

## Phosphorus characterization in freshwater lake sediments using $^{31}\text{P}$ NMR spectroscopy

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Sediments of several shallow bays in Lake Champlain, USA, are a significant source of phosphorus (P) to the water column and to cyanobacteria that bloom over extended lengths of time during late summer. A large part of this P has been shown to be strongly tied to iron oxyhydroxide minerals in the sediment; analysis of redox dynamics in sediment porewaters further indicates these iron oxyhydroxides actively change over seasonal and even diel time scales. We have characterized the total, reactive, and organic P content of sediments collected over three summers (2007-2009) in Missisquoi Bay, Lake Champlain, USA, and utilized both NaOH-EDTA and ascorbic acid to extract organic P from these sediments (this is the first known analysis of organic P from Lake Champlain sediments). For NaOH-EDTA analyses, the organic P content ranged from 18-26% of the total P. Orthophosphate monoesters were the dominant compound class, and both phytate and *scyllo*-inositol phosphate were identified in most sediments. Monoester to diester ratios ranged from 4.6 to 13.1, the highest being in the surface sediments in August 2008. Polyphosphate was only detected in a few samples in 2007, but not in 2008. Pyrophosphate decreased across the 2008 season and was not present in the deeper sediments in October. Organic P was strongly correlated ( $R^2 = 0.89$ ,  $p < 0.05$ ) to porewater Fe(II), indicating that its mobility is associated with the reduction of Fe(III) hydroxides. Organic P was also extracted using ascorbic acid in sediments collected in 2009, a method utilized as it specifically targets nanocrystalline iron oxyhydroxides, the mineral phase of primary importance in P mobility for these systems. This extraction yielded a higher concentration of organic P, and had a speciation distribution that was different compared to identical samples extracted using the more commonly used NaOH-EDTA extraction technique. However, these differences were not extreme and did not change interpretations of the overall behaviour of organic vs. inorganic P mobility in iron-rich freshwater sediments.