Mobilization of P from crystalline and amorphous Fe- and Al-hydroxides

Stella Gypser and Dirk Freese
Faculty of Environment and Natural Sciences, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany (stella.gypser@b-tu.de)

In neutral to acidic soils, the availability of phosphorus (P) is affected by its strong affinity for mineral surfaces. Especially the interaction between P and iron- and aluminum-(oxy)hydroxides (Fe- and Al-hydroxides) plays a crucial role in the immobilization and hence, availability of P for plants. In this context, the fixation of P is mainly determined by processes of adsorption, desorption, and precipitation. In that sense, the kinetics and mechanisms of P desorption from synthetic well crystalline goethite (α-FeO(OH)) and gibbsite (γ-Al(OH)₃) as well as from amorphous ferrihydrite (Fe₂O₃·H₂O) and Al-hydroxide (Al(OH)₃) were characterized.

Different inorganic and organic desorption solutions were selected for these experiments. On the one hand, substance conversion processes take place in the soil system. High-molecular-weight organic compounds formed during humification and mineralization play an important role in soil environment and P mobilization. On the other hand, plants had developed a range of adaptive strategies in case of P demand. Plant roots excrete complex mixtures of organic compounds such as organic acids, amino acids, and sugars. Additionally, there are equilibrium reactions, which are determined by the respective ionic strength of the soil solution itself. For a comparison regarding the efficiency of P mobilization from synthetic Fe- and Al-hydroxides, the desorption solutions CaCl₂, and CaSO₄ were chosen as main components of the soil solution, and humic and citric acid were selected as organic ligands following humification or produced by organisms in the rhizosphere.

Previous P adsorption experiments revealed the formation of adsorbed P surface complexes on crystalline hydroxides by using Fourier-Transform Infrared spectroscopy. Amorphous Al-hydroxides, characterized by a less rigid crystal structure, revealed higher accessibility of P binding sites within the particle structure. The higher accessibility of binding sites was also observed for ferrihydrite. The amorphous character enabled the diffusion of P into the mineral particle, where stable surface complexes and precipitates were formed. Hence, the grade of crystallinity affects the extent of precipitated and low-soluble P complexes.

After 8 weeks of desorption time, the cumulative P desorption increased following the order CaCl₂ < CaSO₄ < humic acid < citric acid. Amorphous ferrihydrite exhibited much less desorption when exposed to inorganic solutions than goethite, gibbsite, or Al-hydroxide. Modeling of the desorption data suggested a diffusion-controlled desorption step for ferrihydrite with citric acid as sorptive.
The determination of $C_{\text{Total}}$ also indicated various release mechanisms of the organic acids: while the use of humic acid led to the accumulation of metal-organic complexes in the solution, citric acid dissolved the mineral phase and hence, also low-soluble precipitated P-complexes. The results suggest organic compounds, especially citric acid, are more important for the mobilization of P from both crystalline and amorphous Fe- and Al-hydroxides than inorganic ions present in the soil solution.