

Clearwater BioLogic LLC

Wild rice waters with sulfate concentration over 10 mg/L should be included in the Impaired Waters list for 2024. Many of the sulfate point sources are identified in the 2018 Tribal Wild Rice Task Force Report. <https://www.mnchippewatribe.org/wildricetaskforce.html> One of these point sources is the Dunka River flowing into Birch Lake near Babbitt. My comments in the attached document are directed specifically at the Dunka River point source and how the sulfate could be reduced. This same approach could be applied to nearly all of the point sources identified. The sulfate can be reduced effectively.

Draft Impaired Waters List 2024

The new Draft Impaired Waters List for 2024 includes several new listings due to elevated sulfate concentrations. Many of these sulfate impairments could be resolved with the biological reduction of sulfate at the source of the excess concentration. My comments here will focus on the particular situation of the Dunka River and Birch Lake near Babbitt as an example of what can be done.

Impaired waters comments: Birch Lake and Dunka River

The data collected by the MPCA related to sulfate concentrations in Birch Lake and the Dunka River clearly show these concentrations to be over the limit of 10 mg/L for wild rice producing waters. And Birch Lake is definitely a wild rice producing lake. Therefore, it is clear that Birch Lake, near Babbitt, MN, must be declared an “Impaired Water for Sulfate Contamination”.

Waters are declared Impaired so that attention will be paid to the problem and action will be initiated to remediate the situation. That way the waters can eventually be removed from the Impaired Waters listing. The question is - what can be done to reduce the sulfate concentrations in Birch Lake to below the wild rice standard of 10 mg/L? Is this a viable objective? I will present a method by which this goal can definitely be achieved.

Clearwater BioLogic LLC, headquartered on the shores of Birch Lake just north of Babbitt, has developed a biological and reactive-iron system to reduce high sulfate concentrations to well below the 10 mg/L wild rice standard, and often to well below 1 mg/L. Details of the system can be seen at www.ClearwaterBioLogic.com.

