

## Isotopic analysis of sulfur cycling in the St. Louis River Watershed, NE Minnesota

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Stable isotope techniques were employed to trace sulfur and oxygen transformations as sulfate ( $\text{SO}_4$ ) from the iron mining region of northeastern Minnesota travels through the St. Louis River watershed. Chemical and biological reactions that can occur during sulfate transport are important due to the potential link between sulfate reduction and production of methyl mercury (MeHg), a toxic form of mercury that bioaccumulates in the food chain. Sampling during the 2012-13 season took place at three locations on the St. Louis River and a number of mine-impacted tributary streams, wetlands, and lakes. Background sulfate concentrations in this region are typically  $\leq 5$  mg/L, with average  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of approximately +6‰ and +4‰, respectively. Mine derived sulfate is distinct, characterized by considerably more negative  $\delta^{18}\text{O}$ , typically between  $\sim -5$  and  $-11$ ‰. Previous work demonstrated that the overall mine-derived sulfate load to the St. Louis River is approximately 35 tons/day, while background sulfate contributes an average of 15 tons/day.

Much, but not all, of the observed sulfate trends can be explained by mixing between these characteristic sulfate sources. We have also identified lake and wetland settings that are impacted to varying degrees by bacterial sulfate reduction. Our results indicate that an additional process is required to fully account for the downstream isotopic evolution of sulfate, which we refer to as “oxygen re-equilibration.” This process is associated with  $\delta^{18}\text{O}_{\text{SO}_4}$  increases between upstream and downstream locations where a corresponding increase in  $\delta^{34}\text{S}_{\text{SO}_4}$  is not observed, and can only partially be explained by mixing relationships. The oxygen re-equilibration process is particularly apparent where high-sulfate, low-DOC mine waters come into contact with low-sulfate, high-DOC background waters.