The role of redox variability in structuring iron cycling in soils

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In environmental systems, natural iron nanoparticles are ubiquitous carriers of contaminates and nutrients; serve as structural components binding aggregates and colloids; and perform numerous electron transfer functions central to functioning ecosystems. In addition, these particles are more susceptible to alteration of their mineral structure than any other solid phase constituents commonly present in environmental systems. The dynamics of iron cycling are defined by the timescales required to shift the amount and/or composition of iron, and this is driven primarily by changes in the oxygen content or redox state of the soil. Our lab has conducted many experiments exposing soils rich in short-range-ordered (SRO) iron (III) phases from the Luquillo CZO to systematic variation in fluctuating redox conditions (e.g., fluctuation frequency, amplitude, or the duration of oxic and anoxic periods), as well as the solution composition. The experiments consistently reveal a sawtooth pattern of Fe(II) concentration that reflects an increase in Fe(II) during the anoxic period, followed by a decrease via oxidation and precipitation of Fe(III) during oxic conditions. Depending on the initial conditions (solid/liquid phase and microbial composition) and redox oscillation characteristics, the trajectory of Fe(II) production can increase or decrease over experimental time. Using selective chemical extractions, $^{57}Fe^{2+}$ spikes, Mössbauer spectroscopy, X-ray absorption spectroscopy, microbial analyses and numerical modeling of these experiments we propose the following: (a) The rates of microbial Fe(III) reduction—and thus the potential for alterative of iron reactivity toward other biogeochemical cycles (e.g., C)—is strongly influenced by two redox fluctuation parameters: the rate of Fe(II) oxidation during the previous oxic half-cycle; and the length of exposure to oxic conditions. Both abiotic and biotic processes are sensitive to these parameters. (b) The Fe(III) phases formed during exposure to oxic conditions are more short-range-ordered and preferentially re-reduced relative to the bulk soil iron phases. However, the precise nature and properties of the most rapidly reducible Fe(III)—the <10% of total soil Fe active in Fe cycling during redox fluctuations—remains challenging to describe suggesting tertiary structure and nano-scale proximity to electron donors and Fe reducing microbes likely plays an important role. Dynamic redox conditions can constrain Fe reduction rates and influence ecosystem processes that depend of iron behavior.