

Phosphorus activators contribute to legacy phosphorus availability in agricultural soils: A review

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1 **Abstract**

2 Phosphorus (P) is one of the most limiting macronutrients for crop productivity and P deficiency is a
3 common phenomenon in agricultural soils worldwide. Despite long-term application of phosphate
4 fertilizers to increase crop yields, P availability is often low, due to the high affinity of phosphate for the
5 soil solid phase. It has been suggested that the accumulated (surplus) P in agricultural soils is sufficient to
6 sustain crop yields worldwide for about 100 years. In this paper, we try to clear up the potential for making
7 use of legacy P in soils for crop growth potentially alleviating the global P resource shortage. Specifically,
8 we try to clear up the potential of soil “P activators” for releasing fixed P. P activators accelerate and
9 strengthen process which transform P into bio-available forms via a range of chemical reactions and
10 biological interactions. They include phosphate solubilizing microorganisms, phosphatase enzymes and
11 enzyme activators, low molecular weight organic acids, humic acids, lignin, crop residues, biochar and
12 zeolites. Although reported performance is variable, there is growing evidence that P activators can
13 promote the release of phosphate from soil and, hence, have potential for mitigating the impending global P
14 crisis. Further basic and applied research is required to better understand the mechanisms of interaction of P
15 activators with natural soils and to maximize activator efficacy.

16
17 **Key words:** Agricultural soils; Potential phosphorus pool; Legacy Phosphorus; Phosphorus activation;
18 Phosphorus bioavailability; Activator

19 20 **1. Introduction**

21 Phosphorus (P) is a major limiting nutrient for crop growth in many agroecosystems and is
22 indispensable in several physiological and biochemical processes (Simpson et al., 2011). Consequently, the
23 availability of P controls the growth and development of all crops (Wyngaard et al., 2016). Plants assimilate
24 P (predominantly as negatively charged primary and secondary orthophosphate ions) from the soil solution.
25 Although most soils contain considerable total P stocks, only a small fraction (<1%) of the total inorganic P
26 (P_i) and organic P (P_o) is dissolved at any given time (Bünemann, 2015). The concentration of P in soil
27 solution remains really low, about 0.05-0.30 $\mu\text{g P mL}^{-1}$ (Bolan, 1991). It is estimated that crop productivity
28 is limited by P deficiency on more than 40% of the world’s arable land (Balemi and Negisho, 2012). P
29 limitations are also a major productivity constraint in many natural (Augustine et al., 2003) and managed
30 (Bünemann et al., 2011) grassland systems. Although other constraints may also limit productivity, soil P
31 often needs to be replenished repeatedly to satisfy plant demand, in part because it is quickly removed from
32 the dissolved (plant available) form by sorption, precipitation and microbial immobilization (Roberts and
33 Johnston, 2015) or is lost through surface runoff (in particulate and dissolved forms), subsurface flow
34 (leaching and throughflow via the soil matrix and macropores), drain flow and even groundwater which
35 may accelerate the eutrophication of P sensitive waters (Heathwaite and Dils, 2000; Hively et al., 2006;
36 Holman et al., 2008; Sims et al., 1998).

37 Historically, chemical fertilizers, such as manufactured water-soluble phosphate have played a
38 significant role in replenishing this P pool. However, these fertilizers are derived from mined
39 rock-phosphate which has a finite (and rapidly diminishing) supply (Gilbert, 2009). Some studies claim that,
40 at current rates of extraction, global commercial phosphate reserves will be depleted in 50-100 years

41 (Abelson, 1999; Sattari et al., 2012). Opinions vary about the reliability of these data because they are
42 principally based on second and third hand information and the figures change all the time (Gilbert, 2009).
43 However, it is likely that remaining reserves will have increasingly lower quality and will be increasingly
44 more costly to extract, which means that the supply of high quality phosphate fertilizer will also become
45 progressively more restricted (Cordell et al., 2009). The rising demand for agricultural commodities in
46 developing countries has put increasing pressure on land resources for higher yields, with associated
47 growth in the demand for phosphate fertilizers (Weber et al., 2014). This realization (sometimes described
48 as a “potential phosphate crisis”) is pushing global fertilizer prices up (Chowdhury et al., 2017).

49 The high P fixing capacity of most soils and the low P use efficiency (around 10-15%) of most crops
50 means that surplus P input from fertilizers tends to accumulate in soils (Withers et al., 2001). This
51 accumulation is known as “legacy P” which can be calculated as the difference between inputs (mineral P
52 fertilizer, atmospheric deposition and weathering) and outputs (lost through surface runoff, subsurface flow,
53 leaching, plus P in crop uptake etc.) (Havens and James, 2005; Sattari et al., 2012). In Oceania and Western
54 Europe, for example, cumulative inputs of P fertilizer to arable land (560 and 1115 kg P ha⁻¹, respectively,
55 for the period 1965-2007) were much greater than the cumulative uptake (100 and 350 kg P ha⁻¹,
56 respectively) (Sattari et al., 2012). In turn, this results in changes to the concentration of P in the soil
57 solution and its association with soil minerals and organic matter which can lead to enhanced phosphate
58 loss (Guppy et al., 2005; Heckrath et al., 1995) and subsequent degradation of freshwater and marine
59 resources where eutrophication can be triggered by additional P inputs (Tilman et al., 2001).

60 It is clear that legacy P stocks in soils have the potential to play a vital role in maintaining agricultural
61 productivity with lower P requirements for inputs and reduced P transfers from land to water, if crops can
62 efficiently access this P (Condrón et al., 2013). It has even been suggested that the accumulated P in
63 agricultural soils would be sufficient to sustain maximum crop yields worldwide for about 100 years if it
64 were available (Khan et al., 2007).

65 Unfortunately, most legacy P is not available for plants to absorb easily. However, it may be possible to
66 manipulate soils to increase the availability of this P for crops. The aims of this review are to clarify our
67 current understanding of the cycling and transformation of legacy P in agricultural soils and to present
68 findings from the published literature about so-called “P activators”. Furthermore, we evaluate the
69 contribution of P activators to soil legacy P availability, assess the advantages and disadvantages of
70 different P activator classes and summarize the key mechanisms involved.

71

72 **2. The forms and mobility of soil P**

73 More than 80% of P applied as fertilizer can become unavailable for plant uptake shortly after
74 application via sorption, precipitation (typically by reaction with Al³⁺ and Fe³⁺ in acidic soils and Ca²⁺ in
75 calcareous soils: Table 1) or microbial immobilization (Gustafsson et al., 2012; Roberts and Johnston, 2015;
76 Yadav and Verma, 2012). To take full advantage of legacy P, it is necessary to understand the long-term

77 dynamics of this P in soil (Liu et al., 2014a).

78 Soil P occurs in a number of different forms (organic and inorganic) which vary greatly in their
79 bioavailability (Fig. 1). Those include constituents of rock minerals from the parent material, which are
80 completely inaccessible, various forms of organic matter (including the constituents of humus and the cells
81 of living organisms: Khan et al., 2014) and bioavailable phosphate in solution (Dollard and Billard, 2003).
82 The environmental behavior of P is also a function of its speciation, which is directly linked to P solubility,
83 reactivity, and bioavailability (Liu et al., 2014b). For example, P associated with Fe (hydr) oxides (Fe-P) is
84 sensitive to reducing conditions (Beauchemin et al., 2003). P sorbed to Al (hydr)oxides (Al-P) or calcium
85 phosphate precipitates is likely to be more sensitive to pH changes (Yan et al., 2014), and some species of
86 organic P tends to be more bioavailable (Li and Brett, 2013).

87 The total P in top soils (0-15 cm) typically ranges from 50 to 3,000 mg P kg⁻¹, depending on parent
88 material, soil texture, vegetation cover and soil management history (Sanyal and De Datta, 1991).
89 According to Stutter et al. (2015), based on 32 soils from the United Kingdom, arable soils tend to be
90 dominated by ortho-P_i with orthophosphate monoester species associated with strongly sorbing Al and Fe
91 soil surfaces. Intensive grasslands tend to be dominated by orthophosphate monoesters and as grazing
92 becomes more extensive labile orthophosphate diesters, associated with labile soil organic matter and
93 microbial turnover, dominate. The diversity of P species in less intensively managed soils can be viewed as
94 a positive indicator of ecosystem function and diversity.

95 P_i generally accounts for 60-80% of total P in agricultural soils (predominantly in minerals). The total
96 P content is usually at least one order of magnitude larger than the amount of P that rapidly cycles through
97 the soil-plant system and two to three orders of magnitude larger than the amount of P present as
98 plant-available P_i in the soil solution (HPO₄²⁻ or H₂PO₄⁻) (Frossard et al., 1995). The dominant form of
99 orthophosphate ion present in the soil is pH dependent. At pH 4-5, orthophosphate usually exists as H₂PO₄⁻
100 ions but as pH increases, first HPO₄²⁻ ions and then PO₄³⁻ ions become more dominant (Yadav and Verma,
101 2012).

