

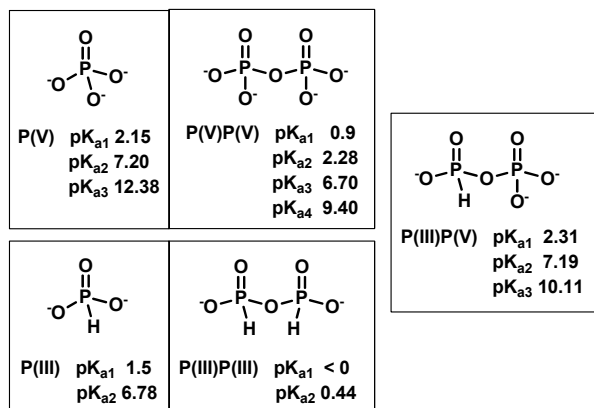
## Phosphorus +III and +V-containing oxyanions in soil interstitial waters: complex formation, adsorption, nucleophilic addition, and oxidation

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The five P(III) and P(V)-containing oxyanions shown below are all used as agricultural soil amendments. logK values for metal ion complex formation and adsorption onto oxyhydroxide minerals are considerably higher for the P(V)P(V) dimer than for the P(V) monomer, owing to the ability of the dimer to form six-membered chelate rings while maintaining much of the basicity of the monomer. In stark contrast, the basicity of the P(III)P(III) dimer is more than six log units lower than for the P(III) monomer, which suppresses metal ion complex formation and adsorption. The mixed P(III)P(V) dimer lies in the middle; it is sufficiently basic to form metal ion complexes and adsorb, but any contribution to these reactions from the chelate effect is small.

Speciation arising from protonation, metal ion complex formation, and adsorption governs reactivity. Dimers hydrolyze to monomers, with rates increasing as solutions become more acidic. In addition to facilitating hydrolysis, metal ions and oxyhydroxide mineral surfaces have the potential to raise concentrations of P(OR)<sub>3</sub> tautomers, thereby boosting P(III) atom electrophilicity. Electrophilicity and nucleophilicity are key features in the reactions of P(III)-containing oxyanions with reduced sulfur species and oxidants.



**Figure 1.** Phosphorus-containing oxyanions used as soil agricultural amendments.