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Redox-induced alterations of soil minerals: Impacts on nutrient and contaminant behavior in terrestrial systems

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A significant fraction of CO_2 fixed in photosynthesis by plants ends up as organic carbon in the below-ground environment, the soil. This organic matter provides energy and nutrients to soil organisms oxidizing organic carbon back to CO_2 under consumption of O_2 as terminal electron acceptor, a process called aerobic respiration. When molecular oxygen in the soil is limited, for example when soils are wet or flooded, some bacteria can utilize alternative electron acceptors such as nitrate (NO_3^-), manganese ($Mn^{III/IV}$), iron (Fe^{III}), or sulfate (SO_4^{2-}). This triggers a multitude of chemical, biological, and physical changes in the soil, with massive implications for the behavior of nutrients and contaminants [1]. Since the redox-active elements Mn, Fe, and S are important structural components of certain minerals in soils, redox processes also greatly affect the chemical reactivity of these minerals and even lead to recrystallization, transformation, and/or neo-formation of minerals. For example, microbial reduction of Mn(III/IV) and Fe(III) oxides or oxyhydroxides causes dissolution and release of aqueous Mn^{2+} and Fe^{2+} to the pore water. Similarly, reduction of sulfate produces dissolved sulfide (HS^-) which readily reacts with Fe(III) oxyhydroxides to form aqueous Fe^{2+}, elemental sulfur, and polysulfides. The Fe^{2+}, in turn, can catalyze recrystallization and/or transformation processes of Fe(III)-bearing minerals by electron transfer and atom exchange, but it may also be oxidized by Fe-bearing clays or Mn(III/IV) oxides to form poorly-crystalline oxyhydroxide surface precipitates. Low concentrations of dissolved sulfide can be effectively scavenged from solution by chalcophile trace metals leading to the formation of metal sulfide nanoparticles (e.g., CuS, HgS, ZnS, CdS). Sufficiently high sulfide and Fe^{2+} concentrations result in the formation of iron sulfide minerals. Many of these redox-active minerals are important host phases and/or sorbents for essential or potentially toxic trace elements in soils, including both metal cations and oxyanions. Some minerals can cause redox reactions of trace elements and thereby affect their speciation and chemical behavior. This keynote will highlight recent studies on redox processes affecting soil minerals with relevance to nutrient and contaminant behavior in soils and sediments.

[1] Borch *et al*. (2010), Environ. Sci. Technol. 44, 15–23.