102 Many abiotic and biotic reactions occur in the soil P cycle (Fig. 1), some occurring within a few
103 seconds, while others occurring slowly over several years (Bünemann and Condron, 2007; Fardeau, 1995;
104 Frossard et al., 2011). The initial breakdown can often be the rate-limiting step for P_o mineralization (Das et
105 al., 2014). P availability is also greatly affected by a series of pH-dependent abiotic reactions that influence
106 the ratio of soluble-to-insoluble P pools in the soil (DeLuca et al., 2009). These include desorption and
107 solubilization of rapidly exchangeable P_i; uptake of P by soil microorganisms and plants (either through
108 their roots or through mycorrhizal hyphae); the release of P_i from the soil solid phase or from fertilizers,
109 induced by the exudation of phosphatases and organic acids from roots or microorganisms; the release of P_i
110 from plant residues or organic fertilizers to the soil solution; and the release of P_i from organic matter
111 mineralization by microorganisms (Frossard et al., 2011).

112 The concentration of P in the soil solution is primarily controlled by adsorption/desorption equilibria

113 between labile P_i in the solid phase (associated with positively charged minerals such as Fe and Al oxides)
114 defined by equilibrium concentration ratios (Haynes and Mokolobate, 2001; Hinsinger, 2001). Specific
115 adsorption (ligand exchange) occurs when P ions replace the hydroxyl groups on the surface of Al and Fe
116 oxides and hydrous oxides (Haynes and Mokolobate, 2001). P ions can also interact chemically with
117 minerals in combination with metals such as calcium phosphate, aluminum phosphate, iron phosphate and
118 the reductant-soluble phosphate extractable after removal of the first three forms (Chang and Jackson,
119 1957). For example, oxygen (O_2) can immobilize iron through Fe(II) oxidation which precipitates as Fe(III)
120 (hydr) oxides, resulting in the generation of H^+ and a decrease in pH (Eq. (1)) (Begg et al., 1994). This
121 process may have some effects on the trapping of phosphate as $FePO_4$ (Eq. (2)) (Silva and Sampaio, 1998).

122



125

126 P_o may constitute 30-50% in most soils, although it can range from as low as 5% to as high as 95%
127 (Sharpley, 1985). P_o is typically present as orthophosphate monoesters, including inositol phosphates, and
128 as orthophosphate diesters, organic polyphosphates and phosphonates (Bünemann, 2015). P_o can be
129 classified into four main fractions: labile, moderately labile, moderately resistant (fulvic-acid P), and highly
130 resistant (humic-acid P) (Bowman and Cole, 1978; Randriamanantsoa et al., 2015). All fractions can be
131 transformed into phosphate that is available to plants via microbially mediated mineralization – but at
132 different rates. Labile P_o is relatively easily mineralized whereas inositol phosphate (up to 50% of P_o) is
133 considered to be stable (Dalai, 1977). The microbial biomass acts as both a source and a sink of soil P and
134 is critical for P cycling (i.e. mineralizing P_o via enzyme-catalyzed transformations and converting P_i into
135 their living cells during P immobilization).

136 Different soil P fractions can also be separated into fractions characterized operationally by the used
137 extractants (Hedley et al., 1982): e.g. resin-P, $NaHCO_3$ -P, microbial-P, NaOH-P, Sonicated/NaOH-P, HCl-P
138 and residual-P. In this kind of P fractionation, only resin-P and $NaHCO_3$ -P are relatively available for crops
139 but these account for a small proportion of total P.

140 Both P_i and P_o are strongly bound (or fixed) to the solid phase under most soil conditions via a series
141 of different reactions. Together with P sorption and net immobilization by the microbial biomass, this can
142 result in low equilibrium P concentrations in the soil solution which can be manifested as P deficiency (e.g.
143 reduced crop growth), even in moderately fertilized soils (Gerke, 2015). This can be reversed via
144 dissolution/precipitation (mineral equilibria), sorption/desorption (interactions between P and mineral
145 surfaces) and mineralization/immobilization (biological transformations between P_o and P_i).

146

147 3. Soil P activators and the application effect

148 P activators refer to a range of different methods intended to accelerate and strengthen soil P

149 transformations to plant-available forms in the soil solution. They can be classified into three types: (1)
150 bio-inoculants and bio-fertilizers, including phosphate solubilizing microorganisms (PSMs) and
151 phosphatase enzymes; (2) organic matter, including low molecular weight organic acids, humic acids,
152 lignin, crop residue, manure and biochar and (3) zeolites and other materials, which have been relatively
153 less well studied and applied.

154 Although activation processes are complex, several key factors have consistently been demonstrated to
155 govern the availability of fixed P. These main factors can be broadly grouped as sorption reactions and
156 changing the chemical and physical properties of the soil (e.g. pH, extractable Al and the net negative
157 charge on surfaces in soil) with the net effect of increased solubility and reduced sorption of P_i in soil. It is
158 complex to elucidate the effect of P activators based on changing of these factors. For a review of this
159 nature, it would be useful to define a common and clearly explained set of responses to P activation. Here,
160 we employ the P activation response based on an increase in plant-available P or on saved phosphate
161 fertilizer inputs – focusing on experimental data (field and glasshouse) that excluded the impacts of
162 management practices (e.g. grazing, intercropping).

163

164 3.1. Bio-inoculant and bio-fertilizer

165 3.1.1. Phosphate solubilizing microorganisms

166 Various organisms are involved in P cycling but microorganisms probably play the most important
167 role. Much of the global cycling of insoluble organic and inorganic soil P can be attributed to bacteria and
168 fungi. Phosphate solubilizing microorganisms are those which are capable of transforming insoluble P into
169 soluble (plant accessible) forms. They are probably the most eco-friendly and inexpensive option for
170 enhancing P availability for plants (Owen et al., 2015). Phosphate solubilizing bacteria (PSB:
171 *Achromobacter*, *Aereobacter*, *Agrobacterium*, *Alcaligenes*, *Arthrobacter*, *Aspergillus*, *Azotobacter*, *Bacillus*,
172 *Bradyrhizobium*, *Burkholderia*, *Chromobacterium*, *Enterbacter*, *Erwinia*, *Escherichia*, *Flavobacterium*,
173 *Klebsiella*, *Micrococcus*, *Pantoea agglomerans*, *Pseudomonas*, *Rhizobium*, *Salmonella*, *Serratia*,
174 *Thiobacillus*) and phosphate solubilizing fungi (PSF: *Alternaria*, *Arbuscular mycorrhiza*, *Aspergillus*,
175 *Fusarium*, *Helminthosporium*, *Penicillium*, *Rhizopus*, *Sclerotium*) make up 1-50% and 0.1-0.5%
176 respectively of the total PSMs in soil with an additional minor role played by phosphate solubilizing
177 actinomycetes (PSA: *Streptomyces*, *Nocardia*) (Khan et al., 2007). It has long been known that there is
178 significant variation in the ability of bacteria to solubilize P in soil. Bacteria which are known to enhance P
179 availability include species of *Pseudomonas*, *Azotobacter*, *Burkholderia*, *Bacillus* and *Rhizobium* (Jones
180 and Oburger, 2011). Generally, PSF produce more acids than bacteria and consequently exhibit greater
181 P-solubilizing activity. Filamentous fungi known to be able to solubilize phosphate include the genera
182 *Aspergillus* and *Penicillium* (Sharma et al., 2013). In recent years, the P-solubilizing ability of
183 actinomycetes has attracted interest because this group of soil organisms are not only capable of surviving
184 in extreme environments (e.g. drought, fire etc.) but also possess other potential features (e.g. production of

185 antibiotics and phytohormone-like compounds etc.) that could simultaneously benefit plant growth
186 (Hamdali et al., 2008).

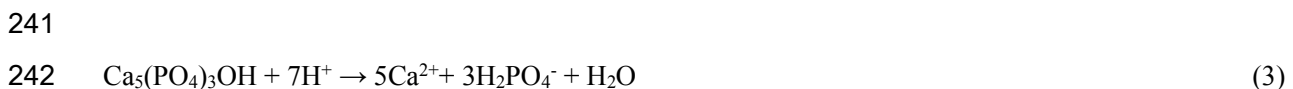
187 The P solubilizing ability of different PSMs varies with species, strain, soil properties (inherent and
188 seasonal) and the plant species (Table 2). A maximum increase in available P of 208% has been reported
189 (Abdul Wahid and Mehana, 2000). However, de Freitas (1997) found that application of PSB (*Bacillus*
190 *sphaericus*, *B. polymyxa* and *B. thuringiensis*) significantly increased plant growth, but not P-uptake. Other
191 studies suggest that mixtures of different PSMs may be more effective than using single organisms (Yu et
192 al., 2011). Kim et al. (1997) reported that when vesicular-arbuscular mycorrhizae (VAM; *Enterobacter*
193 *agglomerans*) and PSB (*Glomus etunicatum*) were applied together, the soil microbial colonization and
194 phosphatase activity response was much higher than when they were used separately, suggesting a
195 synergistic interaction, although the exact mechanisms were not fully understood. It is likely that the
196 additional increase in P resulting from dual inoculation was due to enhanced P solubilization by PSB
197 through the production of organic acids, ion chelation and increasing root cell permeability, as well as
198 supporting the establishment and function of VAM (mycorrhizal colonization alters roots physiologically as
199 well as altering microbial populations: Suri et al., 2011).

