Treatment of Mining-Impacted Waters Using Biological Sulfate Reduction and Direct Reduced Iron Pellets

ClearWater BioLogic

SULFATE SOLUTIONS
FOLLOWING NATURES LEAD

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Why Sulfate Pollution Matters

Potable Water Quality & Health

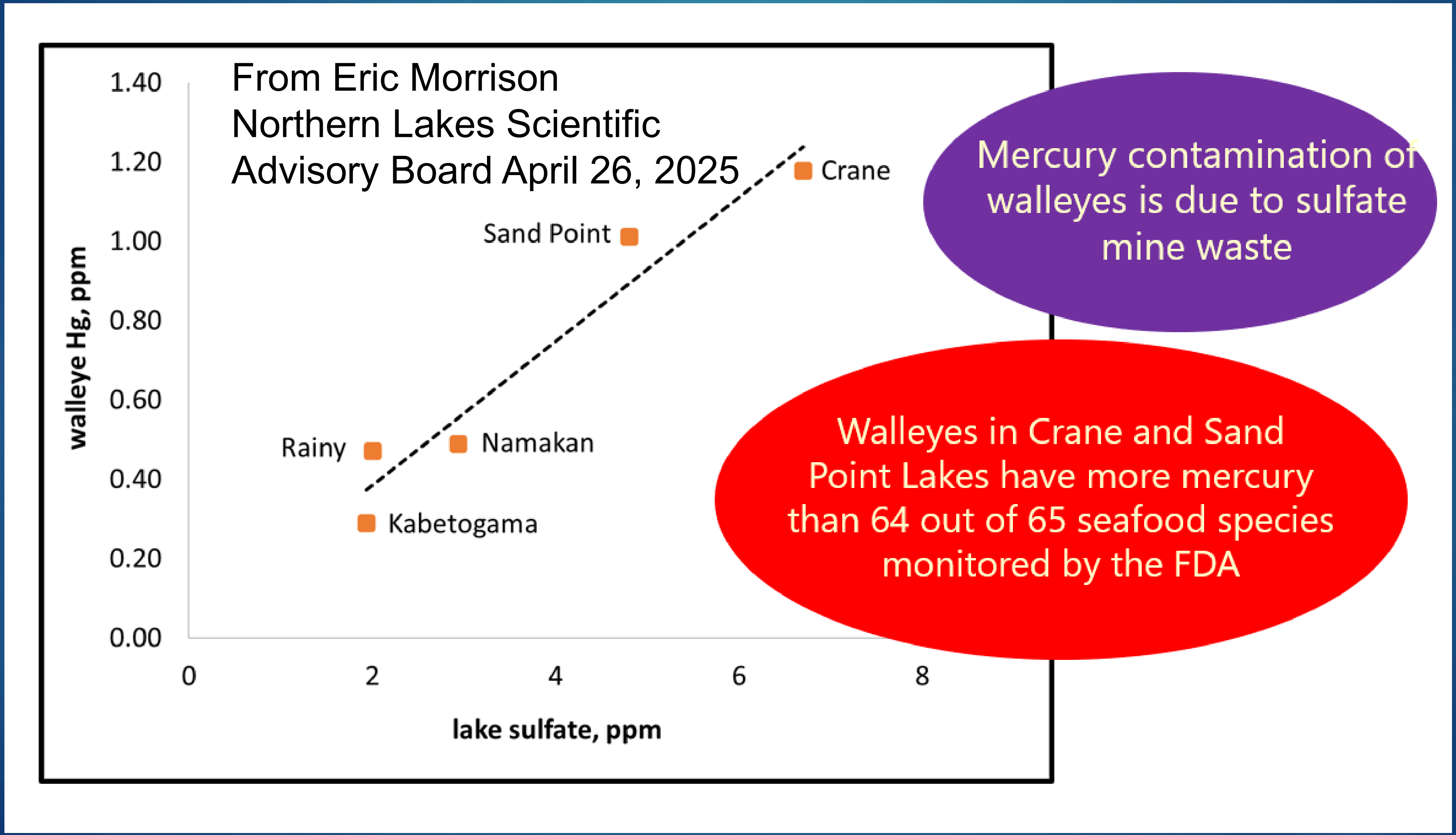
- Unpleasant taste and corrosion.
- High concentrations can act as a laxative and cause dehydration.
- The secondary standard is 250 mg/L. Mining impacted waters often have much higher concentrations.

Why Sulfate Pollution Matters

Environmental Impacts To Surface Waters

- Sulfate in anoxic sediments is an electron acceptor that stimulates the biodegradation of organic matter.
- Biodegradation of organic matter releases sequestered toxic metals, nitrogen, phosphorus and TOC into our wetlands, lakes and streams.
- Sulfate reduction to sulfide stimulates methylation of mercury. Methyl mercury bioaccumulates in fish.
- Sulfate reduction to sulfide harms wild rice. The Minnesota Wild Rice Standard is 10 mg/L.

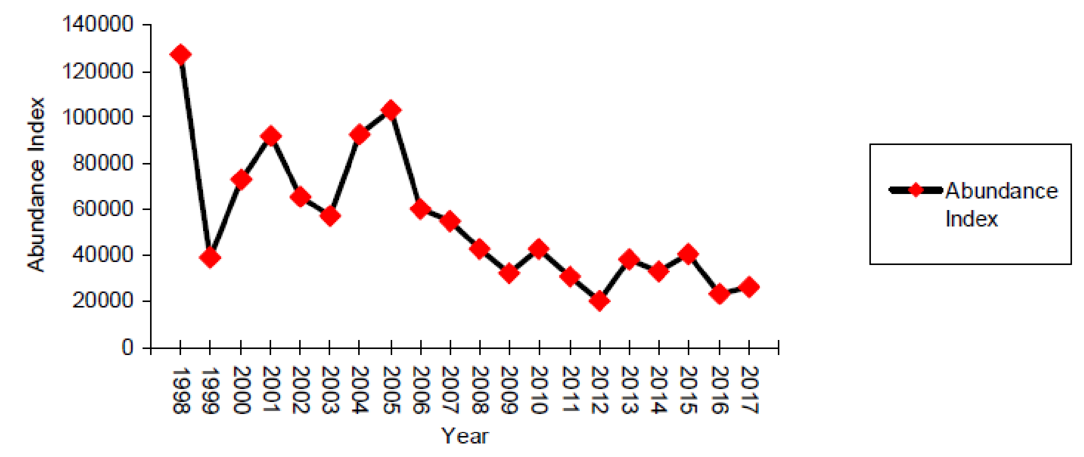
Sulfate Concentrations Correlated With Elevated Methyl Mercury



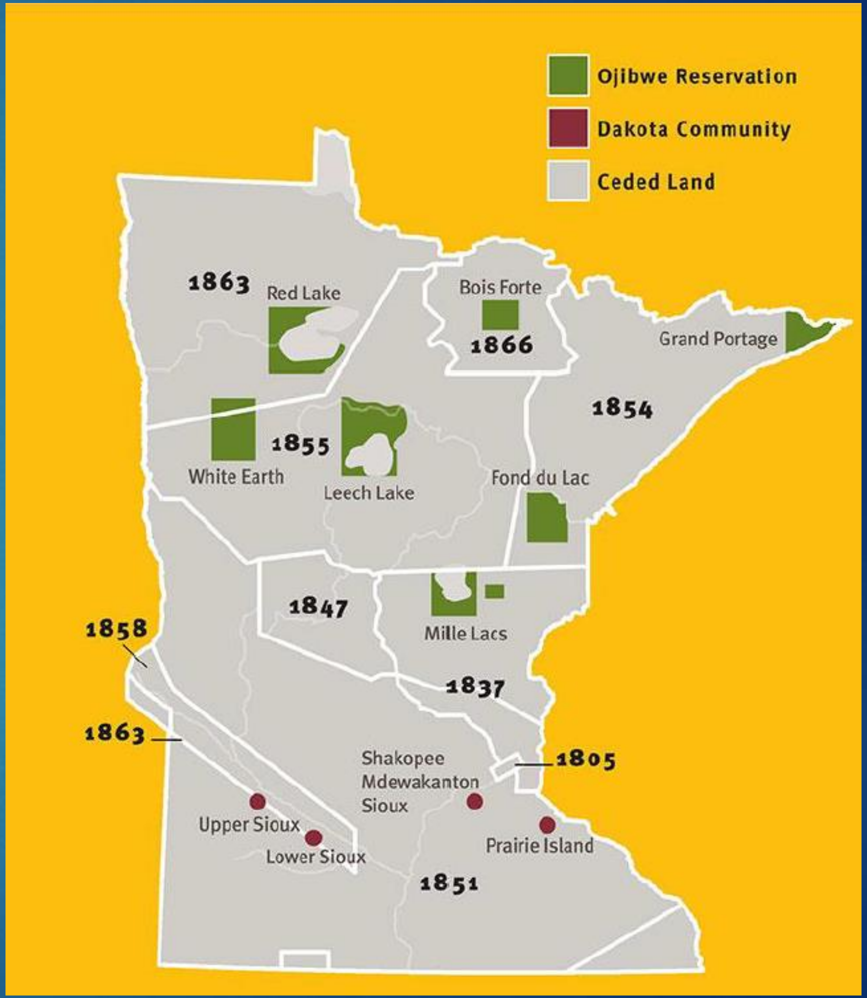
The Cultural Significance of Wild Rice

"You will know the chosen ground has been reached when you come to a land where food grows out of the water."

