

Understanding organic phosphorus cycling in redox-dynamic eutrophic freshwater systems

KUREK, MARTIN R.¹, HARIR, MOURAD², SHUKLE, JOHN.¹, LEDUC, MEAGAN.³, SCHROTH, ANDREW.³, SCHMITT-KOPPLIN, PHILIPPE², DRUSCHEL, GREGORY K.¹

¹Indiana University Purdue University Indianapolis,
Department of Earth Science, makurek@indiana.edu

²Helmholtz Zentrum München, Deutsches
Forschungszentrum für Gesundheit und Umwelt, schmitt-
kopplin@helmholtz-muenchen.de

³University of Vermont, Department of Geology

Organic phosphorus compounds represent a significant fraction of phosphorus species in freshwater lakes and are mobilized via changing redox conditions at the sediment-water interface driven largely by interaction with iron. Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is a powerful analytical technique that can measure atomic masses with remarkable precision, yielding a look at thousands of different molecules in a single sample. This technique has been optimized for characterizing unique organic molecular signatures of dissolved organic matter (DOM) collected from various environments. Water and extracted sediment samples were collected from eutrophic Missisquoi Bay in Lake Champlain, experiencing seasonal redox variations, to assess how biogeochemical redox cycling links to organic phosphorus mobility and bioavailability for cyanobacterial blooms. Additionally, controlled mesocosm work was conducted with sediment cores by varying the redox conditions through manipulation of headspace gases. Water taken from the mesocosms was sampled and compared to unaltered samples from the water column to investigate how short-term variations in the redox conditions affect organic phosphorus mobility. In addition to visualizing FTICR-MS data with classic Van Krevelen diagrams, a novel CHO index plot revealed distinct clusters and homologous series of organic phosphorus molecules. Analyzing the samples in both negative and positive ionization modes revealed differences in the compositional space and provide a more comprehensive representation of the organic phosphorus species in Missisquoi Bay. By oxidizing and reducing the mesocosms, specific release and sequestration of different organic phosphate classes between the bottom water and sediment was observed. This release and adsorption cycle suggest preferential affinities of iron minerals to different phosphate molecules. Major input of organic phosphorus from rivers is quite different from mobilization of phosphorus molecules from the underlying sediment.