200 Various “bio-fertilizers” have been developed which include bacteria (e.g. *Pseudomonas* spp,
201 *Bacillus* spp, *Rhizobium* spp and *Klebsiella* spp), fungi (e.g. *Penicillium* spp, *Aspergillus* spp and *Rhizopus*
202 spp) and actinomycetes (e.g. *Streptomyces* spp). These organisms are intended to solubilize solid phosphate
203 in soils (Mahajan and Gupta, 2009). They are cost effective, have no known environmental issues and can
204 be used to supplement chemical fertilizers (Chesti et al., 2013). It has been estimated that inoculation with
205 arbuscular mycorrhizal fungi (AMF) might result in a reduction of approximately 80% of the recommended
206 phosphate fertilizer rate under certain conditions, with similar crop yields (Liu et al., 2016). The
207 effectiveness of mycorrhizal associations on P uptake from slow-release P compounds has been elucidated
208 in the review of Bolan et al. (1991). They noted that for plants the increase in P uptake associated with
209 mycorrhizal infection was found to vary with source of P. Greatest benefit from mycorrhizal inoculation
210 was obtained with the least soluble source of iron phosphate. Compared to normal phosphate fertilizers,
211 dissolved P microbial mixed fertilizers appear to have a significant effect on the utilization of P – enabling
212 a reduction in phosphate fertilizers by 25-467% (Mukherjee and Sen, 2015; Sundara et al., 2002). The effect
213 of PSMs varies at different phases of plant growth. Sundara et al. (2002) shows that the effect of PSB
214 fertilizer treatment on available P status varied with sugarcane growth stage. PSB fertilizers were more
215 effective in the tilling and growth phases than during the ripening phase.

216 Although it is widely known that PSMs can make P available, the mechanisms underlying this
217 phenomenon are not fully understood. The potential mechanisms are illustrated in Fig. 2 and include the
218 microbial synthesis of a range of exudates (e.g. organic acids and H⁺, metabolites and enzymes including
219 phosphatase) (Behera et al., 2014) The insoluble forms of P_i, such as tricalcium phosphate (Ca₃(PO₄)₂),
220 aluminium phosphate (AlPO₄), iron phosphate (FePO₄), may be converted to soluble P by low molecular

221 weight organic acids as well as facilitated by microbially released H⁺ (Khan et al., 2014). Li et al. (2015)
222 studied mechanisms for solubilizing different types of P by an efficient *Aspergillus niger* strain An2. They
223 found An2 mainly secreted oxalic acid to solubilize Ca-P, Mg-P, Al-P and Fe-P and secreted tartaric acid to
224 solubilize rock phosphate.

225 PSMs can secrete enzymes (phosphatase, phosphohydrolase, phytase, phosphonataase and C-P lyase) which
226 catalyze P_o mineralization. The most commonly secreted enzymes are phosphatase (an enzyme which
227 eliminates P from its substrate by hydrolyzing phosphoric acid monoesters into a P ion and a molecule with
228 a free hydroxyl group.) and phytase because of the predominant presence of their substrates in soil (Othman
229 and Panhwar, 2014). Phosphatases or phosphohydrolases describe a broad group of enzymes that catalyze
230 the hydrolysis of both esters and anhydrides of H₃PO₄ (Jones and Oburger, 2011). Phytase (myo-inositol
231 hexaphosphate phosphohydrolase) can hydrolyze sodium phytate, resulting in the production of P_i (Sharma
232 et al., 2013). Phosphonataase and C-P lyase cleave the C-P of organophosphonate. Wanner (1996) found that
233 many enzymes can function as organic phosphoester scavengers, releasing inorganic phosphates from
234 nucleotides and sugar phosphates. PSMs can also solubilize phosphate via the production of NH₄⁺, CO₂ and
235 H₂S, as well as releasing P during substrate degradation (Khan et al., 2010). The production of H₂S can act
236 with ferric phosphate to yield ferrous sulphate with concomitant release of phosphate. The presence of
237 NH₄⁺ can result in pH depression via the formation of H⁺ during nitrification which contributes to P
238 solubilizing (Khan et al., 2014). Proton release also occurs from the dissociation carbonic acid (H₂CO₃)
239 which is formed from the dissolution of CO₂ generated by biological respiration. These protons can readily
240 solubilize Ca-apatite (Kim et al., 1997):



244 3.1.2. Phosphatase enzyme and enzyme activators

245 Phosphatase enzymes are widely distributed in natural environments and play a major role in P_o
246 regulation (Fig. 3) by hydrolyzing ester-phosphate bonds in P_o, leading to the release of phosphate (Burns
247 and Dick, 2002).

248 Phosphodiesterase and phosphomonoesterase may act sequentially in the mineralization of P_o:
249 phosphomonoesterase can dissociate the phosphate group from phosphate monoester compounds and
250 phosphodiesterase can hydrolyze the phosphate diester bond in nucleic acids. Lipids and nucleic acids
251 typically make up about 7% of soil P_o (Kalsi et al., 2016). The influence of phytase on P_o mineralization is
252 less well understood but is thought to be important in the mineralization of inositol P (which makes up
253 approximately 50% of soil P_o in the form of phytin and its derivatives). Phytase can release lower forms of
254 myo-inositol phosphates and inorganic phosphate by catalyzing the hydrolysis of phosphomonoester bonds
255 in phytate. Xiang et al. (2005) observed that soil phosphatase activity and available P content increased
256 significantly after applying exogenous phytase in potted *Malus hupehensis* experiments.

257 D- α -glycerophosphatase is a rare phosphatase in soil which has been purified and characterized from
258 *Bacillus licheniformisc* (Skraly and Cameron, 1998). The products of the reaction catalyzed by
259 D- α -glycerophosphatase were identified as glycerol and inorganic phosphate. In addition, a kind of
260 inorganic phosphatase (pyrophosphate phosphohydrolase) has been identified which can hydrolyze
261 pyrophosphate (used as a fertilizer) to P_i (Dick and Tabatabai, 1978).

262 It has been shown that the activities of phosphatase (like those of many hydrolases) depend on several
263 factors including soil properties, soil organism interactions, plant cover, leachate inputs and the presence of
264 other inhibitors and activators (Bünemann et al., 2011).

265 Phosphatase activity varies with pH (different phosphatases are classified as either alkaline (pH>7) or
266 acid (pH<6) phosphatase). Generally, enzyme activities of soils increase with increasing soil pH with the
267 exception of acid phosphatase which is predominant in acid soils. It is worth underlining that when the
268 effects of soil pH on enzyme activities are studied, the concentration of organic matter should remain
269 constant (Gianfreda and Ruggiero, 2006). For example, the significantly greater activities of alkaline
270 phosphomonoesterase, inorganic pyrophosphatase and phosphodiesterase reported in manure-treated soils
271 by Acosta-Martínez and Tabatabai (2000) are believed to be due to a combination of greater soil pH values
272 and enhanced microbial activity and diversity resulting from manure input over the years. Martens et al.
273 (1992) studied the activities of ten soil enzymes after the application of different organic amendments
274 (poultry manure, sewage sludge, barley straw and green alfalfa) over a 31-month period. They found that
275 the addition of amendments increased enzyme activity by an average of 2- to 4-fold during the first year of
276 the experiment. Similarly, phosphatase activities (acid phosphate, alkaline phosphatase, phosphodiesterase
277 and inorganic pyrophosphatase) were significantly correlated with the organic carbon content of the 40 soil
278 samples tested by Deng and Tabatabai (1997), confirming that organic matter plays an important role in
279 protecting and maintaining soil enzymes in their active forms.

280 It is well established that phosphatase activities generally decrease with soil depth (Gianfreda and
281 Ruggiero, 2006). Ji et al. (2014) describe a two-year field experiment on the effects of deep tillage on soil
282 microorganisms and phosphatase activity in clay and loam soils. The data showed that tillage and soil
283 texture had a significant influence over soil phosphatase activities and that deep tillage increased soil
284 phosphatase activities, which was affected by soil depth. This may be because deep tillage loosens the soil
285 and mixes organic matter into lower horizons, thereby increasing the abundance of soil
286 microorganisms. Activities of phosphatase in clay soil were higher than those of loam by 10.9%. This may
287 have been due to the fact that the finer particles in clay soils offer more surface area and more small pores
288 which can trap organic matter and offer habitat for soil microorganisms (which are the source of
289 phosphatases). Das et al. (2014) also found that soil phosphatase activity decreases with increasing depth.
290 Soil temperature also has a significant impact on soil phosphatase activity. Higher temperatures can
291 encourage microbial metabolism, increasing phosphatase activity and nutrient availability (Dalai, 1977).
292 However, previous studies have also shown a significant correlation between phosphodiesterase activity

293 and organic carbon content which complicates the explanation for this effect (i.e. the degradation of organic
294 carbon is also correlated with temperature) (Koch et al., 2007; Štursová and Baldrian, 2011).