SEVEN FIRES PROPHECY



Total Abundance Index on all Waters in 1854 Treaty Authority Monitoring Program (1998-2017)



Figures from the 2018 Tribal Wild Rice Task Force

High Sulfate Concentrations Downstream of Taconite Mining Facilities

The 2018 Tribal Wild Rice Task Force identified the sixteen largest sulfate sources affecting wild rice waters.

Two were coal fired power plants the other fourteen are mining operations.

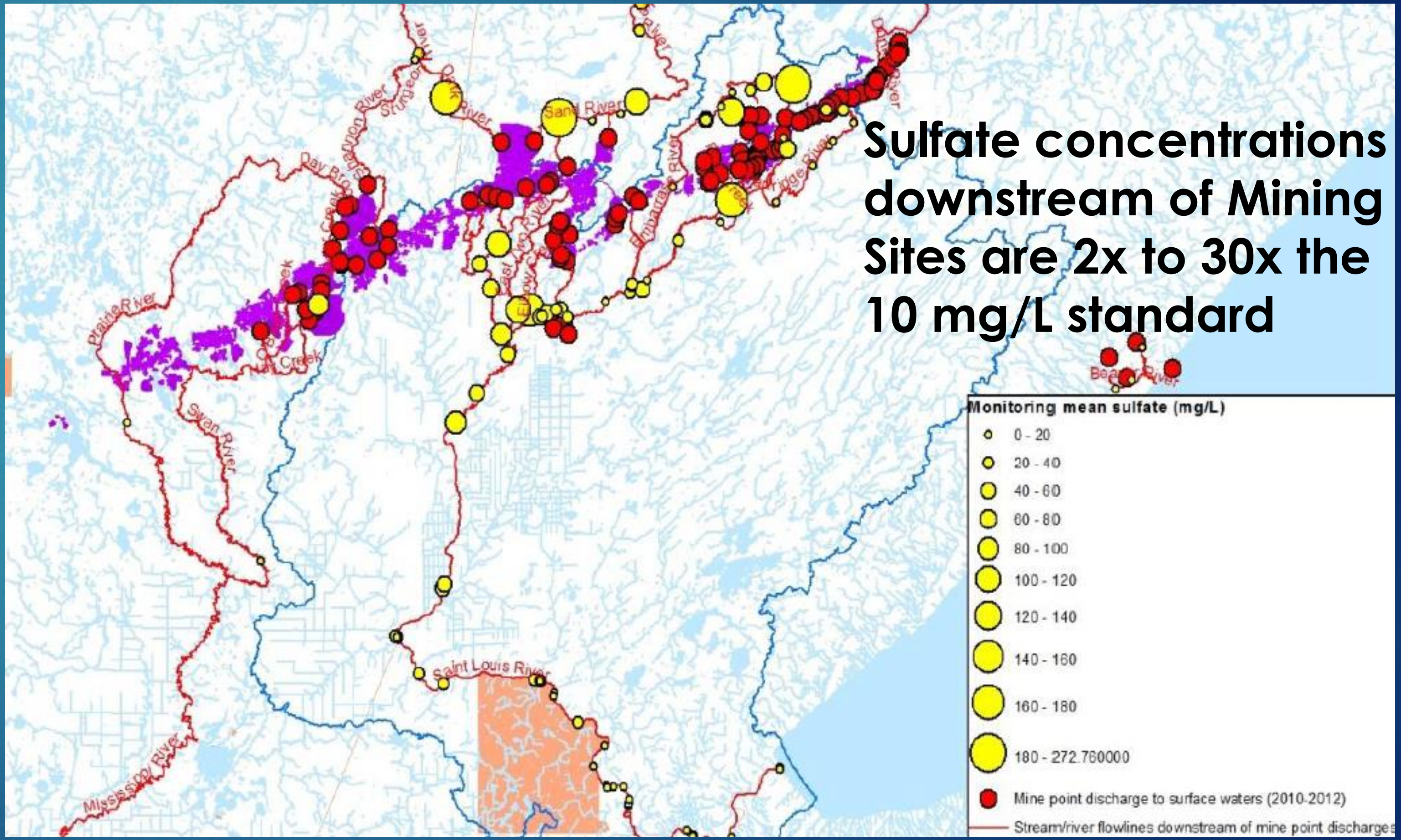
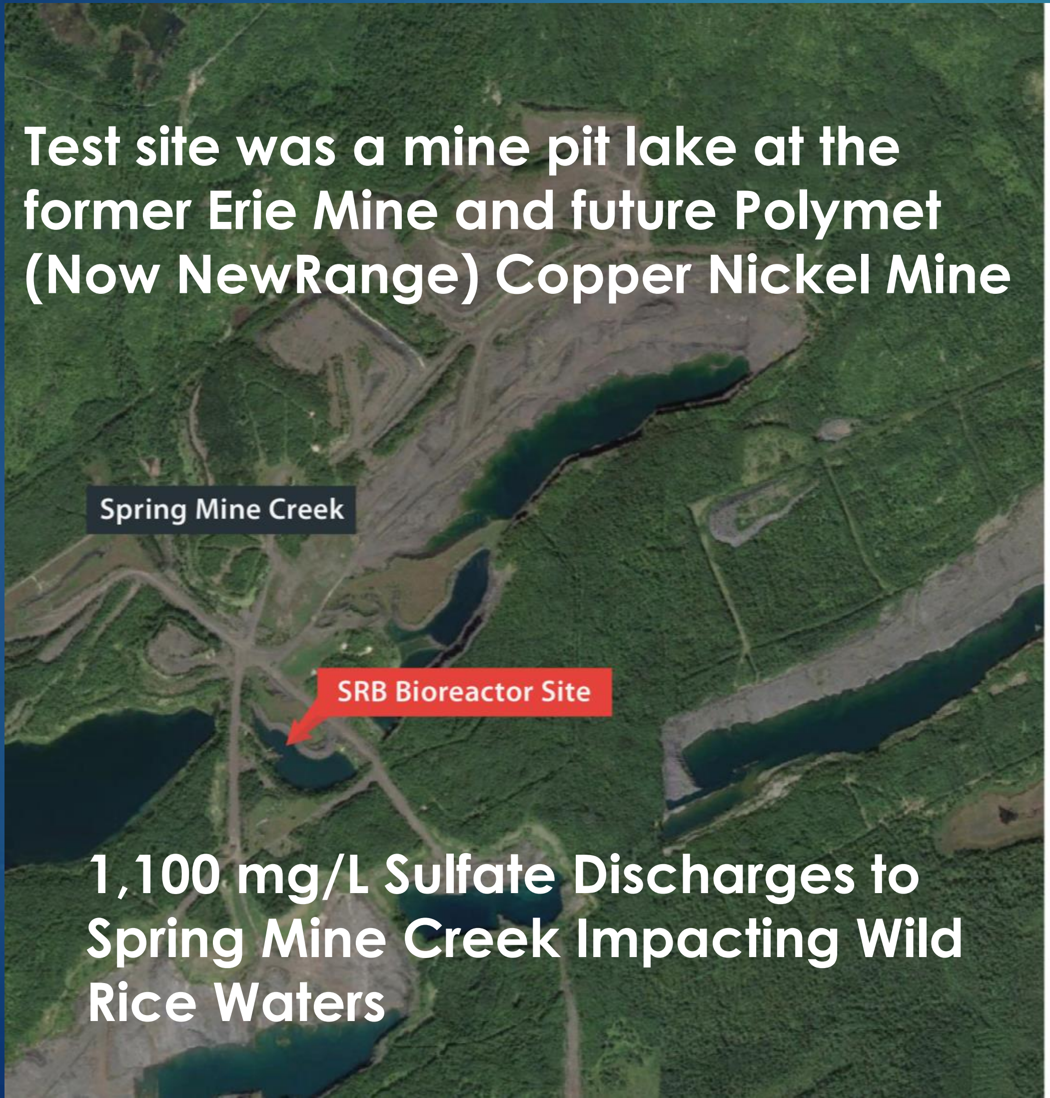
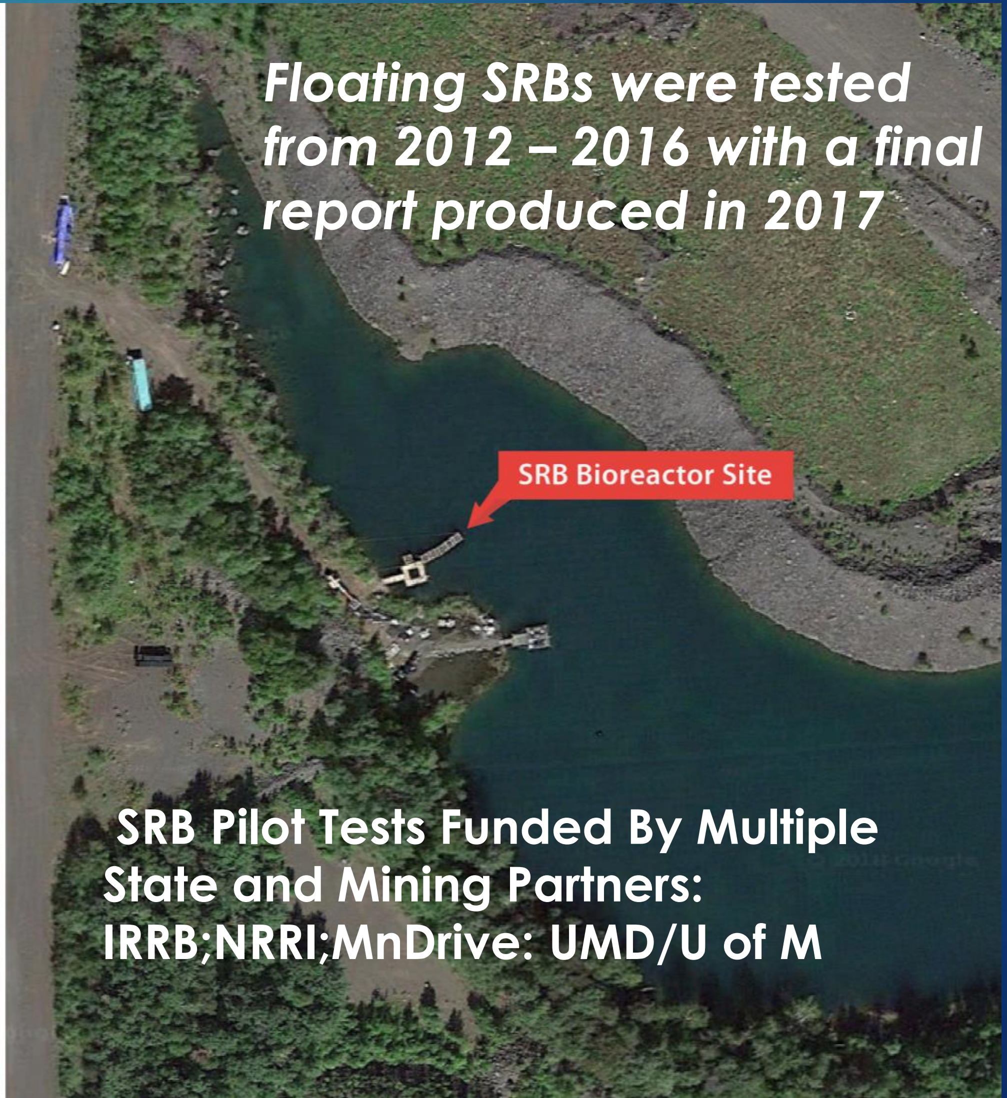


