Manganese dissolution in the CZ – impacts from effects from minerals, organic ligands, and pH

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Manganese controls several important aspects in the Critical Zone, serving as an essential nutrient, electron acceptor/donor, sorbent for adsorption, and potentially toxic element at elevated concentrations. Thus, characterizing its sourcing and transport is important for soil and subsurface geochemical systems. Batch reactors at 25° C were used to test pH (4, 5, 6) and organic acid (citrate, oxalate, catechol, control) effects on rocks (amphibolite, anorthosite), minerals (kyanite, muscovite, orthoclase feldspar), and soils (B and C horizons from Calhoun, Eel River, Luquillo, and Southern Sierra CZOs) Mn sourcing. Amphibolite (1178 mg kg^{-1}) and muscovite (570 mg kg^{-1}) had the higher Mn concentrations kyanite (45 mg kg^{-1}) and anorthosite (529 mg kg^{-1}). However, amphibolite (159 nM m^{-2} d^{-1}) and muscovite (89 nM m^{-2} d^{-1}) had lower Mn dissolution rates than kyanite (652 nM m^{-2} d^{-1}) and anorthosite (562 nM m^{-2} d^{-1}) across treatments. Soils Mn concentrations ranged from 197 mg kg^{-1} at Calhoun C horizon up to 1213 mg kg^{-1} at Eel River CZO C horizon. Despite soils being very different in physicochemical properties and Mn concentrations, Mn dissolution rates were not significantly different, ranging from 507 – 759 nM m^{-2} d^{-1}. Considering treatments across all rocks and minerals, citrate dissolution rate (418 nM m^{-2} d^{-1}) was significantly greater than control (212 nM m^{-2} d^{-1}) and oxalic acid (128 nM m^{-2} d^{-1}). Similarly, soil citrate (1557 nM m^{-2} d^{-1}) and oxalate (638 nM m^{-2} d^{-1}) dissolution rates were significantly higher than control (129 nM m^{-2} d^{-1}) and oxalic acid (196 nM m^{-2} d^{-1}). The pH did not significantly affect mineral dissolution due to larger differences among organic acid treatments and materials. These results highlight that mineral assemblages not total concentrations can control Mn dissolution. Moreover, pH effects can be mineral-specific and mediated by the presence of organic acids.