295 Some stressors such as salinity and high heavy metal concentrations may have adverse effects on the
296 phosphatase activities. Alkaline phosphatase was observed to decline exponentially with increasing salinity
297 and linearly with increasing sodicity by Rietz and Haynes (2003). This was ascribed to the denaturation of
298 enzyme proteins at high salt concentrations and a decrease in microbial biomass and activity. Heavy metals
299 affect enzyme activity by modifying protein conformation, due to interaction with the protein active groups
300 and by inhibiting enzyme synthesis (Karaca et al., 2010). Kandeler et al. (2000) found that phosphatase
301 activities decreased after 10 years of contamination with different levels of Zn, Cu, Ni, V and Cd.

302 Although, in principle, some P activators can strengthen (accelerate) the activity of phosphatase and,
303 hence, activate P_o (Fig. 3b), relatively few studies have been published on this topic. An exception is the
304 work of Fang et al. (2008) which showed that the addition of glutathione enhanced the affinity between
305 enzymes and substrates. Ascorbic acid had a similar effect to glutathione on enzyme activity. They take part
306 in redox reactions and can combine with peroxide and free radicals to protect sulfhydryl from oxidation. As
307 a result, proteins and enzymes containing sulfhydryl in membranes will not deactivate (Wisniewski et al.,
308 2005). Li et al. (2014) found that soil available P content could be increased by 10-91% under the influence
309 of glutathione in paddy soils. They also demonstrated that ascorbic acid promoted the activity of
310 phosphomonoesterase and accelerated the mineralization of P_o . The available P content consequently
311 increased by 2-203%.

312

313 3.2. Organic matter

314 Organic matter applied to soil as an amendment is also reported to increase the availability of existing
315 soil P. A comprehensive review of the competitive sorption reactions between phosphorus and organic
316 matter in soil is given by Guppy et al. (2005). Details of how organic matter contributes to available P in
317 soil is reviewed further in this Section.

318

319 3.2.1. Low molecular weight organic acids

320 Low molecular weight organic acids are organic compounds that contain at least one carboxyl group
321 and a molar mass less than $10,000 \text{ g mol}^{-1}$. They are thought to activate P since plants secrete them under
322 conditions of P deficiency and they are also derived from the decomposition of plant and animal residues
323 (Yuan et al., 2016). The most common low molecular weight organic acids identified in soils are oxalic,
324 malic, citric, fumaric, tartaric and succinic acids (Table 3). The most frequent agents used for mineral
325 phosphate solubilization seem to be gluconic acid and 2-ketogluconic acid (Earl et al., 1979; Moradi et al.,
326 2012). The concentrations of low molecular weight organic acids tend to be low in soils, ranging from
327 10^{-3} - $10^{-5} \text{ mol L}^{-1}$.

328 Different concentrations of low molecular weight organic acids have been added to soil in an attempt

329 to increase P availability. Good P activation responses have been obtained using citric and oxalic acids
330 (Table 4). Low molecular weight organic acids have also been added to soils with phosphatase enzymes in
331 an attempt to activate P. For example, Guan et al. (2013) showed that the application of oxalic acid and
332 phytase together significantly increased available P compared to controls. Amounts of H₂O-P, NaHCO₃-P_i,
333 NaOH-P_i and NaOH-P_o increased by 37.8%, 21.1%, 15.5% and 24.4%, respectively, possibly as a
334 consequence of the transformation of stable P fractions to labile fractions by phytase under the influence of
335 exogenous oxalic acid. However, the detailed mechanisms remain speculative.

336 Low molecular weight organic acids may activate P_i via: (1) changing soil pH which can promote the
337 dissolution of sparingly soluble minerals containing P_i (Fox et al., 1990), including calcium phosphate, e.g.,
338 octacalcium phosphate or apatite (Andersson et al., 2015); (2) forming complexes with Fe, Al and Ca and
339 releasing P combined with these ions (Ström et al., 2005). The release of phosphate occurs via ligand
340 exchange between the carboxylate anion and HPO₄²⁻ or H₂PO₄⁻; (3) organic acid ions compete with P_i for
341 the same sorption sites in soils (Lan et al., 1995). When P and organic acid anions are present in the soil
342 solution, competition is expressed either through direct physical competition for sorption sites or through
343 electrostatic competition.

344 Low molecular weight organic acids may also promote the release of P_o. Giles et al. (2014) found that
345 the addition of organic anions from bacterial sources can improve Ca myo-inositol hexakisphosphate
346 solubilization and, thus, P availability. Organic anion-driven solubilization of Ca myo-inositol
347 hexakisphosphate appears complementary to hydrolysis by plant and bacterial phytases. *In vitro*
348 experiments suggest that Ca myo-inositol hexakisphosphate hydrolysis is improved in the presence of
349 organic anions (e.g., gluconate, citrate, oxalate and acetate), due either to Ca²⁺-mediated phytase activation
350 or solubilization via divalent metal chelation (Patel et al., 2010). However, the exact mechanism about
351 possible dissolution of P_o by organic acids remains unclear. It is possible that low molecular weight organic
352 acids could influence the activity of PSMs and, hence, affect the activity of phosphatases secreted by these
353 organisms (Turner, 2008).

354

355 3.2.2. Humic acids and lignin

356 Humic acids and lignin are natural high molecular weight organic compounds derived from the
357 decomposition of plant litter. Humic acids are composed of a range of aliphatic and aromatic structures
358 with a variety of different functional (mainly oxygen-containing) groups. They can improve soil fertility
359 and increase the availability of nutrient elements including P (Çimrin et al., 2010).

360 Humic acids can activate P via the following mechanisms: (1) Shifting soil pH; H⁺ is produced during
361 the decomposition of humic acids in soil (Hue, 1991) which can increase soluble P concentrations in
362 calcareous soil by decreasing precipitation rates of Ca-P minerals. H⁺ from humic acids can also inhibit the
363 precipitation of hydroxyapatite, and favor the formation of dicalcium phosphate dihydrate over other, more
364 thermodynamically stable and less soluble phosphates. The effects appear to be more effective than low

365 molecular weight acids (Grossl and Inskip, 1991); (2) Formation of simple organic ligands; Humic acids
366 contain some active functional groups such as carboxyl and phenolic hydroxyl groups that can complex
367 metal ions, especially Fe and Al (which are often associated with phosphate fixing). P availability increases
368 when these metals are removed (Antelo et al., 2007; Gerke and Hermann, 1992). (3) Colloid interactions;
369 Humic acids are colloidal substances and can adsorb metal and metal oxides in soil and strengthen the
370 competitive ability of phosphate (Regelink et al., 2015). Competition between humic acids and P for
371 sorption onto soil colloids may result in higher P dissolved concentrations.

372 It is worth noting that humic acids may also act as P-sorbing surfaces in some circumstances. Othieno
373 (1973) added humic acids and P to highly weathered soils and repeatedly observed wheat yield decreases
374 and lower tissue P concentrations, suggesting that humic acids can have a detrimental effect on P
375 availability for plants. Further elucidation of the relationships between humic acids and P in competitive
376 sorption processes is necessary, because both the increase and decrease of P bioavailability may occur in
377 the presence of humic acids.

378 Furthermore, the addition of humic acids can also increase the distance of P movement and the
379 concentration of extractable P in soil surrounding phosphate fertilizer placements (Du et al., 2013). A
380 similar conclusion was reached by Jones et al. (2007). They found that soluble P concentrations were nearly
381 identical between soils prior to fertilization (ranging from 0.1 to 0.2 mg L⁻¹). Soluble P concentrations 3.8
382 cm below the mono-ammonium phosphate band in the calcareous soil were significantly higher when
383 humic acids were applied than in the control after 16 and 32 days, suggesting that humic acids may have
384 increased P solubility and mobility. Fig. 4 demonstrates that P can move relatively far from a phosphate
385 fertilizer band in a neutral pH, non-calcareous soil after humic acids addition (Jones et al., 2007). Soluble P
386 concentrations were higher 3.8 cm below the band (Fig. 4c) than 3.8 cm to the side of the band (Fig. 4b),
387 indicating that there was some downward advection of P.

