Lakes, allows for tracking of concentrations over the last four years. The close relationship between specific conductance and sulfate levels in the Sand River (Figure 5) also allows for tracking sulfate levels in the Sand River over the four year period. The measured specific conductance and predicted sulfate levels compare very closely to the measurements taken by the 1854 Treat Authority (Figures 2 and 6) and by GLIFWC (Table 1).

The records reported here tell a story similar to that told by other data sets, high levels of minerals moving down the Sand River from the Minntac basin, but allow for a clearer view of the seasonal range of specific conductance and sulfate in the Sand River (Figures 4 and 7). Specific conductance levels were typically lowest in the spring and fall when inputs of precipitation/snowmelt were greatest. In mid winter and summer specific conductance levels were much higher because precipitation inputs were greatly reduced. During those "dry" periods specific conductance was typically in the range of 1500 to 2500 uS/cm.

Observed and predicted sulfate concentrations showed a similar pattern. In the spring and fall sulfate was typically lowest (Figure 7). In winter and summer sulfate concentrations were much higher, typically in the 600 to 800 mg/L range (Figure 7).

The readings reported here help demonstrate that in the Sand River contaminants are high (spring and fall) to very high (winter and summer) and exceed limits appropriate to protect aquatic life and wild rice. It is apparent that the contaminants are a large fraction of the levels found within the tailings basin itself. USS's chloride data (USS 2021, Appendix F) support this conclusion, showing that in February 2021 chloride levels in the Sand River entering the Twin Lakes were 83% of the levels observed in the basin itself. In August of that year chloride levels in the river were 97% of those observed in the basin. Given that chloride is a conservative tracer of contaminants it is apparent that during those and other "dry" periods the Sand River is made up of mostly contaminated tailings basin water.

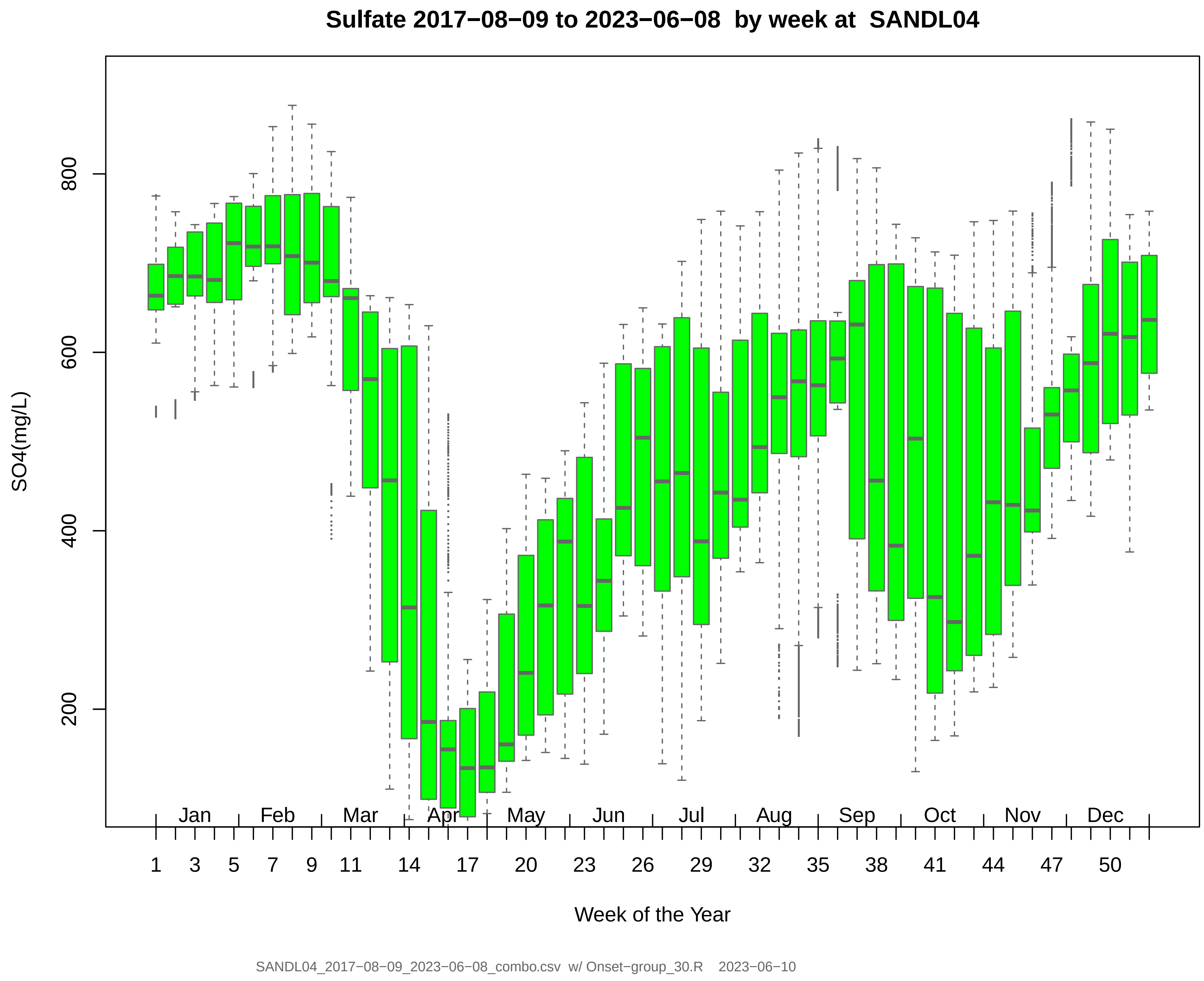
Because these data show that sulfate and other mineral content of the Sand River fluctuates greatly over the year in a predictable pattern, measures need to be implemented to eliminate the very high pollutant concentrations that occur for long periods.

Citations

1854 Treaty Authority. 2010-2021. Sandy Lake and Little Sandy Lake Monitoring. Technical reports 2010 to 2021.

USS 2021. Hydrological Investigation Report Minntac Tailings Basin. NPDES Permit MN0057207 U. S. Steel Corporation December 22, 2021.

cc: Jonathan Gilbert, Director, GLIFWC Biological Services Division
Ann McCammon Soltis, Director, GLIFWC Division of Intergovernmental Affairs


Sulfate 2017−08−09 to 2023−06−08 by week at SANDL04
SO4(mg/L)
200
400
600
800
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
1
3
5
7
9
11
14
17
20
23
26
29
32
35
38
41
44
47
50
Week of the Year
SANDL04_2017−08−09_2023−06−08_combo.csv w/ Onset−group_30.R 2023−06−10