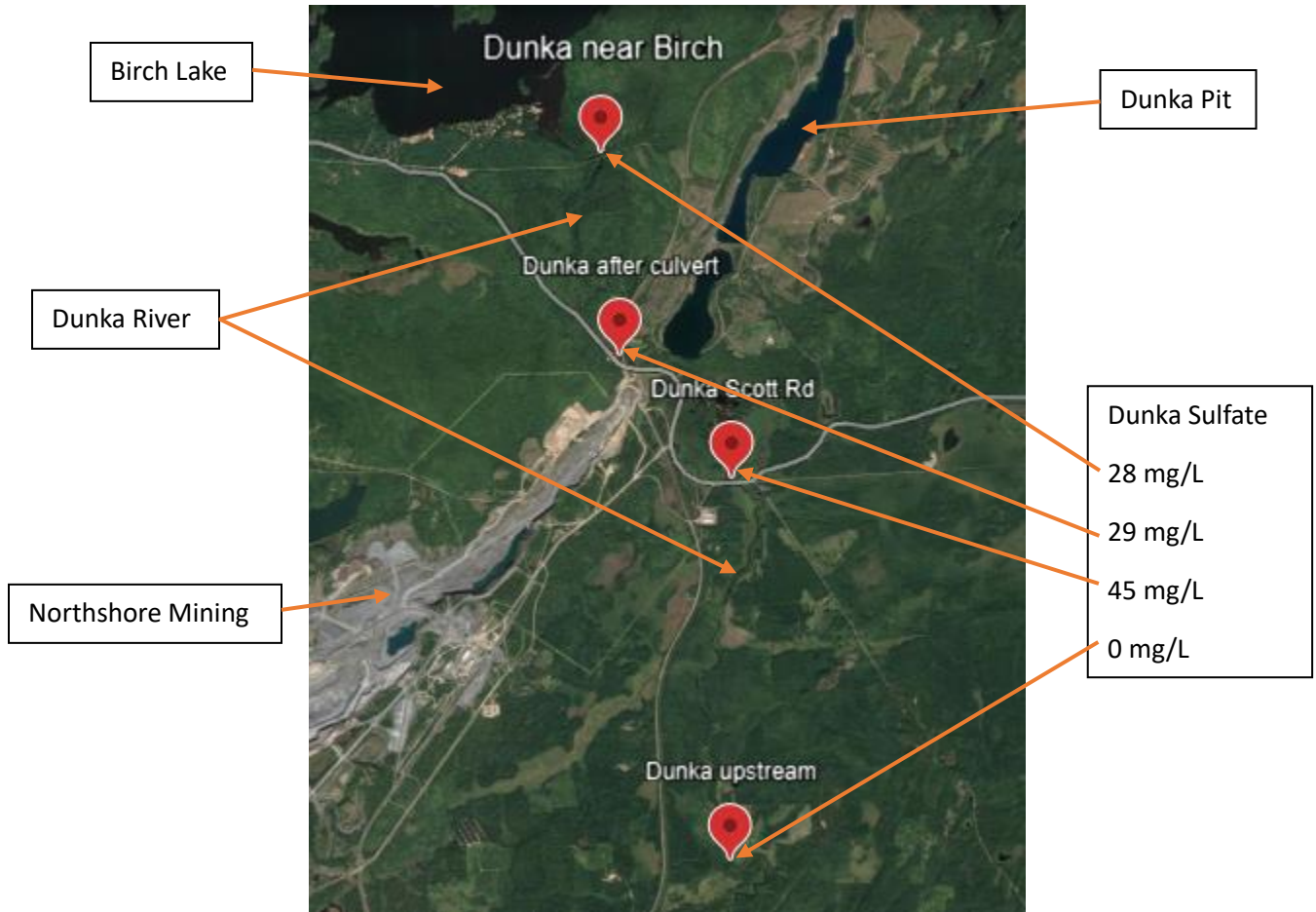
The Clearwater BioLogic system reduces sulfate in waters being discharged from mine pit lakes, active mine pits, and tailings basins. Field tests conducted over a span of 5 years in the 5NEC mine pit lake on the inactive Erie Mining site regularly reduced about 1,100 mg/L to well under 10 mg/L. These Area 5 legacy mine pit lakes form the headwaters of Spring Mine Creek, which flows north into the Embarrass River. In recent years Clearwater BioLogic has conducted successful lab testing to reduce sulfate in water from Spring Mine Creek (which runs 250-750 mg/L) to well below 10 mg/L.

The most recent lab testing using water from the St James Mine Pit Lake near Aurora has consistently reduced 300 to 400 mg/L sulfate concentrations to non-detect levels (defined as <3 mg/L). These tests have been running since May 2023 with St James water and continue to biologically convert +99.9% of the sulfate to hydrogen sulfide. The hydrogen sulfide is then reacted with direct reduced iron (DRI) to form insoluble iron sulfide. The iron sulfide can then be precipitated out and removed from the system. This effectively removes the sulfur from the discharge water thereby avoiding any recreation of sulfate downstream.

The question then is, where does the sulfate in the Dunka River and Birch Lake come from? Can it be intercepted at the source for biological sulfate reduction and removal?