388 Lignin is an important precursor in the formation of humic substances and can form humic acids as a
389 result of microbial activity in soil (Bååth et al., 1995). The major chemical functional groups in lignin
390 include hydroxyl, methoxyl, carbonyl and carboxyl groups in various amounts and proportions. Lignin can
391 facilitate the activation of P via similar mechanisms to those described above for humic acids (Sun et al.,
392 2011), as they share similar functional and structural properties (Tahir et al., 2011). Lignin has been
393 reported to increase available P in calcareous, red ferrallitic (rich in iron-aluminum oxides), yellow
394 ferrallitic (rich in ferric oxide hydrate), sandy and humid-thermo ferrallitic soils. Increases in available P of
395 35% in calcareous soil and 33% in red clay loam have been reported - probably from Al-P complexes
396 (Chen et al., 2003).

397 Lignin can be extracted, recycled and modified from black liquor (a waste product from paper pulp
398 manufacture), bagasse by-products (fibrous sugar cane or sorghum residues) and crop straw. The lignin
399 content in black liquor solids (which are now regularly applied to agricultural soils) can be up to 35% (Tian
400 et al., 2015). Dotaniya et al. (2014) reported that organic residues such as press mud and bagasse

401 by-products could release organic acids and enhance P availability in soil. About 600 million tonnes of crop
402 straw are produced every year in China (Zeng et al., 2007) which is often re-incorporated into soil –
403 increasing both the lignin and organic matter contents. As a result, the content of available P, total P and the
404 activity of phosphatase have been observed to increase (Ding et al., 2012).

405

406 3.2.3. Crop residues, manure and biochar

407 Like chemical phosphate fertilizer, crop residues, manure and biochar (charcoal produced from crop
408 residues) can also act as P sources. Land application is the predominant method for disposing of
409 agricultural residues, thereby recycling their nutrients Fig. 5) (Dai et al., 2016). The magnitude and
410 direction of available P change after the application of these materials to soil depends on the properties of
411 the P source and the receiving soil environment.

412 All of these materials contain highly soluble P_i (e.g. orthophosphate) which can act as a primary
413 source of nutrients. They also contain labile P_o which can be mineralized to release soluble P in the
414 short-term. This soluble orthophosphate can also be assimilated by microorganisms and subsequently
415 released back into soil when these organisms die and are subject to decomposition. Results from a
416 dual-labelling experiment suggest that, on average, 16% of the P contained in surface-applied residues
417 could be classed as labile P (Noack et al., 2014).

418 A review by Damon et al. (2014) concluded that several key factors govern the mineralization and
419 availability of crop residue-derived P including the quality of the crop residues, the activity of the soil
420 microbial biomass, and the subsequent sorption reactions of mineralized P in soil. The addition of organic
421 residues can also alter the chemical and physical properties of the soil and, hence, affect P availability
422 indirectly. For example, increased organic matter usually provides microbes with a more favorable habitat,
423 enhancing P cycling via mineralization (Lone et al., 2015). However, a general finding is that the transfer of
424 P from break crop residues incorporated into the soil is relatively low (2-20%) and is quite variable
425 (Espinosa et al., 2017). This could be due to variable P concentrations in the crop residues, which depend
426 on the soil P status, the physiological maturity of the residues, and on the extent of the translocation of
427 shoot-P to the developing grain in the break crops under considerations (Thibaud et al., 1988).

428 Manure P is a valuable resource, comparable to inorganic fertilizer P for crop production. Compared to
429 crop residues, manure can contain even more labile P. A large fraction of the phosphorus in manure is
430 considered to be plant-available immediately after application. Estimated values of phosphorus availability
431 ranged between 12% and 100% (Bahl and Toor, 2002). The total P content in manure varies depending on
432 the animal species, age, diet and how the manure has been stored. Jia et al. (2015) predicted that if manure
433 P inputs from 2012 to 2030 were assumed to continue in soil, Olsen-P could increase to values close to or
434 exceeding the environmentally critical value of 60 mg kg^{-1} , the tipping point above which P leaching has
435 been shown to be significant (Heckrath et al., 1995). In addition to supplying labile P, manure can also help
436 in mobilizing native P. This mobilization occurs by conversion of insoluble Ca, Al and Fe forms of P to

437 soluble forms through the action of organic acids and chelates that are produced during manure
438 decomposition of manures (El-Baruni and Olsen, 1979). Hountin et al. (2000) found that labile (resin- P_i +
439 $\text{NaHCO}_3\text{-P} + \text{NaOH-P}$) in animal manure-amended soil increased from 61% to 79% and the amounts of P
440 generally increased in the following order: moderately labile NaOH-P_i and $\text{NaOH-P}_o >$ labile P extracted by
441 resin and $\text{NaHCO}_3 >$ stable P. However, the potential environmental P hazard of swine manure should be
442 considered, especially in agricultural systems in which soils receive high rates of manure application.
443 Although P is considered immobile in agricultural soils, a decrease in the P adsorption capacity of soil
444 following manure addition at rates greater than the nutritional requirements of plants for P may increase the
445 potential for leaching of soluble P (Sutton et al., 1982).

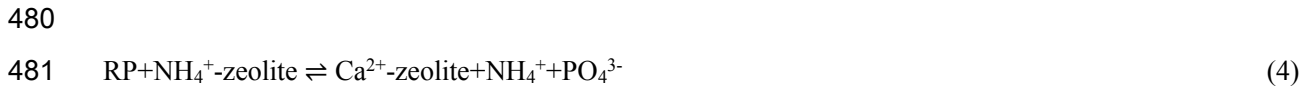
446 The effects of biochar on P availability are variable: in some soils, biochar application has been
447 observed to increase P availability, while in others, P availability was not affected or was observed to
448 decrease, mainly due to increased P sorption (Chaturika et al., 2016). Biochar can induce changes in the
449 soil ion exchange capacity. Fresh biochar in the acid pH range has a high anion exchange capacity, which
450 can initially be in excess of the total cation exchange capacity of the biochar (DeLuca et al., 2009). It is
451 possible that these positively charged exchange sites compete with Al and Fe oxides (e.g., gibbsite and
452 goethite) for sorption of soluble P, similar to that observed for humic acids and fulvic acids (Hunt et al.,
453 2007). P associated with biochar can be more labile than that associated with Al or Fe oxides. To date,
454 however, there is noted lack of studies evaluating the effect of short-term anion exchange capacity on P
455 cycling and availability. Biochar may also alter P availability through sorption of chelating organic
456 molecules like phenolic acids, amino acids and complex proteins or carbohydrates (Joseph et al., 2010).
457 Sorption of organic molecules on biochar surfaces can directly adsorb cations such as Al^{3+} , Fe^{3+} and Ca^{2+} ,
458 resulting in delayed P adsorption or precipitation in soil (Xu et al., 2014). A microcosm incubation study by
459 Jin et al. (2016) suggested that soil P availability was enhanced after the addition of manure biochar
460 (biochar from manure wastes) due to the fact that orthophosphate and pyrophosphate are the major P
461 species in manure biochar and due to enhanced decomposition of some P_o (e.g. monoesters) by enhanced
462 alkaline phosphomonoesterase activities. Xu et al. (2016) reported that biochar application can decrease P
463 availability in saline sodic soil due to enhanced P sorption and precipitation.

464

465 3.3. Zeolites and other materials

466 Zeolites are minerals of hydrated sodium, potassium, calcium and barium aluminosilicates which are
467 often used as cation exchangers (the net negative structural charge of zeolites results in the favorable
468 ion-exchange selectivity for many cations) (Pabalan and Bertetti, 2001). They can increase soil available P
469 concentrations and plant uptake of P. Wei et al. (2001) found that zeolite application could increase soil
470 available P by up to 183%. Some modified zeolites can increase the available P even more (Yang et al.,
471 2015). Fig. 6 gives a summary of several methods for the modification of natural zeolites (Dai et al., 2011)
472 to enhance cation exchange capacity (due to the favorable ion-exchange selectivity of natural zeolites for

473 certain cations, such as Cs^+ , Sr^{2+} , and NH_4^+) and to the pH change induced by zeolites. Acid modified
474 zeolites can decrease the pH of soil and alkali modified zeolites can enhance cation exchange through alkali
475 metal ions. As a result, the release of P can be enhanced (Fadaeeraeyeni et al., 2015). Modification at high
476 temperatures can remove organic matter in zeolite crevices and increase adsorptive capacity, thereby
477 enhancing the capacity of zeolite to activate P (Quin et al., 1998). The combination of zeolite and NH_4^+ can
478 also increase the cation exchange effects of zeolite. The exchange-induced dissolution of rock phosphate
479 proposed can be summarized for an ammonium saturated zeolite as Eq. (4):



482
483 where RP is rock phosphate (Allen et al., 1993). The zeolite/RP combination was intended to act as an
484 exchange-fertilizer, with Ca^{2+} exchanging onto the zeolite. It is proposed that the plant uptake of NH_4^+ or
485 K^+ frees exchange sites which can then be occupied by Ca^{2+} , lowering the soil solution Ca^{2+} concentration
486 and inducing further dissolution of rock phosphate (Pickering et al., 2002).

