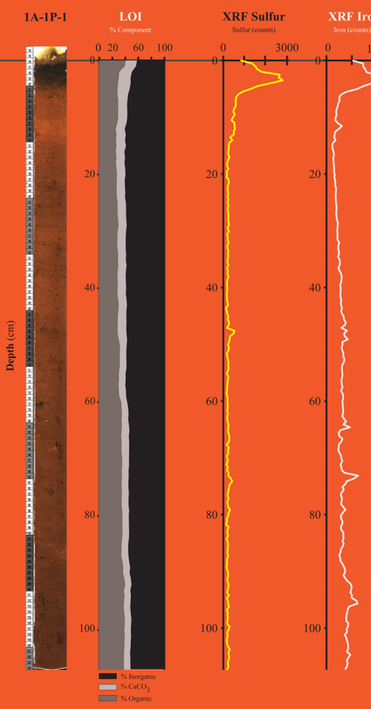
RECONSTRUCTING PAST SULFUR LOADING IN LITTLE SANDY LAKE, A WILD RICE LAKE IN NORTHERN MINNESOTA

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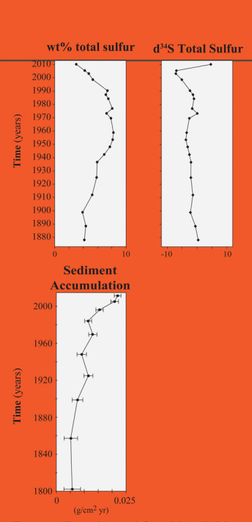


Figure 1: (Top to bottom, left to right): Weight percent and $d^{34}S$ total sulfur data from stable isotope ratio mass spectrometer at Gilhooly Lab (IUPUI). Lead-210 dating and sediment accumulation data from St. Croix Watershed Research Station (SCWRS).



Figure 2: Coring Site 1A



Figure 3: Coring Site 1A. First observations of core sediments. Water depth 110 cm.



Figure 4: Coring Site 2: Just a few feet from shore. Water depth 42 cm.



Figure 5: Coring Site 3: Setting up the coring equipment. Water depth 85 cm.

ABSTRACT: Iron mining has increased dissolved sulfate concentrations in northern Minnesota waterways throughout the 20th century and the proposed copper-nickel mining ("sulfide mining") in the Duluth Complex may release additional sulfate to the surrounding lakes and rivers. This potential pollution is of concern because of the risks to wild rice (Zizania sp.), which is a sacred plant to the Ojibwe and the state grain of Minnesota. Wild rice is observed to grow poorly in waters with sulfate levels above 10 mg/L, which is the legal standard for Minnesota wild rice water bodies. Little Sandy Lake, located in St. Louis County near Virginia, Minnesota, lies approximately one mile downstream from a taconite tailings basin that was constructed in 1966. Sediment cores were extracted from Little Sandy Lake to determine whether the lake has been impacted by mining activity. The tops of the three surface cores showed a 5-10 cm layer of black sediment, which is an indicator of the presence of iron sulfide compounds. The cores were analyzed for sulfur counts using scanning x-ray fluorescence (XRF) and dated using lead-210 (^{210}Pb) radiometric dating. The data show that there is a significant increase in sulfur levels after the 1960's, following hundreds of years of very low sulfur levels. Current water sample data show sulfate values in Little Sandy Lake are 80-200 mg/L, down from 300-400 mg/L and even higher levels in the past. Sulfur geochemical data are being used to understand historical sulfur inputs to the lake and the effects of land use changes on wild rice abundance. Sediment accumulation data show earlier periods of erosion in Little Sandy Lake, possibly related to other anthropogenic activities such as logging. The sedimentology of a near shore core shows that lake level has recently increased, but this event cannot be dated directly. The increases in lake level could have contributed to the decline of wild rice, as wild rice grows in shallow waters. Beaver damming of the lake's outlet stream may have been the cause of the water level rise.

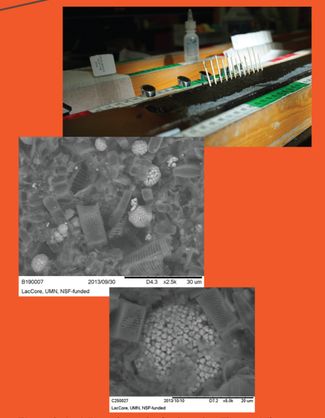


Figure 8: (top) Preparing stubs for Scanning Electron Microscope (SEM) imaging. SEM image of pyrite from core 1A-1P-1 at 19 cm (middle) and at 25 cm (bottom). There was an abundance of pyrite found within this depth range.