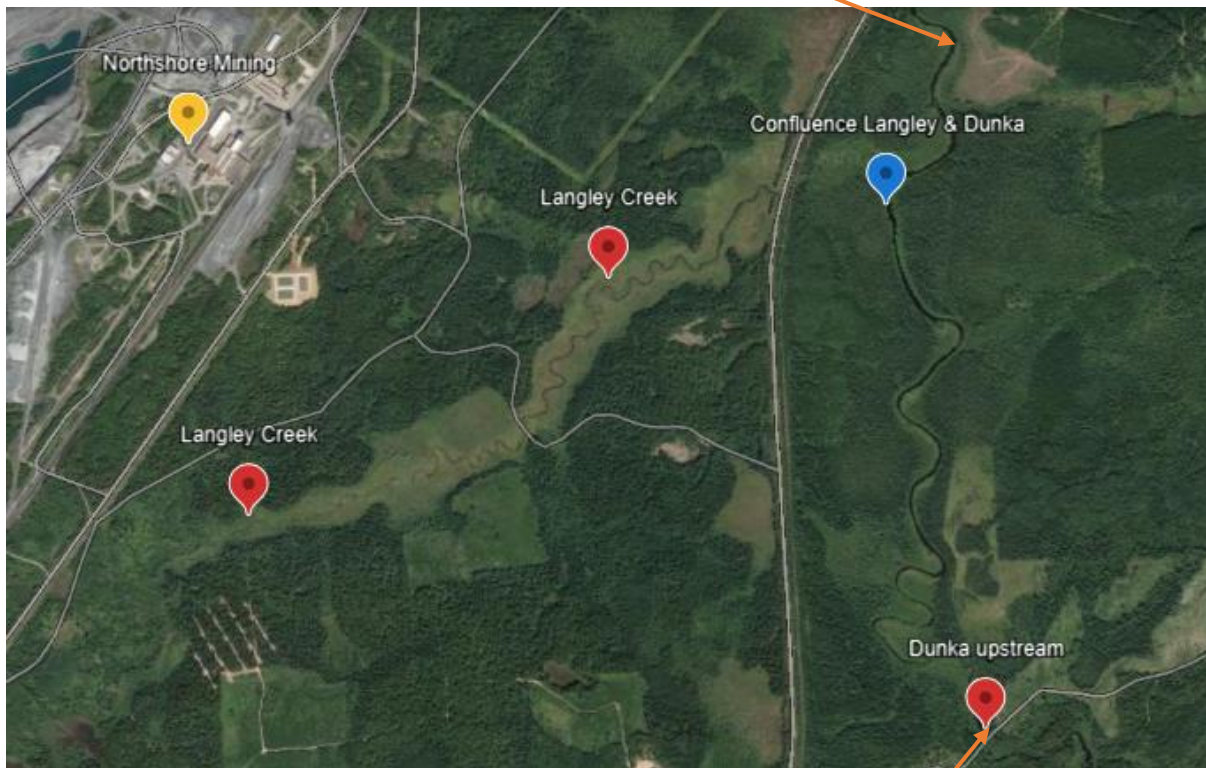
The following map from Google Earth shows the Dunka River from where it flows into Birch Lake at the top and, at the bottom, the upstream source. Sulfate concentrations in tests from December 2023 were 28 mg/L at the mouth of the river near Birch Lake. Concentrations increased upstream to 45 mg/L where the Dunka River goes under Scott Road. Further upstream, where the Dunka River goes under Forest Service Road 116, there is non-detect sulfate (defined as <3 mg/L by our test method). This sampling site

can be reached by going south off Scott Road on Dunka Lake Road #112, turning right onto #114 and continuing onto #116 to the bridge over the Dunka River where a gate blocks further access. This last is a sampling spot upstream of any mine pit water that is discharged into Dunka River or Langley Creek and shows essentially no sulfate.



These samplings of Dunka River clearly show that the sulfate in the river is coming into the river downstream of road #116 and upstream of Scott Road. This area is in close proximity to the Northshore Mining pit and crushing plant. The second Google map below shows where Langley Creek comes even closer to Northshore Mining and flows into the Dunka River. This is a likely place where sump water from Northshore Mining is pumped into Langley Creek and on into Dunka River.

Dunka downstream of Langley Creek – 45+ mg/L sulfate



Dunka River upstream of Langley Creek – 0 mg/L sulfate

This review explains what the point source of the elevated sulfate most likely is. This is important to determine the prospects for remediating the elevated sulfate in the river. It is much easier to reduce high levels of sulfate in low volumes of water than it is to reduce lower levels of sulfate in much larger flows. Treating the discharge flow of sump water from the Northshore mine pit can remove the sulfate before it goes into Langley Creek and Dunka River. This would effectively reduce the sulfate concentrations in Dunka River to well below the 10 mg/L wild rice standard. Within a short time Dunka River would recover enough so it could be removed from the Impaired Waters List for Sulfate.