487 Fly ash, a coal combustion product (Parab et al., 2015) and wood ash can also be used to activate P in
488 soil (Demeyer et al., 2001). One possible reason for the significant improvement of P availability by fly ash
489 in acid soil was that ash addition had a liming effect which can enhance bioavailable P concentrations
490 (Parab et al., 2015). However, fly ash may also be associated with high heavy metal loads. Compared to
491 coal ash, reported concentrations of Mn, Zn and Cd in wood ash are higher while As, Se and Cr contents
492 are lower (Someshwar, 1996). In addition to P, wood ash is a direct source of other major elements, notably
493 Ca, Mg and especially K in soils. The dissolution of wood ash in soil, and the rate at which P becomes
494 plant-available is complicated. The change in soil nutrient availability is a combination of three factors: (1)
495 P addition from the ash; (2) shifts in pH-dependent soil chemical equilibria; (3) changes (mostly increases)
496 in microbial activity (Demeyer et al., 2001). Furfural is an important organic compound produced from
497 agro-industrial wastes and residues. When applied to soil, it can decrease pH and release Ca^{2+} - bound
498 phosphate (García-Domínguez et al., 2015).

499 Other P activators include water-dissolved organic polymeric compounds, bentonite, mugineic acid
500 and ABT rooting powder (ABT has the ability to promote rooting and to increase the survival rate of plants
501 under abiotic stress). Polyvinyl alcohol, polyacrylamide and polyethylene glycol have been shown to
502 increase P sorption and pH in red ferralitic soils (rich in ferric oxide hydrate). Polyvinyl alcohol is a
503 polymer containing hydroxyl groups, which has low permeability and high water adsorption capability
504 (Chai et al., 2012). Polyacrylamide is a polymer of acrylamide which is soluble in polar solvents and
505 nontoxic in nature. Polyethylene glycol has special solubility and chain-folding properties. Phosphate is
506 released as a consequence of the protonation of hydroxyl and amide groups in these water-dissolved
507 organic polymers and their interaction with Al^{3+} and Fe^{3+} -phosphate (Hua et al., 2005). Bentonite can also
508 increase P_i in soil (principally $\text{Ca}_2\text{-P}$ followed by $\text{Ca}_8\text{-P}$, Al-P and Fe-P) (Liu and Sun, 2004). Mugineic acid

509 has a high affinity for Fe and can activate Fe-P (Zhang et al., 1989). ABT rooting powder is an efficient
510 plant growth promoter developed by the Chinese Academy of Forestry, which can promote root P
511 absorption and plant growth. The active components of ABT rooting powder include indole-3-butyric acid
512 and indole-3-acetic acid, which are regulators of plant growth (Zhang et al., 2010). Liu et al. (2002) found
513 that the phosphate fertilizer utilization ratio of wheat increased by 12% when ABT rooting powder was
514 used.

515

516 **4. Discussion**

517 *4.1. Practical applications*

518 A variety of different soil P activators have been reported to activate legacy P over the last few
519 decades. These include PSMs, phosphatase enzymes, enzyme activators, low molecular weight organic
520 acids, humic acids, lignin, crop residues, manure, biochar, zeolites, fly and wood ash, water-dissolved
521 organic polymers, bentonite, mugineic acid and ABT rooting powder.

522 Each P activator can act in one or more ways to promote the solubilization of insoluble P_i and or the
523 mineralization of P_o . The range of mechanisms is illustrated in Fig. 7. The most common activation
524 pathways are: (1) Dissolution. P activators change the chemical structure of the sorbing components –
525 principally via metal complexation and removal; (2) Competitive inhibition of P sorption. P activators
526 compete with phosphate for sorption sites or compete with metal oxides for exchange sites in soil; (3)
527 Organic ligands. Functional groups such as carboxyl and phenolic hydroxyl can complex metal ions and
528 release P bound to these cations; (4) Enzymolysis. P activators catalyze the hydrolysis of ester-phosphate
529 bonds, leading to the release of phosphate; (5) P release. Bio-resource P activators contain both P_i and P_o
530 which can be released into the soil.

531 Each type of P activator has its own specific advantages and disadvantages (Table 5), so activator
532 selection should be tailored to the specific context in which the activator is to be used. Key factors to be
533 considered include: (1) Specific optimum conditions, including soil physico-chemical properties. This is
534 particularly the case for PSMs; (2) the nature of the legacy P pool targeted (P_i or P_o or both); (3) the cost
535 and access to the P activators under consideration; (4) the influence of the P activator on crops, the
536 prevailing microbial community and soil physical and chemical characteristics.

537 All types of bio-resource P activator, such as crop residues, manure and biochar, have both primary
538 and secondary P supply functions. They can be usefully separated according to their form and principal
539 mode of action: i.e. direct inorganic nutrient supply for direct uptake and the input of organic nutrients
540 which are subsequently mineralized. They may also contain microbial populations (e.g. rhizobacteria)
541 which can affect secondary nutrient (P) supply and other plant growth promotion functions.
542 P-solubilization in the field tends to be much more difficult to demonstrate than solubilization of P in the
543 laboratory. Crops respond differently to P activator amendments and are dependent on several factors such
544 as soil temperature, moisture content, pH, salinity, organic matter content, microorganisms, the rhizosphere

545 effect and soil fauna. The effects of these factors on the role of P activators need to be studied more
546 extensively at the field scale before P activators can be used reliably.

547

548 *4.2. Environmental considerations*

549 Making full use of legacy P in soil is an environmentally desirable and economically feasible strategy
550 for improving crop production, particularly in P-deficient soils. Agricultural P loss is a global concern due
551 to the effects of P in receiving water bodies (eutrophication). By reducing the need for P fertilizer addition
552 and enabling crops to efficiently access legacy P, the transfer of P from land to water can be reduced. There
553 is now increasing evidence that P availability can be controlled by P activators. However, increasing P
554 availability using P activators in soil can also increase the risk of P losses to surface and ground waters via
555 dissolved and colloid-facilitated transport (Hens and Merckx, 2001).

556 Some P activators can contain potential toxicants, such as heavy metals (As, Cr, Zn, Cd). For example,
557 ashes originating from co-firing of bark or wood with tyres can contain high levels of Zn (1%) (Someswar,
558 1996). Such sources should be avoided (or at least rates should be controlled) in order to avoid
559 contamination of both soil and receiving water bodies after P activator addition.

560 Although generally regarded as environmentally-friendly, P activators such as PSMs may also have
561 some negative impacts such as triggering plant diseases or problems for native organisms (i.e. they can
562 potentially act as biological invasions in soil: Amsellem et al., 2017). That said, they may also act to curb
563 invasions of other invasive species (i.e. they can act as a biological control) (Santini et al., 2013).

564

565 *4.3. Future research directions*

566 Despite the fact that P activators have been shown to increase available P, precise mechanisms remain
567 uncertain in most cases and additional insight is required. For example, further elucidation of the
568 relationships between organic P activators and P in competitive sorption processes is necessary. Similarly,
569 the available literature regarding the effects of biochar on P availability is inconsistent and mechanistic
570 understanding of biochar-P interactions remains poor. Moreover, the response of plants to soil P activators
571 in the field is often difficult to predict. Future research is, therefore, required to identify underlying
572 biochemical and physical processes, which alter the bioavailability of legacy soil P.

573 Application of single activators may be insufficient to activate the broad range of P forms typically
574 present in soil and the use of several activators together may produce better results. For instance, some
575 studies have reported that the addition of citric acid and phosphatase together can be beneficial, although
576 the exact mechanism by which additional P is released in this case is uncertain. Further research is required
577 to uncover the mechanisms underpinning the compound effects of different P activators used in concert.
578 Specifically, long-term field experiments should be conducted to address the interactions of P activators
579 with natural soil and their impacts on crop yield.

580 Even though, various amendments have been reported for managing legacy P in different soils, some

581 of these can be costly and or practically difficult to implement. Although P-solubilizing microorganisms
582 have yet to fulfill their promise as commercial bio-inoculants, scientists need to address certain issues, like
583 how to improve the efficacy of bio-fertilizers, what the optimal delivery system should be, how to stabilize
584 these microbes in soil systems, and how nutritional and root exudation aspects can be controlled in order to
585 get maximum benefits from PSM application. Finally, research is also required to discover and enable
586 efficient, feasible, cheap and environmentally-friendly solutions for improving access to legacy P stocks in
587 soil.

588

589 **5. Conclusion**

590 P is a major macronutrient needed for plant growth and development. It has been historically
591 oversupplied as phosphate fertilizers in many agricultural systems to increase crop yields. However, there
592 are a number of adverse environmental impacts associated with the use of inorganic P fertilizers. These
593 include increasing risk of P loss from soils with elevated P concentrations (so-called legacy P), which may
594 lead to eutrophication in water bodies receiving phosphate in agricultural runoff (diffuse-source pollution),
595 and the depletion of finite resources of high grade phosphate rocks with associated price increases in the
596 context of ever-increasing global demands for food and bioenergy. A more sustainable approach to
597 managing P availability in agriculture is, therefore, required.

