

## Effect of Dissolved Mn(II) and Organic Acids on Mn Oxide Structure and Metal Binding

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Manganese oxide minerals are ubiquitous in soils, occurring as lamellar, nanocrystalline phases with high surface areas and high reactivity. Despite their lower abundance compared to other reactive phases, like iron oxides, these minerals often are major controls on the fate and availability of trace metals, including Ni and Zn. Such metals are important micronutrients required for microbial carbon and nitrogen cycling but are also toxic at higher concentrations, such as in soils impacted by mining, smelting, or other industrial processes. The reactivity of Mn oxides towards metals is controlled by their structure and composition, with materials having a low Mn(III) content and a large number of vacancies showing the greatest reactivity. We have investigated chemical processes that may alter vacancy content and the structure of Mn oxides, thereby modifying their affinity and capacity for metal binding. Dissolved Mn(II), which is often present at redox interfaces, causes substantial structural changes at acidic pH conditions, whereas Mn oxide structures are stable at neutral pH until the onset of phase transformations into MnOOH minerals. This pH-dependent structural response directly impacts metal binding, with trace metals ejected from binding over vacancy sites upon Mn(II) addition at low pH but maintaining strong binding to such sites under neutral conditions. The small organic acids oxalate and citrate, produced via organic matter decomposition and as root exudates, are known to reduce Mn oxides and thus may also impact mineral structure and metal binding. Aging of Mn oxides with these organic acids at both pH 4 and 7 causes partial Mn reduction but does not substantially alter the overall phyllosulfate structure. Citrate, which causes greater Mn reduction, drives Ni to weaker binding sites on the edges of mineral particles, whereas oxalate promotes Ni incorporation into the mineral sheet at pH 7 and has no effect on binding at pH 4. These studies show that Mn oxides undergo dynamic structural changes in response to changing chemical conditions. This in turn may increase or decrease the stability of bound metals, altering micronutrient availability and contaminant fate.