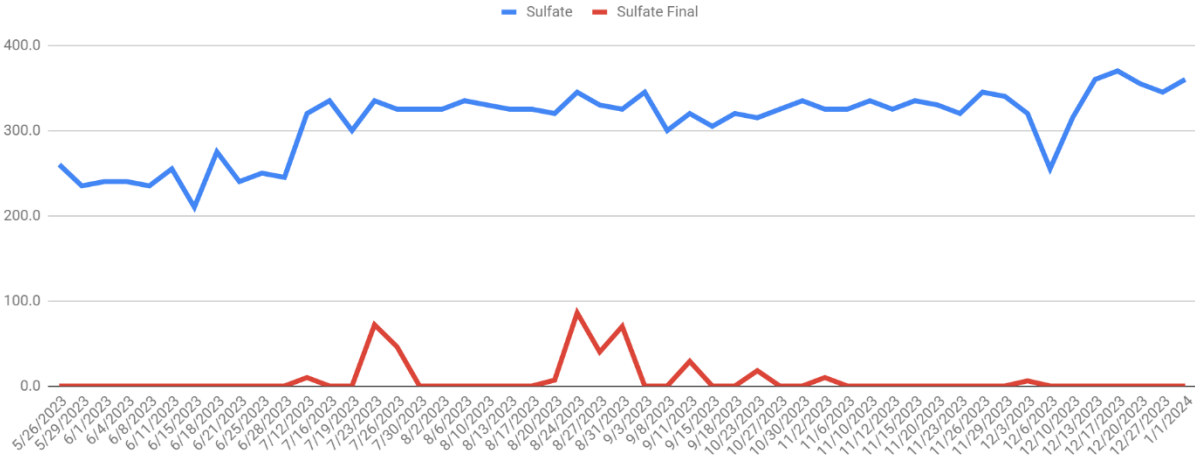
If the flow of sulfate coming into Birch Lake from Dunka River is reduced to less than 10 mg/L, The Birch Lake concentrations should also drop. Other sulfate inflows from the Dunka Pit Lake, via Unnamed Creek and Bob Bay, contribute additional sulfate loading to Birch Lake. But this sulfate source can also be treated with the Clearwater Biologic sulfate reduction system to reduce sulfate from the Dunka Pit Lake to well under the 10 mg/L wild rice standard. With both the Dunka River and Dunka Pit Lake water flows below 10 mg/L, there is little doubt that the sulfate concentrations in Birch Lake would drop below 10 mg/L over time. This would allow Birch Lake to recover from elevated sulfate and be removed from the Sulfate Impaired Waters List.

Recent Bench Scale Tests

Currently running bench scale tests at Clearwater BioLogic **continue** to demonstrate the effectiveness of the system. In early spring of 2023 tests were running with Spring Mine Creek water from Area 5 of the inactive Erie Mining pit lakes. This water had about 250 mg/L of sulfate, **the exact amount varying** depending on rain and snowmelt events. Sulfate concentrations were consistently reduced to below 3 mg/L.