598 Legacy P that has accumulated in soils represents a significant potential secondary P source that could
599 substitute (at least in part) manufactured fertilizers, if ways can be found for unlocking it (P activation). A
600 number of P activators have been proposed which have been reviewed here. However, soil P cycling is
601 extremely complex and varies with soil morphogenesis, mineralogy, organic matter content, pH, water
602 relations, etc. Taking full advantage of legacy P, therefore, remains a significant challenge. Complicating
603 influences include tillage, residue management and fertilization practices, as well as the effects of
604 interactions between soil microbes, soil structure and organic matter on operational soil P fractions.

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References

- Abdul Wahid, O.A., Mehana, T.A., 2000. Impact of phosphate-solubilizing fungi on the yield and phosphorus-uptake by wheat and faba bean plants. *Microbiol. Res.* 155, 221-227.
- Abelson, P.H., 1999. A potential phosphate crisis. *Science* 283, 2015.
- Acosta-Martínez, V., Tabatabai, M.A., 2000. Enzyme activities in a limed agricultural soil. *Biol. Fert. Soils* 31, 85-91.
- Allen, E.R., Hossner, L.R., Ming, D.W., Henninger, D.L., 1993. Solubility and cation exchange in phosphate rock and saturated clinoptilolite mixtures. *Soil Sci. Soc. Am. J.* 57, 1368-1374.
- Amsellem, L., Brouat, C., Duron, O., Porter, S.S., Vilcinskis A., Facon B., 2017. Importance of microorganisms to macroorganisms invasions. *Adv. Ecol. Res.* 57, 99-146.
- Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J., McLaren, T.I., 2015. Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils. *Geoderma* 259, 35-44.
- Antelo, J., Arce, F., Avena, M., Fiol, S., López, R., Macías, F., 2007. Adsorption of a soil humic acid at the surface of goethite and its competitive interaction with phosphate. *Geoderma* 138, 12-19.
- Augustine, D.J., McNaughton, S.J., Frank, D.A. 2003. Feedbacks between soil nutrients and large herbivores in a managed savanna ecosystem. *Ecol. Appl.* 13(5), 1325-1337.
- Bååth, E., Frostegård, Å., Pennanen, T., Fritze, H., 1995. Microbial community structure and pH response in relation to soil organic matter quality in wood-ash fertilized, clear-cut or burned coniferous forest soils. *Soil Biol. Biochem.* 27, 229-240.
- Bünemann, E.K., 2015. Assessment of gross and net mineralization rates of soil organic phosphorus – A review. *Soil Biol. Biochem.* 89, 82-98.
- Bünemann, E.K., Condon, L.M., 2007. Phosphorus and sulphur cycling in terrestrial ecosystems, In: Marschner, P., Rengel, Z. (Eds.), *Nutrient Cycling in Terrestrial Ecosystems*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 65-92.
- Bünemann, E.K., Oberson, A., Frossard, E., 2011. *Phosphorus in action*. Springer Berlin Heidelberg, London New York.
- Bahl, G.S., Toor, G.S., 2002. Influence of poultry manure on phosphorus availability and the standard phosphate requirement of crop estimated from quantity-intensity relationships in different soils. *Bioresour. Technol.* 85, 317-322.
- Balemi, T., Negisho, K., 2012. Management of soil phosphorus and plant adaptation mechanisms to phosphorus stress for sustainable crop production: a review. *J. Soil Sci. Plant Nutr.* 12, 574-562.
- Beauchemin, S., Hesterberg, D., Chou J., Beauchemin, M., Simard, R.R., Sayers, D.E., 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-Ray absorption near-edge structure spectroscopy and chemical fractionation contribution. *J. Environ. Qual.* 32, 1809-1819.
- Begg, C.B.M., Kirk, G.J.D., Mackenzie, A.F., Neue, H.U., 1994. Root-induced iron oxidation and pH changes in the lowland rice rhizosphere. *New Phytol.* 128, 469-477.
- Behera, B.C., Singdevsachan, S.K., Mishra, R.R., Dutta, S.K., Thatoi, H.N., 2014. Diversity, mechanism and biotechnology of phosphate solubilising microorganism in mangrove – A review. *Biocatal. Agric. Biotechnol.* 3, 97-110.
- Bolan, N.S., 1991. A critical review on the role of mycorrhizal fungi in the uptake of phosphorus by plants. *Plant Soil* 134, 189-207.
- Bolan, N.S., Naidu, R., Mahimairaja, S., Baskaran, S., 1994. Influence of low-molecular-weight organic acids on the solubilization of phosphates. *Biol. Fert. Soils* 18, 311-319.
- Bowman, R., Cole, C., 1978. An exploratory method for fractionation of organic phosphorus from grassland soils. *Soil Sci.* 125, 95-101.
- Burns, R.G., Dick, R.P., 2002. *Enzymes in the Environment: Activity, Ecology, and Applications*. Marcel Dekker, Inc, New York, United States.
- Chai, W.L., Chow, J.D., Chen, C.C., 2012. Effects of modified starch and different molecular weight polyvinyl alcohols on biodegradable characteristics of polyvinyl alcohol/starch blends. *J. Polym. Environ.* 20, 550-564.

- Chang, S., Jackson, M.L., 1957. Fractionation of soil phosphorus. *Soil Sci.* 84, 133-144.
- Chathurika, J.A.S., Kumaragamage, D., Zvomuya, F., Akinremi, O.O., Flaten, D.N., Indraratne, S.P., Dandeniya, W.S., 2016. Woodchip biochar with or without synthetic fertilizers affects soil properties and available phosphorus in two alkaline, chernozemic soils. *Can. J. Soil Sci.* 96, 472-484.
- Chen, Q., Mu, H., Huang, Y., Yang, W., 2003. Influence of lignin on transformation of phosphorus fractions and its validity. *J. Agro-Environ. Sci.* 22, 745-748.
- Chesti, M.U.H., Qadri, T.N., Hamid, A., Qadri, J., Azooz, M.M., Ahmad, P., 2013. Role of bio-fertilizers in crop improvement, In: Hakeem, K.R., Ahmad, P., Ozturk, M. (Eds.), *Crop Improvement: New Approaches and Modern Techniques*. Springer US, Boston, MA, pp. 189-208.
- Chowdhury, R.B., Moore, G.A., Weatherley, A.J., Arora, M., 2015. Key sustainability challenges for the global phosphorus resource, their implications for global food security, and options for mitigation. *J. Clean. Prod.* 140, 945-963
- Çimrin, K.M., Türkmen, Ö., Turan, M., Tuncer, B., 2010. Phosphorus and humic acid application alleviate salinity stress of pepper seedling. *Afr. J. Biotechnol.* 9, 5845-5851.
- Condron, L.M., Spears, B.M., Haygarth, P.M., Turner, B.L., Richardson, A.E., 2013. Role of legacy phosphorus in improving global phosphorus-use efficiency. *Environ. Dev.* 8, 147-148.
- Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Global Environ. Chang.* 19, 292-305.
- Dai, L., Li, H., Tan, F., Zhu, N., He, M., Hu, G., 2016. Biochar: a potential route for recycling of phosphorus in agricultural residues. *GCB Bioenergy* 8, 852-858.
- Dai, S.L., Wang, R.C., Zhao, J.F., 2011. Mechanism and application of modified zeolite for nitrogen and phosphorus removal in wastewater treatment. *Water Purifi. Technol.* 30, 53-57.
- Dalai, R.C., 1977. Soil Organic Phosphorus, In: Brady, N.C. (Eds.), *Advances in Agronomy*. Academic Press, pp. 83-117.
- Damon, P.M., Bowden, B., Rose, T., Rengel, Z., 2014. Crop residue contributions to phosphorus pools in agricultural soils: A review. *Soil Biol. Biochem.* 74, 127-137.
- Das, S., Jana, T.K., De, T.K., 2014. Vertical profile of phosphatase activity in the Sundarban mangrove forest, north east coast of bay of Bengal, India. *Geomicrobiol. J.* 31, 716-725.
- DeLuca, T.H., Gundale, M.J., MacKenzie, M.D., 2009. Biochar effects on soil nutrient transformations, In: Lehmann, J., S., J. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan, London, UK, pp. 251-270.
- de Freitas, J.R., Banerjee, M.R., Germida, J.J., 1997. Phosphate-solubilizing rhizobacteria enhance the growth and yield but not phosphorus uptake of canola (*Brassica napus* L.). *Biol. Fert. Soils* 24, 358-364.
- Demeyer, A., Voundi Nkana, J.C., Verloo, M.G., 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresour. Technol.* 77, 287-295.
- Deng, S.P., Tabatabai, M.A., 1997. Effect of tillage and residue management on enzyme activities in soils: III. Phosphatases and arylsulfatase. *Biol. Fert. Soils* 24, 141-146.
- Dick, W.A., Tabatabai, M.A., 1978. Inorganic pyrophosphatase activity of soils. *Soil Biol. Biochem.* 10, 58-65.
- Ding, L., Wu, J., Xiao, H., Zhou, P., Syers, J.K., 2012. Mobilisation of inorganic phosphorus induced by rice straw in aggregates of a highly weathered upland soil. *J. Sci. Food Agric.* 92, 1073-1079.
- Dollard, M.A., Billard, P., 2003. Whole-cell bacterial sensors for the monitoring of phosphate bioavailability. *J. Microbiol. Methods* 55, 221-229.
- Dotaniya, M.L., Datta, S.C., Biswas, D.R., Meena, H.M., Kumar, K., 2014. Production of oxalic acid as influenced by the application of organic residue and its effect on phosphorus uptake by wheat (*Triticum aestivum* L.) in an inceptisol of North India. *Natl. Acad. Sci. Lett.* 37, 401-405.
- Du, Z.Y., Wang, Q.H., Liu, F.C., Ma, H.L., Ma, B.Y., Malhi, S.S., 2013. Movement of phosphorus in a calcareous soil as affected by humic acid. *Pedosphere* 23, 229-235.
- Earl, K.D., Syers, J.K., McLaughlin, J.R., 1979. Origin of the effects of citrate, tartrate, and acetate on phosphate sorption by

