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P speciation affects the pathways and end-products of Fe(III) oxidative precipitation in porewaters

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Iron (Fe) redox cycling significantly impacts partitioning of elements between solution and solid phases, including phosphorus (P). In soils, P retained by Fe oxides can be released under reducing conditions and re-precipitated with newly forming Fe precipitates when oxidizing conditions are re-established. Soil porewaters contain ligands and electrolytes like silicate (SiO_4) and calcium (Ca), which affect structures of Fe(III)-precipitates and P retention mechanisms. Interactions among Fe, Ca, SiO_4, inorganic P (P_{in}) have been extensively studied in the past[1], whereas interactions of organic P (P_{org}) with Ca and SiO_4 in Fe precipitate formation remain unexplored. Former research showed that inositol hexaphosphate – the most common P_{org} compound in soil – accelerates Fe(II) oxidation, leading to the formation of Fe-P co-precipitates[2]. This study examines how P_{in} and P_{org}, along with key dissolved species (i.e. SiO_4 and Ca) in porewater, influence the kinetics and pathways of Fe(III)-precipitate formation and their P retention mechanisms.

Fe(III)-precipitates were formed at pH 6.0 (in 20 mM MES buffer) via oxidation of 2 mM Fe(II) in the presence of 0.04 (P/Fe = 0.02) or 0.4 mM (P/Fe = 0.2) P as NaH_2PO_4 (P_{in}) or inositol hexaphosphate (P_{org}), and 0.4 mM SiO_4 or 1 mM Ca. Aliquots of solutions were analyzed for aqueous Fe(II) and dissolved P concentrations photometrically. Fe(III)-precipitates were characterized by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) to determine their mineral composition and P binding environment.

Results indicate that P_{org} had less influence on Fe(III)-precipitate structure compared to P_{in}. XRD showed that lepidocrocite crystallization was suppressed at P_{in}/Fe=0.02, while the same was not true for P_{org}. Lepidocrocite formation was completely suppressed by SiO_4, resulting in ferrihydrite formation regardless of P form and initial P/Fe. Conversely, Ca presence did not affect Fe(III)-precipitate structure, as lepidocrocite formed in most cases. Precipitation of solid Fe(III) resulted in the uptake of more than 99% of the P present in solution irrespective of P form and initial P/Fe. Further characterization of the precipitates will include ^{31}P nuclear magnetic spectroscopy and Fe X-ray absorption spectroscopy.

[1] Nenonen et al. (2023), GeCA 360, 207-230

[2] Santoro et al. (2019), Geoderma 348, 168-180