

The effect of high amplitude redox cycles on soil Fe reduction rates and mineral composition

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Iron plays important roles in ecosystems, as part of the soil and colloid matrix; as a sorbent for nutrients, carbon and trace elements; and as a mediator of electron-transfer reactions. Fluctuations in oxygen concentration control the biogeochemical cycling of Fe through dissolution and co-precipitation of iron-oxide minerals. Our recent work on soils from the Luquillo Critical Zone Observatory in Puerto Rico explores how fluctuations in redox conditions influence Fe reduction rates and mineralogy. We imposed systematic redox oscillations to soil slurries and examined the dynamic behaviour of Fe in the aqueous and dilute acid extractable phases. We constrained these oscillations using three fundamental parameters: (1) The oscillation frequency, (2) the amplitude of those fluctuations; and (3) the length of time that oxic or anoxic conditions persist. We show that Fe-reduction rates increase dramatically over 28 - 56 days when high amplitude (0 - 21% O₂) redox oscillations are imposed across frequencies ranging from 3.5 to 14 days. The stimulation of iron reduction coincides with the formation of an iron(III) phase that can be rapidly reduced in microbial Fe reduction assays. We also present results from sequential extractions targeting different Fe pools, mineral composition based on Mössbauer and XAFS, and a numerical model describing Fe(II) behaviour in the system. These results highlight how the dynamics of redox conditions can constrain rates of Fe reduction and influence ecosystem processes that depend of iron behaviour.