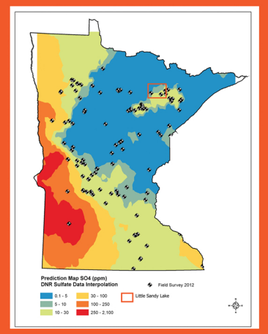


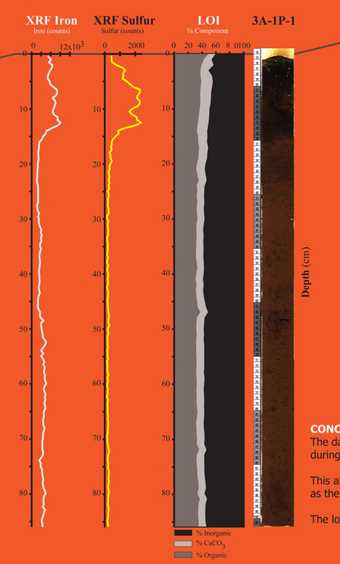
Figure 6: Surface water sulfate contour map with wild rice bodies overlain
Everything pale green and warmer is over *10 mg/L sulfate
Most wild rice lakes are within the <10 mg/L area

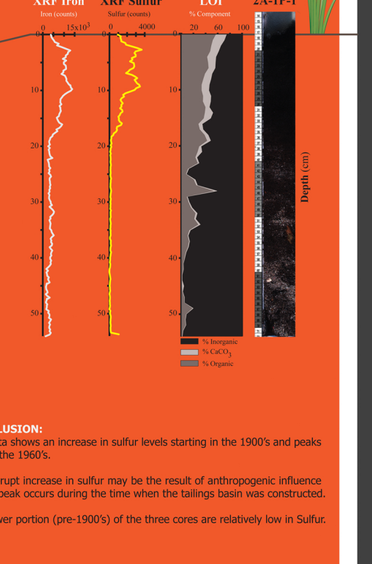
*Minnesota state standard for wild rice waters



Figure 7: Little Sandy Lake, engineered seep along the tailings basin dike wall, where millions of gallons a day used to 'seep' out into the adjacent wetlands.
Photo courtesy of John Coleman of Great Lakes Indian Fish & Wildlife Commission (GLIFWC) 2007.

HYPOTHESIS:
Increased levels of sulfate (SO_4^{2-}) to the lakes, rivers, and wetlands in northeastern Minnesota may cause a decrease in the abundance of wild rice (Zizania spp).
Empirical evidence (Moyle, 1944) suggests that wild rice grows poorly in water containing sulfate at a level greater than 10 mg/L.
The sulfate concentrations of Little Sandy Lake were as high as 353-483 mg/L in 2010.
SO_4, the chemical weathering and oxidation product of sulfide (S^{2-}), is the main solute produced when mining iron or metal sulfides.
The primary focus here is to understanding whether iron mining has had adverse effects on wild rice over time.





CONCLUSION:
The data shows an increase in sulfur levels starting in the 1900's and peaks during the 1960's.

This abrupt increase in sulfur may be the result of anthropogenic influence as the peak occurs during the time when the tailings basin was constructed.

The lower portion (pre-1900's) of the three cores are relatively low in Sulfur.



FUTURE:
Complete the Scanning Electron Microscope (SEM) analysis to identify and quantify the abundance of pyrite (FeS_2) in the sediment.
Analyze core sediment from Little Sandy Lake using Energy Dispersive X-ray Spectroscopy (EDS) for the elemental distribution in the sample surface.

METHODS:
Sulfur and Iron XRF data were obtained at the Large Lakes Observatory (LLO), University of Minnesota - Duluth using an ITRAX x-ray fluorescence core scanner.

Weight percent (wt%) and $d^{34}S$ total sulfur data were obtained at the Gilhooly Lab at Indiana University Purdue University Indianapolis (IUPUI) using Delta V Plus with Costech EA and Zero Blank autosampler stable isotope ratio mass spectrometer.

Lead-210 (^{210}Pb) and sediment accumulation data were obtained at the St. Croix Watershed Research Station (SCWRS).

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Fond du Lac Resource Management

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