Figure from the 2018 Tribal Wild Rice Task Force

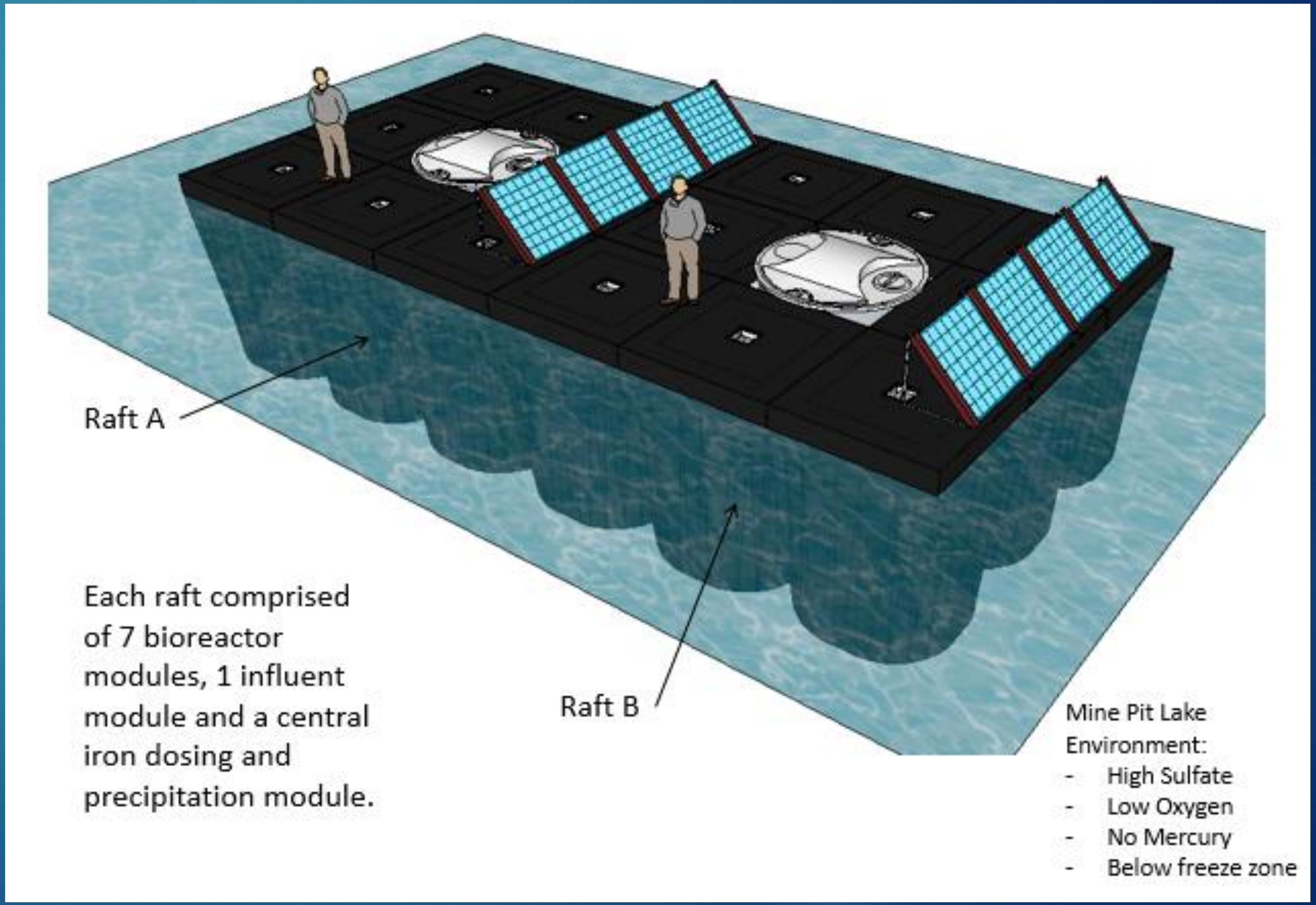
Area 5 Floating Sulfate Reducing Bioreactor (SRB) Pilot Tests





