

Inhibition of chromium(III) oxidation by manganese(IV) oxide passivation and Fe(II) abiotic reduction

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Manganese (Mn) oxides are ubiquitous, strong oxidants in soils that can oxidize redox active metals, including chromium (Cr). In soil environments, trivalent chromium [Cr(III)] species are relatively benign, immobile micronutrients, whereas the hexavalent [Cr(VI)] form is predominantly present as a highly mobile, toxic chromate oxyanion that presents a contamination risk for drinking water. Although many studies have characterized the capacity of Mn oxides to oxidize Cr(III) to toxic Cr(VI), the oxidative capacity of the Mn(IV) oxides in the presence of other potentially passivating soil constituents, such as Fe(II), within diffusion-limited soil environments, such as within soil aggregates, remains unresolved. We hypothesize that such redox interfaces within soils provide conditions where Cr(VI) production is inhibited due to Mn(IV) oxide passivation by Fe(II).

A multi-chamber reactor to stimulate the diffusion-limited transport at soil redox interfaces was used to investigate the capacity of poorly-crystalline and crystalline Mn(IV) oxides (birnessite and pyrolusite, respectively) to oxidize Cr(III) hydroxides to soluble Cr(VI) in the presence of aqueous Fe(II). X-ray absorption spectroscopic analysis was used to determine solid phase speciation and mineral transformations. In the absence of Fe(II), Cr(VI) was generated in the Mn oxide chamber at a rate controlled by the solubility of Cr(OH)₃. When Fe(II) was introduced into the Cr/Mn system, aqueous Cr(VI) generation decreased as a function of Fe(II) concentration, where high concentrations of Fe(II) completely inhibited Cr(VI) production likely through both Mn oxide passivation and Cr(VI) back reduction. At both high and low Fe(II) concentrations, hematite (Fe₂O₃) and goethite (α -FeOOH) formed on the Mn oxide surface as evidence that surface passivation likely plays a role in decreasing the extent of Cr oxidation. Additionally, Cr(III) oxidation rate and extent decreased with increasing crystallinity of the Mn oxides due to lower specific surface area of the Mn oxide.