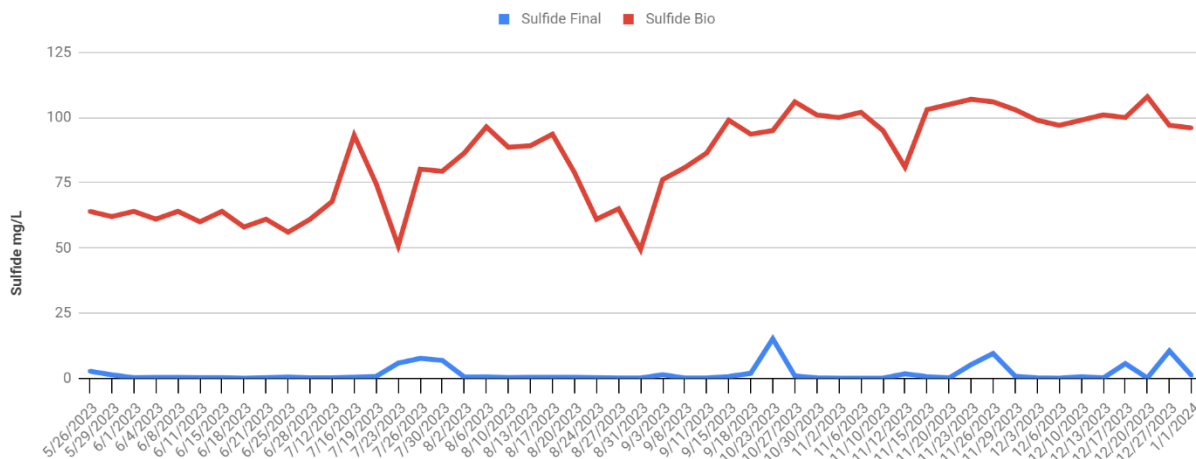
In July 2023 we switched to St James Mine Pit water from near Aurora. This water is more consistent and runs from 330 to 370 mg/L of sulfate. This increase in sulfate concentration in July and an increase in flow rate in August caused a temporary increase in final sulfate concentrations. Once the biological reduction of sulfate adapted to the increased sulfate concentration and an increase in flow rate, nearly 100% sulfate reduction rate to below 3 mg/L was again achieved. The graph below illustrates the actual test results from May 2023 to January 2024 with some early fluctuation due to the system adapting to increased sulfate concentration and an increase in flow rate.

Sulfate and Sulfate Final - May 2023 to January 2024



The biological reduction of sulfate produces hydrogen sulfide. Hydrogen sulfide is not an acceptable final result. The Clearwater BioLogic system treats this hydrogen sulfide by reacting it with reduced iron to produce insoluble iron sulfide. The system effectively eliminates the hydrogen sulfide. The sulfur is removed from the system as iron sulfide. Over 99% of the hydrogen sulfide was eliminated consistently throughout these tests. The graph below of actual bench scale results illustrates this hydrogen sulfide elimination.

Sulfide Control with Iron - May 2023 to January 2024



These current and continuing test results confirm the effectiveness of removing sulfate in mining impacted water to well below the 10 mg/L wild rice standard. This system is applicable to low sulfate concentrations up to concentrations well over 1,000 mg/L. And because it is a modular system, it is scalable to any flow necessary. Once the point sources of sulfate entering the Dunka River and Birch Lake are identified and quantified, a system can be designed and installed to effectively eliminate this sulfate.

Previous Field Tests and Cost Estimates

The previous field tests conducted from 2012 to 2017 are highlighted on the Clearwater Biologic website <http://www.ClearwaterBioLogic.com>. The full report of these tests can be seen in the NRRI report at the following link.

<https://clearwaterbiologic.com/wp-content/uploads/2021/10/TR-2017-17.pdf>

This report confirmed in field tests that 90% of sulfate that started at over 1,000 mg/L was regularly reduced and that sulfate reduction varied from 60 to 100%, with 100% reduction being achieved even in winter.

The report further confirmed that the generated hydrogen sulfide was eliminated chemically. But the system of hydrogen sulfide was complicated and had an estimated cost of \$12.50/ 1,000 gallons for chemical reagents. This cost accounted for the major portion of overall system costs.

With the more recent developments of the Clearwater BioLogic system using reactive iron for hydrogen sulfide elimination, the overall costs have been significantly reduced. Actual costs can vary significantly due to sulfate concentration, system water flow, and other factors. But current test results have provided cost estimates for the complete system of less than \$4.50 down to under \$1.00 per 1,000 gallons. In general, higher sulfate concentrations and lower flow tend to have lower costs per gallon treated or cost per pound of sulfur removed. Accurate cost estimates must be calculated on a site-specific basis. This is possible for almost any level of sulfate concentration and flow rate.