Modular Floating SRB Systems

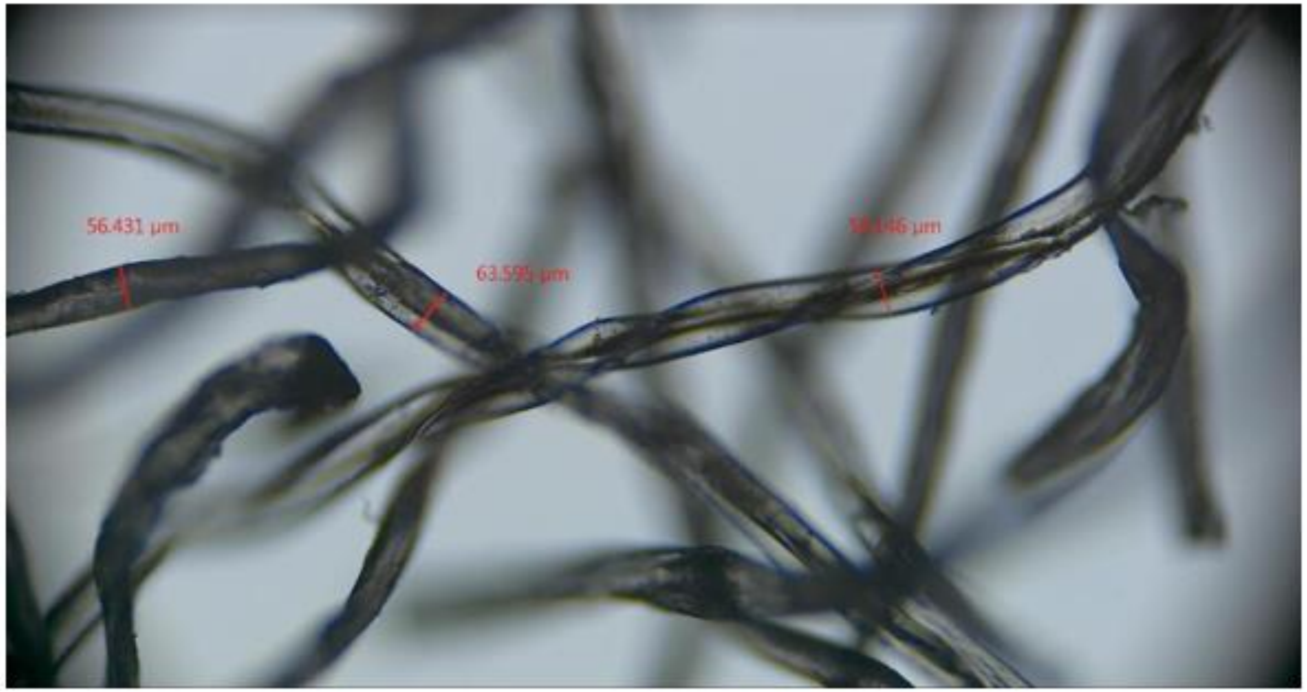
Flexible 4,000 Gallon Floating Modules
Filled With Fiber Attachment Media



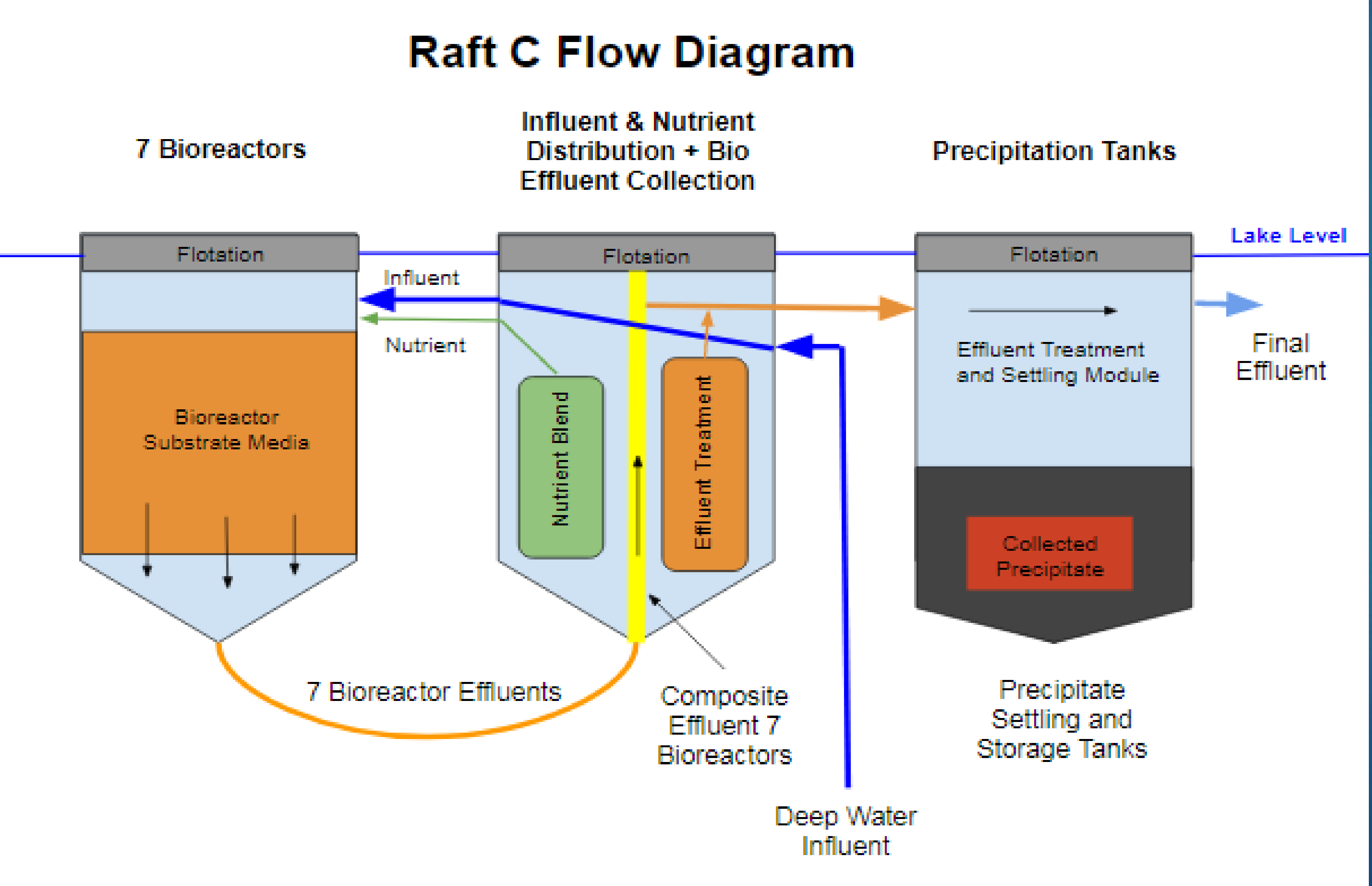
Low Cost High Surface Area Fiber Media Supports Sulfide Reducing Bacteria

SRB Attachment Surface Area

- Gravel bed 149 M^2/M^3 <50% void volume
- Large bio-carriers 100 M^2/M^3 ~95% void volume
- Mini bio-carriers 500 M^2/M^3 ~90% void volume
- Clearwater fibers 7,000 M^2/M^3 >90% void volume
- <10% cost on volume and 0.7% on area of mini bio-carriers



Area 5 Bioreactor Raft C



- Seven modules in the raft with effluent flows to a chemical treatment module and precipitation settling module.
- Buoyant polypropylene fiber media with downflow allows beds to expand to prevent biofouling.
- Taconite pellets for ballast in the cone bottom.

Floating SRBs Allow for Year-Round Operation in any Weather

Floating Bioreactors Operated Continuously in Winter From 2013 – 2014 Temperatures as low as -40 Celsius

Summer Operation – Some hoses damaged by beaver and muskrats. Bear scat on one raft !

