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Modeling the effects of manganese bioavailability on carbon storage in the Critical Zone

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Predictions of soil carbon storage under future climate scenarios are limited by incomplete understanding and representation of complex biogeochemical processes that influence decomposition. Current earth system models parameterize organic matter decomposition as a function of litter quality and climate with limited inclusion of microbial and geochemical factors. We developed a novel reactive transport model in PFLOTRAN to simulate the effects of soil Mn bioavailability on organic matter decomposition and C storage. Manganese is a critical component of enzymatic lignin oxidation, but the effects of Mn-promoted decomposition on soil C storage are unknown. The model configuration represents a soil profile in a temperate forest based on observations at the Susquehanna Shale Hills Critical Zone Observatory in central Pennsylvania, U.S.A. Reactive soil Mn is contained the biogenic Mn(IV)-oxide birnessite. Birnessite dissolution is modeled as a function of pH and redox over a range of dissolution/precipitation rate constants representing the sensitivity of birnessite dissolution to mineral properties (e.g., crystallinity, surface area) and other environmental factors. Birnessite dissolution produces bioavailable aqueous Mn^{2+} that is taken up by tree roots and stored temporarily in vegetation, then returned to surface soil in litterfall at the end of each year. During litter decomposition, soil fungi convert Mn^{2+} into reactive Mn^{3+} that is chelated to produce a highly reactive compound that oxidizes lignin. Litter degradation is therefore enhanced by Mn redistribution to surface soils. We also explored how effects of manganese on C storage interact with nitrogen deposition and warming associated with climate change. We determined that high levels of Mn uptake by plants in moderately acidic soils produce Mn-rich surface soils that enhance litter decomposition, increase CO_2 emissions, and decrease C stocks. Soil C losses at high Mn bioavailability were partially offset by increases in mineral-associated organic matter derived from lignin oxidation products. Nitrogen deposition increased C storage by inhibiting effects of Mn on decomposition. Decomposition increased with warming but was inhibited by low manganese bioavailability. Based on our simulations, we predict that Mn becomes limiting to litter decomposition when poorly soluble or inhibited by N, potentially constraining the response of organic C stocks to warming.