45 - Impacts of manganese oxides on the retention, speciation, and lability of soil organic carbon

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Abstract: Carbon exchange between the Earth’s surface and atmosphere is a fundamental regulator of our climate system. Collectively, soils and sediments account for the greatest quantity of short-term organic C on the planet. Therefore, a process-level understanding of C storage and fluxes within the land surface is paramount to projecting future climatic conditions. The growing consensus of the predominant means by which soils store and stabilize C is by mineral protection. Organomineral complexes may hinder the efficacy of microbial enzymes to degrade organic C. Progress has been made in determining the roles of Fe oxides, Al oxides, and silicate minerals in controlling C cycling in soils. However, the impacts of the highly reactive Mn oxides present a major confounding gap in our understanding of C cycling in soils. Manganese oxides have the capacity to oxidize organic C into chemically simpler compounds, but also have been suggested to catalyze transformation to more complex compounds. Here we show that at high initial C:(Mn/Fe) ratios, hydrous Mn oxide (HMO) sorbs a larger quantity of forest-litter extracted-organic C (DOC), but in a more chemically labile form, than does goethite (FeOOH). The sorption maximum at pH 5 for DOC on HMO and goethite is 88 mg C g\(^{-1}\) and 63 mg C g\(^{-1}\), respectively. Upon reaction with 0.1 M Na\(_2\)HPO\(_4\), HMO and goethite retain 26 – 31 % and 41 – 68 % of the initially sorbed C, respectively. Carbon near edge X-ray absorption fine structure (NEXAFS) spectroscopy shows the HMO-sorbed organic C is enriched in carboxyl C and depleted in aromatic and phenolic C relative to the native DOC. The high capacity of HMO to sorb DOC in a relatively labile and oxidized form, suggests that Mn oxides may play an important role in governing organic C partitioning in soils. The impacts of Mn oxide-induced changes to organic C speciation and chemical lability on the microbial availability of the organic C warrant further investigation.