Summary of Four Years of MnDrive Area 5 Pilot Testing

- Modular System Effective Year-Round for over 4 years
- 90%+ Sulfate Reduction achieved regularly
- Up To 100% Sulfate Removal Even in Winter
- Methyl Mercury Production Insignificant
- Needed further work for consistent sulfate reduction
- Needed more cost-effective hydrogen sulfide treatment

Improvements Developed By Clearwater BioLogic Since 2018

Better Electron Donor Feed Needed: *Area 5 Bioreactors used a pulsed ethanol electron donor feed which resulted in variable effluent quality.*

Electron Donor Feed Improvement: A more continuous feed of a glycerin ethanol blend provides consistent effluent quality, ND sulfate (< 3 mg/L). The low-cost electron donor blend stays liquid even at -75 Celsius which allows outside storage in any weather.

The Clearwater BioLogic floating modular bioreactor system was patented under US-10.597.318-B2 and US-11.104.596.

Improvements Developed By Clearwater BioLogic Since 2018

Cost Effective Sulfide Treatment Needed: NRRI and UMD/U of M treated effluent sulfide with Ferric Chloride to create an iron sulfide precipitate. The ferric chloride treatment added more than 1000 mg/L chloride to the effluent! They also implemented partial oxidation to elemental sulfur using pH adjustment and hydrogen peroxide. Both treatment methods were effective but expensive.

Cost Effective Sulfide Treatment Solution: Two Direct Reduced Iron (DRI) sulfide treatment methods were tested. A DRI electrode system creates iron cations without adding undesired chloride and produces iron sulfide precipitates. The second method adsorbs sulfur onto the DRI surfaces.

Both DRI treatment methods are patent pending

Direct Reduced Iron Pellets – DRI

What is a DRI pellet?

Hematite or magnetite iron ore is reduced with hydrogen gas and/or carbon monoxide to form sponge iron pellets.

- **Used in electric arc furnace steel mills – DRI pellets conduct electricity.**
- **Greater than 97% iron content.**
- **One third of square meter of reactive surface area per gram.**
- **Low cost – About $200/ton.**

Proof of Concept Bench Testing – DRI Pellet Electrodes

- Jar test with DRI anode and cathode made from DRI pellets in plastic mesh tubes.
- Bioreactor effluent with 40 mg/L HS^- reduced to less than 1 mg/L
- Iron Sulfide precipitate observed at the sacrificial anode.
- Small amounts of hydrogen gas generated at the anode.

