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Extractability of different forms of mineral-associated phosphorus

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The sequential phosphorus (P) extraction introduced by Hedley et al. (1982) and modified by Tiessen and Moir (2006) has become the preeminent measure for estimating the biological availability and binding forms of P in soil. However, the assumptions on the origin of P released into certain extractants have never been tested under defined conditions and verified for soils.

Thus, in a first step, we tested the P extractability from artificial soils containing 10 weight-% of P-loaded mineral and 90 weight-% of silt-sized quartz. P-loaded minerals were produced by reacting different P forms (orthophosphate, phytic acid, RNA) with various mineral phases (kaolinite, montmorillonite, goethite, ferrihydrite, Al hydroxide, and allophane) at pH 4. All artificial soil samples were subjected to sequential extraction in line with the Hedley fractionation scheme (water–resin extraction, 0.5 M $NaHCO_3$, 0.1 M NaOH, 1 M HCl, and conc. HCl at 80°C). The extracts were analyzed for P as well as for the main elements composing the respective mineral phases by ICP-OES. In a second step, we applied the Hedley fractionation to soil horizons of five well characterized forest soils of a German geosequence (Lang et al. 2017). In addition to P, we measured Fe, Al, and Ca in the extracts by ICP-OES.

Extractability of the artificial soils differed between P forms and mineral phases. Phosphorus contributed to all extracts for almost all P-loaded minerals. Aluminum hydroxide and allophane dissolved partly in NaOH and partly in HCl. The Fe oxides withstood the alkaline extraction and dissolved only in HCl, which is in agreement with the theoretical solubility but in contrast to the assumptions underlying the Hedley fractionation. The assumption of the Hedley fractionation that the 1 M HCl extract represents exclusively Ca-bound P, thus, is obviously wrong. For the extracted soil horizons, Al in both the NaOH and 1 M HCl extracts correlated with oxalate-extractable Al. Iron in both HCl extracts correlated with P in the respective extracts and with oxalate- and dithionite extractable Fe. Also P and Ca in the 1 M HCl extract correlated. Thus, results from extraction of the artificial soils were conferrable to real soils.

In summary, P forms bound to different minerals contribute to all extracts. Thus, the individual extraction steps of the Hedley fractionation do not represent P bound to certain compounds but P bound to various mineral phases via bonds of different strength. Additional measurement of Fe, Al, and Ca in the extracts gives more evidence on the origin of extracted P; for instance, P in the 1 M HCl extract can be attributed to Fe oxides, Al oxides and/or Ca phosphates.