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Organic carbon induced transformation of phosphorus speciation at the manganese oxide-solution interface

DANE LAMB[1], MARJANA YEASMIN[1], OLUWADUNSIN ADEDEJI OYETUNJI[1], OLIVER JONES[1] AND SURESH SUBCHANDERBOSE[2]

[1]RMIT University

[2]LoamBio

Presenting Author: dane.lamb@rmit.edu.au

Manganese (Mn) oxides, such as birnessite, play a crucial role in soil processes, including organic carbon sequestration, humification, and nutrient release, particularly phosphorus (P). Their high redox activity facilitates soil P cycling, catalyzing the release of P from organic compounds and polyphosphates. Research has shown manganese oxides can liberate P from synthetic organic P compounds, such as glyphosate and polyphosphates, primarily through C-P and C-O-P bond cleavage, along with catalyzed oxygen incorporation. Additionally, manganese oxides may affect P mobility via precipitation and co-precipitation reactions. Despite these findings, the role of manganese oxides in P dynamics in natural systems remains underexplored.

This study focuses on the release and transformation of P from natural organic matter using birnessite under reducing conditions, employing wet chemistry techniques alongside P K-edge XANES, C and O K-edge NEXAFS, and Mn L-XANES analyses. It uses two organic matter sources: a natural dissolved organic matter extract from vermicompost, rich in organic P, and commercial humic acid. In a glovebox under anaerobic conditions, hexagonal birnessite was reacted with organic matter at varying Mn:C ratios and pH levels (4, 6, and 8). Samples were taken at 1, 6, 12, and 16 days.

The results indicated modest reduction of Mn oxides in the systems containing vermicompost-derived organic matter compared to those with commercial humic acid, attributed to lower dissolved organic carbon concentrations in the former systems. The Mn L-edge XANES revealed a partial reduction of hexagonal birnessite to Mn(II), ranging from 9-20% in the humic acid systems and 2-12% in the vermicompost systems. This difference in reduction led to a higher formation of manganous phosphate (up to 19 % P) in the humic acid systems over the 16-day period across all pH levels compared to the vermicompost systems, highlighting the role of organic matter on manganese oxides stability and soil P dynamics under reducing conditions.