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Temperature and pH affect the sorption and transformation of dissolved organic carbon by birnessite

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Soil mineralogy plays a vital role in soil carbon retention. Birnessite is a ubiquitous manganese oxide mineral capable of facilitating molecular C transformations via diverse interactive mechanisms. Despite its widespread occurrence, limited studies are exploring the interactions between soil organic C and manganese oxide minerals. This study investigated the influence of triclinic birnessite on the retention and transformation of vermicompost-derived dissolved organic C (DOC) at different pH (4 and 8) and temperature (25^{o}C and 50^{o}C) conditions. The resultant impact of the reaction on mineral stability was also assessed.

Batch adsorption kinetic studies were conducted at pH 4 and 8 and 25^{o}C and 50^{o}C. These experiments involved controlled additions of birnessite to varied concentrations of DOC (15 and 25 mg/L) followed by wet chemical evaluation of C and Mn compositional changes. Spectroscopic evaluations of C and mineral transformations were carried out using fluorescence spectroscopy, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and X-ray absorption Spectroscopy (XAS).

Enhanced adsorption and transformation of dissolved organic C, particularly at pH 4 and 50°C was observed. The use of $SUVA_{254}$ and fluorescence spectroscopy demonstrated an increase in C aromaticity, with the highest degree observed at pH 4 at 50^{o}C. X-ray photoelectron spectroscopy and Near-Edge X-ray Absorption Fine Structure C 1s analysis showed an 8-fold increase in sorbed C aromaticity at 50°C compared to the unreacted dissolved organic C, the catalysis of esterification and/or etherification reactions at pH 4 was also demonstrated. Linear Combination Fitting of the X-ray absorption near-edge structure of reacted and unreacted triclinic birnessite showed modest changes to Mn II, III and IV proportions and the average oxidation state. Extended X-ray Absorption Fine Structure analysis showed the formation of hexagonal birnessite at pH 4, the temperature-induced formation of manganite at 50^{o}C, and the formation of up to 6% ramsdellite at 25^{o}C. This study provides insights into the role of triclinic birnessite in soil C retention and possible mineral transformation pathways under relevant environmental pH and temperature conditions.