Clearwater Biologic Column Tests

Nutrient drip feed

Bioreactor A

Nutrient Infusion Pump

Bioreactor B

DRI Column 1

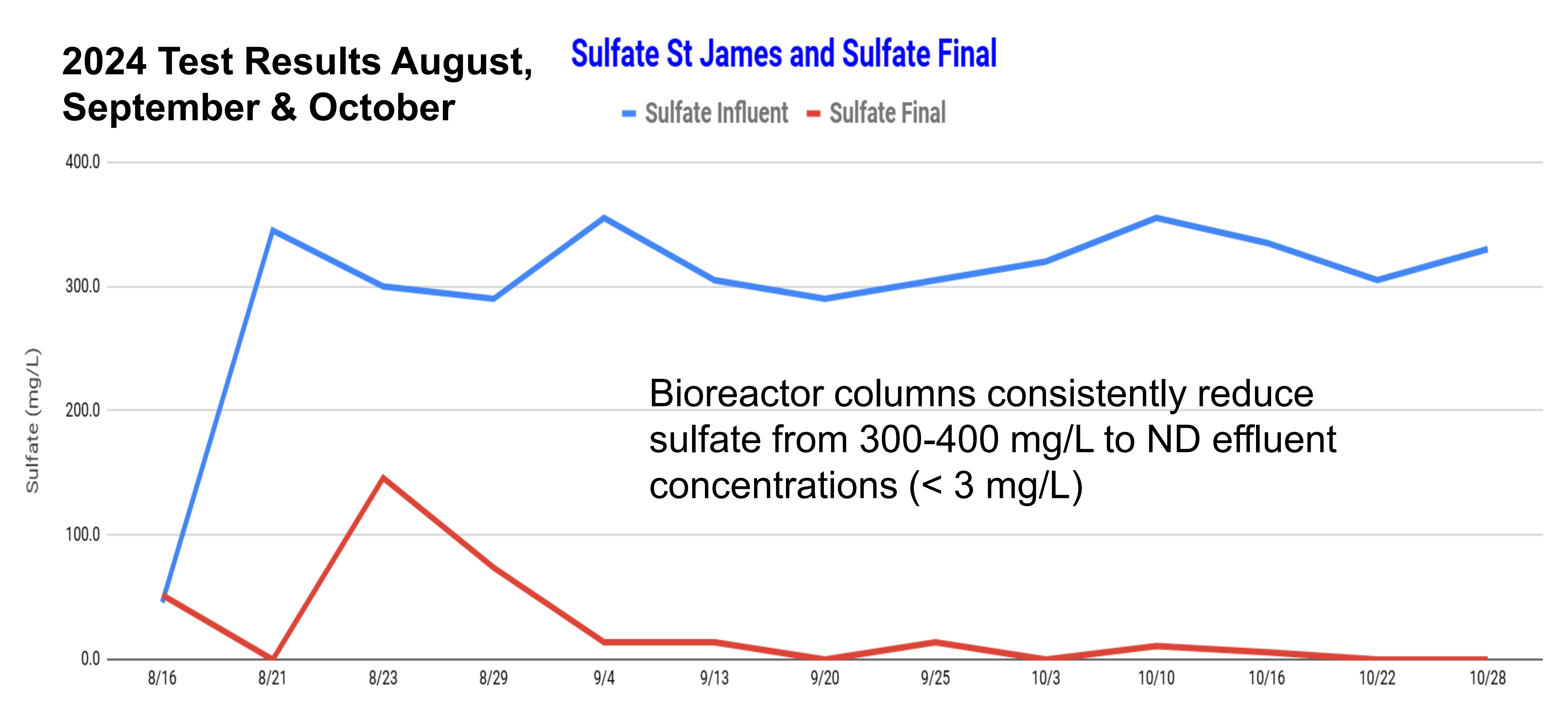
Electrode Tank

DRI Column 2

Influent Water & Nutrient Injection

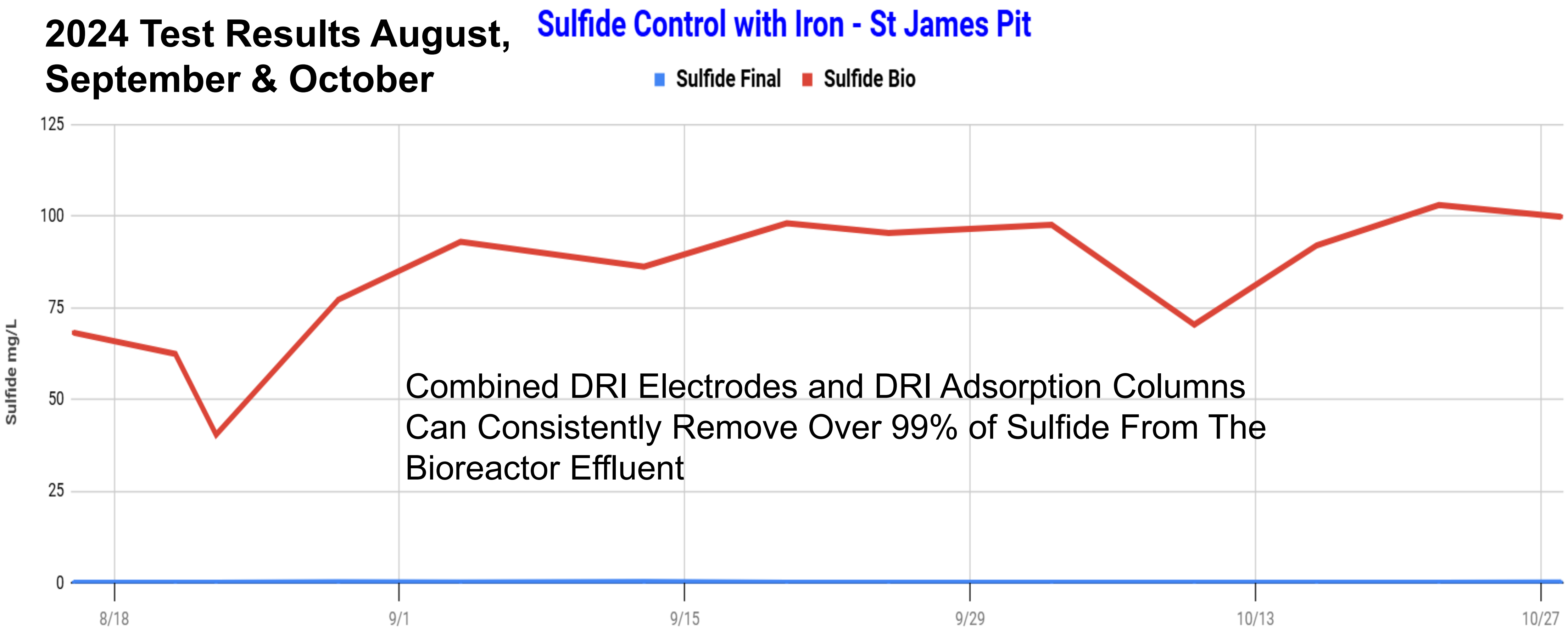
Influent Pump

Column Tests With Fiber SRBs Plus DRI Sulfide Treatment



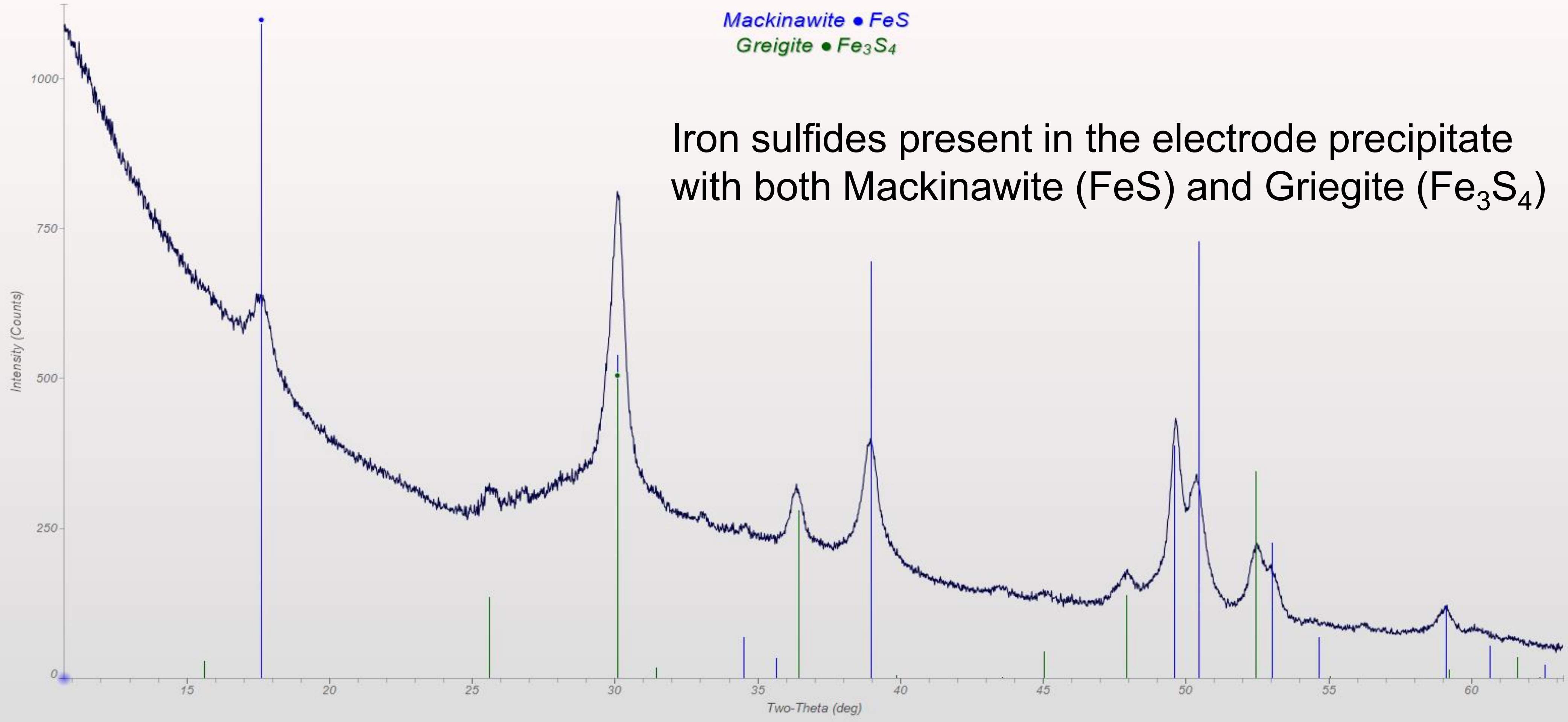
Column Tests With Fiber SRBs Plus DRI Sulfide Treatment

2024 Test Results August, September & October



Combined DRI Electrodes and DRI Adsorption Columns Can Consistently Remove Over 99% of Sulfide From The Bioreactor Effluent

Qualitative Analysis of Electrode Precipitate XRF – Characterization Facility, UMN



Iron sulfides present in the electrode precipitate with both Mackinawite (FeS) and Griegite (Fe_3S_4)

Treatment Lab and Field Test Results

- Area 5 field tests confirmed year-round operation in northern Minnesota. Sulfate concentrations of 1,100 mg/L or higher were at times reduced to less than the 10 mg/L wild rice standard in the floating SRBs.

- Column studies with the improved electron donor feed was tested water from three mining impacted sites with sulfate concentrations ranging from 25 mg/L to over 700 mg/L. The SRB columns consistently reduced sulfate concentrations to non-detect (< 3 mg/L).

- Effluent from the bioreactor columns was treated using a combination of DRI electrodes and DRI adsorption columns consistently reducing sulfide to less than 1 mg/L.

- Minimal change in pH effluent, no increase in TDS or specific conductance – in some cases a reduction in TDS and specific conductance via electrocoagulation is possible.

Next Steps for Scaleup and Deployment

The Clearwater BioLogic mobile pilot test trailer can be operated off solar power at remote mining impacted water locations. The treatment capacity is one seventh of the 4,000-gallon modules used at Area 5. Two fiber filled SRB tanks test biological sulfate reduction. DRI electrodes and DRI adsorption columns test sulfide removal. A field lab and office space is located in the front of the trailer.

Pilot Test Trailer Opportunities

- **Maximum Bioreactor Flow Rates:** Determine maximum flow rates that can achieve a less than 10 mg/L sulfate effluent.

