

## Effect of pH and soil P content on phosphate solubilization mechanisms by different organic acids in soil

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The release of organic anions (e.g. citrate, malate, etc.) and protons (rhizosphere acidification) by plant roots are considered important plant response mechanisms to increase phosphate ( $P_i$ ) availability in the soil solution and are often observed to occur simultaneously. In non-calcareous soils a major proportion of  $P_i$  is strongly sorbed to metal oxi(hydr)oxides of mainly Fe and Al and organic anions are known to compete with  $P_i$  for the same sorption sites (ligand exchange) or solubilize  $P_i$  via ligand-promoted mineral dissolution. However, the efficiency of these solubilization mechanisms is clearly soil-type dependent (sorption sites, P coverage, pH) and conclusive information on the P solubilizing mechanisms of carboxylates in natural soils is scarce. Also, the effect of concurrent rhizosphere acidification on P mobilization by organic anions is not well understood.

To gain a better mechanistic understanding of the solubilizing mechanisms of carboxylates in soil, the  $P_i$  solubilizing efficiency and the concurrent Fe, Al and Ca solubilization by four different organic anions (citrate, malate, oxalate, malonate,  $2.5 \mu\text{mol g}^{-1}$ ) was investigated in 5 different, non-calcareous soils (Cambisol, Podzol top and subsoil, and 2 Andosols) previously amended with  $25 \text{ mg kg}^{-1}$  and  $356 \text{ mg kg}^{-1}$  P, respectively. To minimise pH effects, the carboxylate solution pH was adjusted with KOH (1M) to the natural soil pH. The effect of rhizosphere acidification was simulated by adding carboxylate solutions with a pH of 3.3 and potassium chloride (KCl, 1 mM) was used as background electrolyte and control for all treatments.

Results of this study indicate that in medium to high sorbing, non-calcareous soils, ligand-promoted mineral dissolution of Al- and Fe-oxides is mainly responsible for a carboxylate-driven increase in  $P_i$  solubility, with the importance of ligand exchange increasing with increasing P sorption site coverage. The relative  $P_i$  solubilizing effect of carboxylates compared to KCl was the greatest in soils with medium to high amounts of anionic binding sites, but decreased on average by 50% at a higher P sorption site coverage (high P treatment).

Simulated rhizosphere acidification generally further increased the  $P_i$  solubilization at low P concentrations while little or the reverse effect was observed in the high P treatment. In soils with high amounts of exchangeable Ca, the proton-induced Ca solubilization reduced soluble  $P_i$ , presumably due to ionic-strength-driven changes in the electric surface potential of the soil matrix favoring a higher  $P_i$  retention.

We conclude that the efficiency of carboxylates in solubilizing  $P_i$  in different soils is a function of both, the amount of anionic binding sites and their coverage together with the corresponding  $P_i$  concentration in the soil solution, with the largest effects being observed at medium to high amount of sorption sites and coverage.