Microscale characterization of sedimentary sulfur speciation in prairie pothole lakes

TENG ZENG[1,3], WILLIAM A. ARNOLD[1] AND BRANDY M. TONER[2]*

[1]Department of Civil Engineering, University of Minnesota, Minneapolis, MN 55455, USA
[2]Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108, USA (*correspondence: toner@umn.edu)
[3]Present addresss: Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA

The Prairie Pothole Region, which extends from north-central United States into south-central Canada, hosts numerous glacially-derived water basins known as prairie pothole lakes (PPLs). Due to recharge by gypsum-saturated groundwaters, many PPLs evolve high levels of sedimentary sulfur. Elucidating suflur speciation in PPL sediments is essential for evaluating the ecosystem functions of these water bodies.

In this study, we seek to define and quantify the solid-phase sulfur pools in PPL sediment samples collected from North Dakota, USA. A quantitative X-ray microprobe method was developed based on sulfur *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy and X-ray fluorescence (XRF) mapping. For each sample, XRF maps were collected at multiple energies spanning the sulfur *K*-edge. Individual XRF maps were then stacked to create a composite sulfur chemical map having a seven-point absorption spectrum at each pixel within the area of interest. These sulfur chemical maps were subsequently fit with reference XANES spectra of identified sulfur species to extract quantitative information of sulfur speciation.

Three sulfur pools – pyritic sulfur, reduced organic sulfur (organic mono- and disulfide), and oxidized sulfur (inorganic sulfate, ester sulfate, and sulfonate) – were identified in PPL sediments. No significant seasonal variation was evident for the total sedimentary sulfur level, but sulfur speciation showed a seasonal response. During the spring-summer transition, the reduced organic sulfur decreased with a concomitant rise in the oxidized sulfur. During the summer-fall transition, the trend reversed and the reduced organic sulfur grew at the expense of the oxidized sulfur. The pyritic sulfur remained relatively constant over time. The seasonal dynamics of sulfur speciation observed herein could have profound impacts on the transformation and mobilization of toxic trace elements such as mercury.