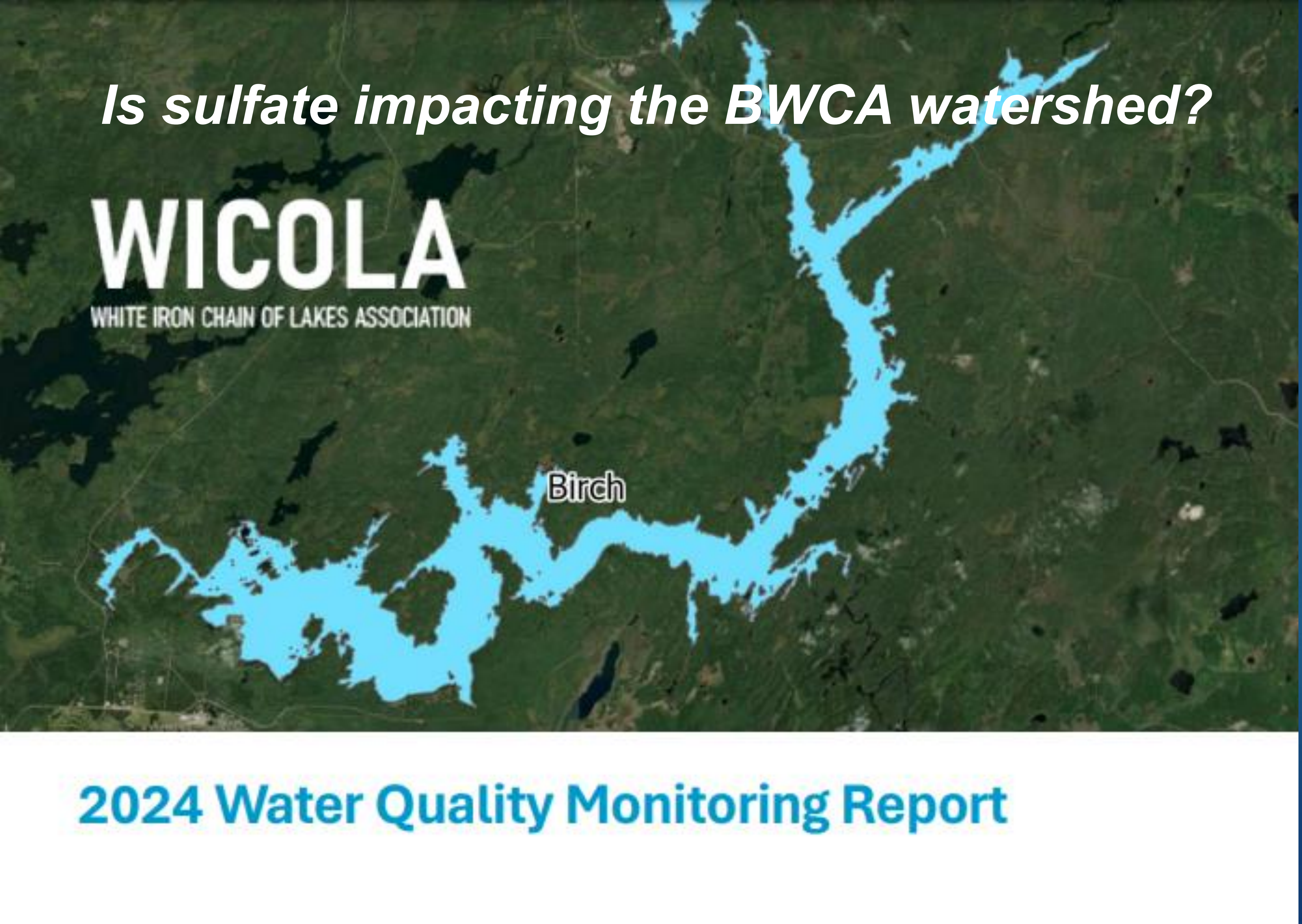
- **Minimize Electron Donor Costs:** Determine electron donor needs and optimal N&P nutrients.

- **Maximum DRI Treatment Flow Rates:** Optimize sulfide treatment in the electrode tanks and DRI adsorption columns.

- **DRI Electrode Parameters:** Determine optimal voltage and current and estimate power needs.

- **Evaluate Effluent Quality:** Determine final effluent quality sulfate concentrations, specific conductance, pH, TDS and hardness.

Is sulfate impacting the BWCA watershed?



