

Carbon-mediated dissolution of Fe-Mn oxides, colloid formation, and (re)precipitation at oxic-anoxic interfaces

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Manganese (Mn) and iron (Fe) oxides are critical constituents of soils/sediments, driving key biogeochemical processes. Mn oxides act as powerful oxidants, while Fe oxides exhibit a high adsorption capacity. Together, they can undergo redox-driven dissolution and (re)precipitation, significantly influencing metals and organic carbon interactions. Natural organic matter (NOM) from different sources varies in molecular weight and functional groups, affecting its ability to promote Fe and Mn mineral dissolution, metal release and complexation. To better understand how NOM drives competitive release of Fe and Mn from mixed Fe-Mn oxides, we examine how different types of NOM, carbon concentration, and carbon oxidation state influence the competitive release of Fe and Mn and colloid formation. Fe-Mn oxides were synthesized at a molar ratio of 3 before being reacted with standard and reduced Pahokee peat humic acid (PPSHA_{ox} and PPSHA_{red}) and Suwannee River fulvic acid (SRFA_{ox} and SRFA_{red}) in respective oxic and anoxic batch experiments. Filtered samples (< 0.2 µm) were collected over 72 hours to assess generation of dissolved and colloidal Fe and Mn using ICP-OES. Upon experiment termination, the distribution of Fe and Mn among the <3 nm and <200 nm size fractions was quantified. While no measurable Mn or Fe was observed in either oxic or anoxic conditions in carbon free systems, Mn and Fe release scaled with C concentration for all conditions. Preferential dissolution of Mn was observed for both PPSHA and SRFA under all conditions. For PPSHA, the C concentration influences the extent of Mn dissolution relative to Fe dissolution, while for SRFA all C concentrations yield similar Fe:Mn ratios. Under oxic conditions, PPSHA_{ox} promoted continuous aqueous Fe release, while in the presence of both SRFA_{ox} and SRFA_{red}, a re-precipitation trend of aqueous Fe was observed with re-precipitation being more pronounced in the presence of SRFA_{red}. The decline in Fe release in the presence of SRFA_{red} highlights the importance of secondary mineral formation. This, together with the differing effects of lower versus higher molecular weight C compounds on the redox stability of generated metal colloids, has important implications for contaminant transport and nutrient cycling.