

Abiotic transformation of plant-derived carbon by Mn Oxides: Breakdown of cellobiose by δ -MnO₂

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Soil carbon (C) cycling is controlled by a complex interplay of microbial and mineralogical processes. While minerals often provide important physical protection of soil organic matter from microbial respiration, studies have shown that dissolved organic matter (OM) can undergo significant abiotic transformation upon contact with mineral surfaces [1]. Mn oxides, ubiquitous in soil systems and one of nature's strongest oxidants, have been shown to facilitate degradation of OM [1, 2] although conflicting studies have observed OM stabilization through adsorption or polymerization [3].

In this study, we investigate the extent and mechanism of cellobiose oxidation in the presence of abiotic layer-type Mn oxides at pH 7. Cellobiose, the repeating unit of plant cellulose, was added to batch reactors containing δ -MnO₂ at three different Mn:C molar ratios, ranging from excess electron donating capacity (EDC) to excess electron accepting capacity (EAC). Cellobiose oxidation was tracked over time. Oxidation products were identified and quantified using liquid chromatography-mass spectrometry and ion chromatography. In order to quantify concomitant Mn reduction and the electron flux over the course of the reaction, solid-phase Mn(III) generation was measured together with average Mn oxidation number (AMON).

Our results show significant abiotic transformation of cellobiose via both hydrolysis (e.g., glucose) and oxidation pathways (e.g., formic acid, glyoxylic acid), although neither complete oxidation to CO₂ nor sorption of cellobiose or its breakdown products was observed. While solid-phase Mn(III) was generated within all treatments (13-40%), aqueous Mn(II) was not a good predictor of overall Mn reduction and was only observed when EDC exceeded EAC. Understanding the capacity of Mn oxides to transform OM has broad implications for C storage and is critical for more accurate prediction of C oxidation rates in soils.

[1] Chorover and Amistadi (2001) *GCA*, **65** (1), 95-109. [2] Sunda and Kieber (1994) *Nature*, **367**, 62-64. [3] Johnson et al. (2015) *Nat. Commun.* **6**, 7628.