DRAFT
2024
Houston
Engineering

Sulfate Already Impacts the BWCA Watershed

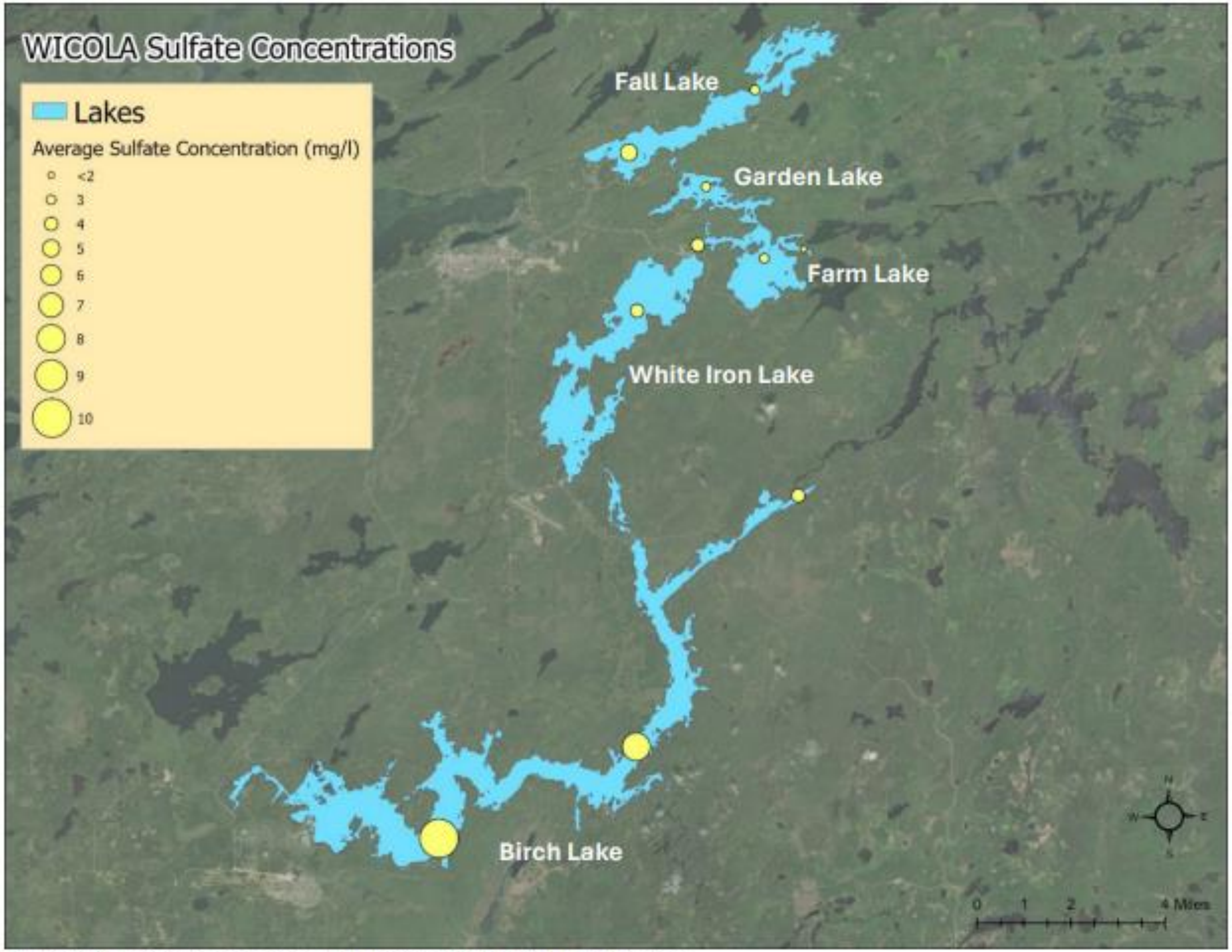


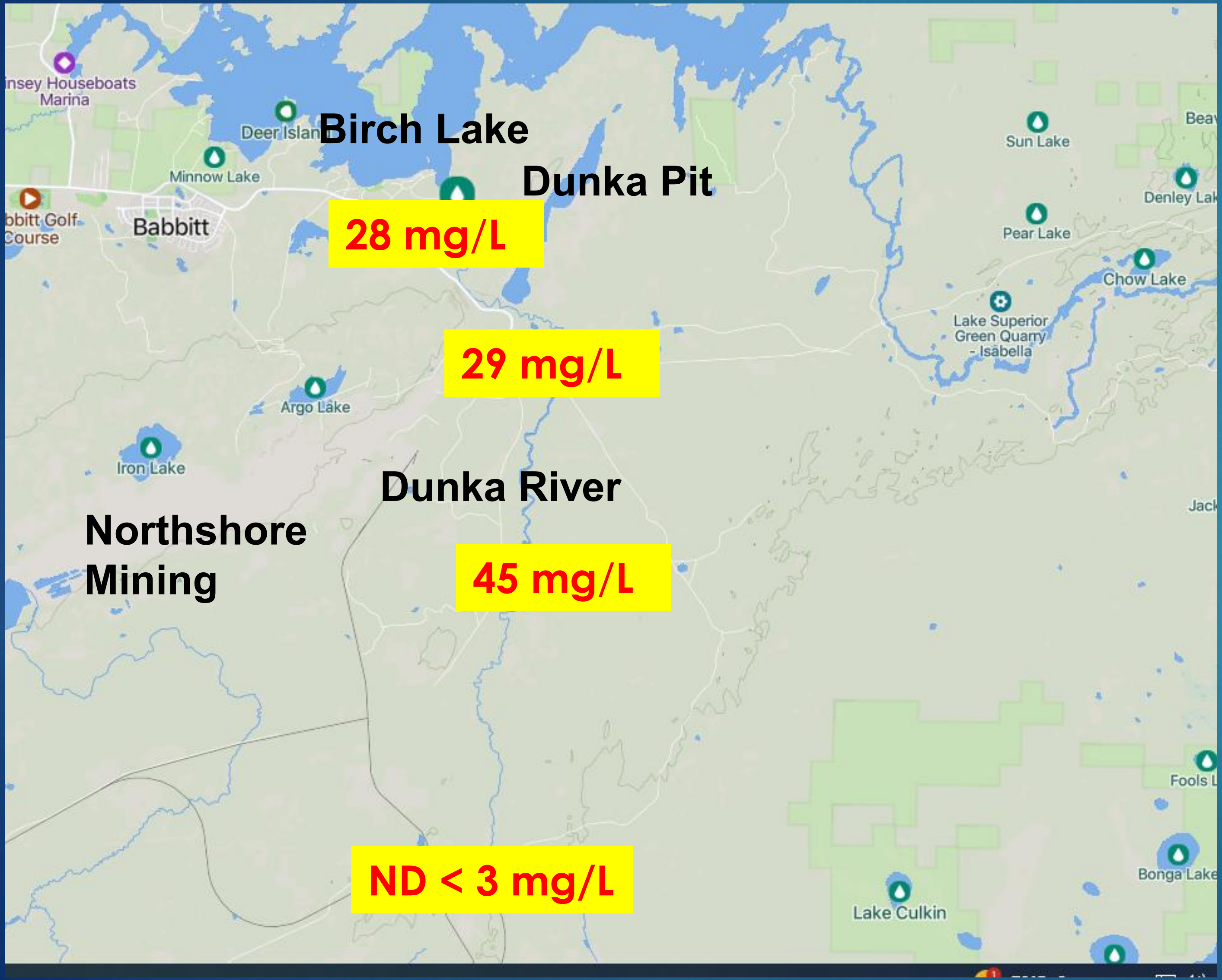
Figure 30. Average sulfate concentrations from WICOLA sampling locations.

Birch Lake - Impaired waters from Elevated Sulfate

Birch and the White Iron Chain Of Lakes contribute one third of the water flow through the BWCA

Mining impacted waters are the primary source of sulfate.

Clearwater BioLogic Dunka River Sulfate Data



Background sulfate in the Dunka River is non-detect less than 3 mg/L.

It peaks at 45 mg/L just downstream of mining discharges from Northshore Mining and the Dunka Pit.

Water entering Birch Lake from the Dunka River contains 28 mg/L of sulfate.

WICOLA LCCMR Proposal

2026-424 Restoring Wild Rice Waters: Sulfate and Mercury Treatment$727,000
White Iron Chain of Lakes Association Dave Holt

WICOLA is the lead organization for this grant. Clearwater BioLogic and Bay West will operate the Clearwater BioLogic pilot test trailer for 12 months at a site within the Dunka River watershed. All data will be made public. We will welcome the public for tours of the system and to learn about the technology.

Electron Donor Needs

Hydrogen Production and Hydrogen Demand

Electron Donor	Hydrogen Production	Kilos H_2/Kilo
Ethanol	$C_2H_6O + 5\ H_2O \rightarrow 2\ HCO_3^- + 2\ H^+ + 6\ H_2$	0.261
Methanol	$CH_4O + 2\ H_2O \rightarrow HCO_3^- + H^+ + 3\ H_2$	0.188
Glycerol	$C_3H_5(OH)_3 + 6\ H_2O \rightarrow 3HCO_3^- + 3H^+ + 7\ H_2$	0.152
QR90	55% glycerol and 34.3 % SDA-3C	0.17

Electron Acceptor	Stoichiometric Hydrogen Demand	Kilos H_2/Kilo
Sulfate	$H^+ + 4\ H_2 + SO_4^{2-} \rightarrow HS^- + 2H_2O$	0.0833
Dissolved Oxygen	$2\ H_2 + O_2 \rightarrow 2H_2O$	0.125

Electron Donor Costs

In the SRB columns we fed 3x to 4x of the calculated stoichiometric hydrogen demand. **We expect to reduce this to 3x or less for full scale treatment.**

Ethanol SDA-3C $1.99/pound of molecular hydrogen based on the bulk tanker load cost of $0.52/pound.

Crude glycerin (80% glycerin typical) $1.64-$2.88/pound of hydrogen based on bulk tanker load costs $0.20-$0.35/pound.

Electron Donor Cost To Reduce 1000 Kilos of Sulfate to Sulfide

Stoichiometric Hydrogen Demand is 83.3 kilos of molecular hydrogen – 318 kilos of SDA-3C ethanol.

2x Hydrogen Demand Costs $732 for SDA-3C ethanol

3x Hydrogen Demand Costs $1098 for SDA-3C ethanol.

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DRI Needed To Remove Sulfide Produced By 1000 Kilos of Sulfate Using Electrodes

DRI Sacrificial Anode $HS^- + 2e^- + Fe^{2+} \rightarrow FeS$

- At 100% Efficiency - 581 Kilos of DRI converted to Fe^{2+}
- DRI Cost $116 based on $200/metric ton
- Electric Costs: 558 Kilowatt Hours $33.50-$55.80

(Solar Power $0.06-$0.10/KWH)

DRI Needs To Remove Sulfide Produced By 1000 Kilos of Sulfate by Adsorption

HS^{-} + Fe → FeS Surface → Sulfidized Iron

- DRI Cost: $3,269 for DRI adsorption alone.
- DRI and Power: Only $488 if we remove 90% sulfide by electrodes and 10% by DRI adsorption total
- At 2% S We make 1669 kilos of sulfidized iron pellets based on 10% of the sulfide removed by adsorption and 90% by electrodes

FeS Electrode Precipitates Have Value

Redox Technology LLC sells FeS (Mackinawite) based products for treating mercury and other toxic metals. Ferroblack product sells for $2.25/kilo ($22.50/kilo of FeS solids).

Our electrode precipitate is FeS and other iron sulfides. If our FeS solids sold at just $2.25/kilo this could yield over $1,850 in revenue for each 1000 kilos of sulfate.

Sulfidized DRI Pellets Have Value

- Sulfidized Zero valent iron (ZVI) products are sold for groundwater remediation. Sulfidized ZVI is reactive for long periods of time unlike ZVI.
- Our sulfidized DRI pellets may be more valuable than DRI. They could be used for groundwater PRBs or above ground water treatment.
- Sulfidized DRI pellets could be used to adsorb both organic contaminants and toxic metals in sediments. Reductive dechlorination of TCDDs, and PCBs *in situ* is possible.

Example Project Cost Estimates

Keetac sulfate permit compliance costs estimated by Barr Engineering for four RO based systems. 600-800 million dollars capital cost. Flow capacity totals 13,000 gpm. Operating costs 105 million per year.

Sulfate mass removal expectations for the proposed Keetac RO based systems are not defined. At the 13,000 gpm design capacity and a concentration of 100 mg/L sulfate – up to 2,586 metric tons per year of sulfate removed. At an operating cost of 105 million dollars per year $40,603 per metric ton of sulfate removed.

The Clearwater BioLogic bioreactor and DRI System Capital Costs are $3,000-$5000 per module (10-30 gpm flow capacity expected). Capital cost 2-6 million dollars. Operating costs scale to sulfate mass removed. For electron donor, DRI, power, labor, and an operating margin the total treatment costs should be **less than $2000 per metric ton of sulfate removed** not including sales of byproducts.

Conclusions

- Treatment costs and energy inputs are much lower than reverse osmosis.
- The bioreactor fiber media comes from reclaimed carpet fiber. Low cost and less waste going to landfills.
- The systems can operate on green energy, crop derived electron donor and potentially green DRI made from green energy and hydrogen.
- No harmful chemicals added in the treatment process. Only DRI, electron donor and DC current required for treatment.
- We believe the iron sulfide precipitate and sulfidated DRI pellets may have commercial value.

Questions?

ClearWater BioLogic

SULFATE SOLUTIONS
FOLLOWING NATURES LEAD

Delivering a Triple Bottom Line:

- ***Good for mining and business***
- ***Good for jobs and culture***
- ***Good for the Environment***