Geophysical Research Abstracts
Vol. 20, EGU2018-846, 2018
EGU General Assembly 2018

Retention of organic P during Fe(II) oxidative coprecipitation

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The sorption of phosphorus (P) on soil minerals is known to strongly influence P cycling and control its retention and bioavailability. Considering the high affinity of Fe (oxy)hydroxides for P, the cycling of these two elements is often closely coupled, particularly in hydromorphic soils where Fe redox chemistry can bring about important mineral transformations. While surface adsorption of P is a well-known and widely studied process, less attention had been devoted to the understanding of Fe-P coprecipitation, although it may greatly affect the extent, kinetics and mechanisms of retention of various P forms, especially in soils subjected to alternating redox conditions.

In this work we synthesized Fe-P systems with increasing P/Fe ratio, prepared by either surface adsorption on ferrihydrite (Fh) or oxidative coprecipitation of Fe(II) with inorganic phosphate (Pi), inositol hexaphosphate (*myo*InsP6) or phosphatidylcholine (PC). P and Fe contents, specific surface area (SSA), porosity, surface charge and particle size of the obtained materials were determined, while XRD, TEM, XPS and FT-IR techniques were used to study their properties.

Coprecipitation resulted in a higher P retention with respect to adsorption, and for both processes retention decreased in the order *myo*InsP6>Pi>PC. The presence of Pi reduced the rate of Fe precipitation with respect to the P-free system. At low Pi concentrations, Pi interference and poisoning of the crystallisation resulted in nanometric particles, with phosphate concentrated on the surface, while with increasing Pi concentrations more aggregated particles with a lower SSA and higher porosity were obtained. Although XRD showed the formation of amorphous $FePO_4$, the surface charge of the particles was negative, indicating the simultaneous formation of Fh which provided new surfaces for Pi sorption. Conversely, *myo*InsP6 accelerated the precipitation of Fe through the formation of Fe-*myo*InsP6 complexes, leading to coprecipitates bearing *myo*InsP6 within the structure. This was deduced from the lower surface P/Fe ratios (by XPS) with respect to the total elemental ones, and from the less negative surface charge than the respective adsorbed systems. The prevailing mechanism involved in PC interaction with Fe was physical retention, confirming the weaker stabilization of P diesters in soils. Irrespective of the P/Fe ratio, PC did not influence the rate of Fe(II) oxidation and precipitation, although its presence led to a decrease of SSA and pore volume.

Coprecipitation of Fe(II) in the presence of P is therefore a more complex process than simple formation of a Fe(III)-hydroxide coupled with ion adsorption. Several types of processes may occur during Fe(II) oxidation, mainly depending on the initial P/Fe ratio and P species. Our results also highlight the important contribution of coprecipitation to the stabilization and selective accumulation of *myo*InsP6 with respect to other organic P forms with important implications on its retention and bioavailability.