- soils and synthetic gels. *Soil Sci. Soc. Am. J.* 43, 674-678.
- El-Baruni, B., Olsen, S.R., 1979. Effect of manure on solubility of phosphorus in calcareous soils. *Soil Sci.* 128, 219-225.
- Espinosa, D., Sale, P., Tang, C., 2017. Effect of soil phosphorus availability and residue quality on phosphorus transfer from crop residues to the following wheat. *Plant Soil.*
- Fadaerayeni, S., Sohrabi, M., Royae, S.J., 2015. Kinetic modeling of MTO process applying ZSM-5 zeolite modified with phosphorus as the reaction catalyst. *Pet. Sci. Technol.* 33, 1093-1100.
- Fardeau, J.C., 1995. Dynamics of phosphate in soils. An isotopic outlook. *Fert. Res.* 45, 91-100.
- Fang, N.N., Wu, Z.J., Chen, L.J., 2008. The kinetic characteristics of soil phosphatase as influenced by glutathione reduced. *Chin. J. Soil Sci.* 39, 840-844.
- Fox, T.R., Comerford, N.B., McFee, W.W., 1990. Kinetics of phosphorus release from spodosols: Effects of oxalate and formate. *Soil Sci. Soc. Am. J.* 54, 1441-1447.
- Frossard, E., Achat, D.L., Bernasconi, S.M., Bünemann, E.K., Fardeau, J.C., Jansa, J., Morel, C., Rabeharisoa, L., Randriamanantsoa, L., Sinaj, S., Tamburini, F., Oberson, A., 2011. The use of tracers to investigate phosphate cycling in soil-plant systems, In: Bünemann, E., Oberson, A., Frossard, E. (Eds.), *Phosphorus in Action: Biological Processes in Soil Phosphorus Cycling*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 59-91.
- Frossard, E., Brossard, M., Hedley, M.J., Metherell, A., 1995. Reactions controlling the cycling of P in soils. In : Tiessen, H., (Eds.), *Phosphorus in the Global Environment: Transfers, Cycles and Management*. Jones Wiley & Sons, Chichester, pp. 107-137.
- García-Domínguez, M.T., García-Domínguez, J.C., López, F., de Diego, C.M., Díaz, M.J., 2015. Maximizing furfural concentration from wheat straw and *Eucalyptus globulus* by nonisothermal autohydrolysis. *Environ. Prog. Sustain. Energy* 34, 1236-1242.
- García-López, A.M., Avilés, M., Delgado, A., 2016. Effect of various microorganisms on phosphorus uptake from insoluble Ca-phosphates by cucumber plants. *J. Plant Nutr. Soil Sci.* 179, 454-465.
- Gerke, J., 2015. The acquisition of phosphate by higher plants: Effect of carboxylate release by the roots. A critical review. *J. Plant Nutr. Soil Sci.* 178, 351-364.
- Gerke, J., Hermann, R., 1992. Adsorption of orthophosphate to humic-Fe-complexes and to amorphous Fe-oxide. *Z. Pflanzenernahr. Bodenk.* 155, 233-236.
- Gianfreda, L., Ruggiero, P., 2006. Enzyme Activities in Soil, In: Nannipieri, P., Smalla, K. (Eds.), *Nucleic Acids and Proteins in Soil*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 257-311.
- Gilbert, N., 2009. Environment: The disappearing nutrient. *Nature* 461, 716.
- Giles, C.D., Hsu, P.C., Richardson, A.E., Hurst, M.R.H., Hill, J.E., 2014. Plant assimilation of phosphorus from an insoluble organic form is improved by addition of an organic anion producing *Pseudomonas* sp. *Soil Biol. Biochem.* 68, 263-269.
- Gomez, D.A., Carpena, R.O., 2014. Effect of 1-naphthaleneacetic acid on organic acid exudation by the roots of white lupin plants grown under phosphorus-deficient conditions. *J. Plant Physiol.* 171, 1354-1361.
- Grossl, P.R., Inskeep, W.P., 1991. Precipitation of dicalcium phosphate dihydrate in the presence of organic acids. *Soil Sci. Soc. Am. J.* 55, 670-675.
- Guan, L.Z., Yang, Z.H., Cao, H.L., Zhang, G.C., Zhang, Y., 2013. Effects of phytase on phosphorus release under the influence of exogenous oxalic acid. *Soil Fert. Sci. in China* 5, 19-23.
- Guppy, C.N., Menzies, N.W., Moody, P.W., Blamey, F.P.C., 2005. Competitive sorption reactions between phosphorus and organic matter in soil: a review. *Soil Res.* 43, 189-202.
- Gupta, M., Kiran, S., Gulati, A., Singh, B., Tewari, R., 2012. Isolation and identification of phosphate solubilizing bacteria able to enhance the growth and aloin – A biosynthesis of *Aloe barbadensis* Miller. *Microbiol. Res.* 167, 358-363.
- Gustafsson, J.P., Mwamila, L.B., Kergoat, K., 2012. The pH dependence of phosphate sorption and desorption in Swedish agricultural soils. *Geoderma* 189, 304-311.

- Hamdali, H., Hafidi, M., Virolle, M.J., Ouhdouch, Y., 2008. Rock phosphate-solubilizing Actinomycetes: screening for plant growth-promoting activities. *World J. Microbiol. Biotechnol.* 24, 2565-2575.
- Hariprasad, P., Niranjana, S.R., 2009. Isolation and characterization of phosphate solubilizing rhizobacteria to improve plant health of tomato. *Plant Soil* 316, 13-24.
- Havens, K.E., James, R.T., 2005. The phosphorus mass balance of Lake Okeechobee, Florida: Implications for eutrophication management. *Lake Reserv. Manage.* 21, 139-148.
- Haynes, R.J., Mokolobate, M.S., 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. *Nutr. Cycl. Agroecosyst.* 59, 47-63.
- Heathwaite, A.L., Dils, R.M., 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. *Sci. Total Environ.* 251, 523-538.
- Heckrath, G., Brookes, P.C., Poulton, P.R., Goulding, K.W.T., 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the broadbalk experiment. *J. Environ. Qual.* 24, 904-910.
- Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46, 970-976.
- Hens, M., Merckx, R., 2001. Functional characterization of colloidal phosphorus species in the soil solution of sandy soils. *Environ. Sci. Technol.* 35, 493-500.
- Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil* 237, 173-195.
- Hively, W.D., Gerard-Marchant, P., Steenhuis, T.S., 2006. Distributed hydrological modeling of total dissolved phosphorus transport in an agricultural landscape. II. Dissolved phosphorus transport. *Hydrol. Earth Syst. Sci.* 10, 263-276.
- Ho, B., Huang, E.h., Ho, T.K., Ho, T.W., 2013. Microorganisms, microbial phosphate fertilizers and methods for preparing such microbial phosphate fertilizers. Foshan Jinkuizi Plant Nutriment Co., Ltd., United States.
- Holman, I.P., Whelan, M.J., Howden, N.J.K., Bellamy, P.H., Willby, N.J., Rivas-Casado, M., McConvey, P., 2008. Phosphorus in groundwater – an overlooked contributor to eutrophication? *Hydrol. Processes* 22, 5121-5127.
- Hountin, J.A., Karam, A., Couillard, D., Cescas, M.P., 2000. Use of a fractionation procedure to assess the potential for P movement in a soil profile after 14 years of liquid pig manure fertilization. *Agric. Ecosyst. Environ.* 78, 77-84.
- Hua, Q.X., Zhou, J.M., Wang, H.Y., Chang wen, D.U., 2005. Effects of water-dissolved organic polymeric compounds application on P adsorption in red soils. *J. Soil Water Conserv.* 19, 5-8.
- Hue, N.V., 1991. Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. *Soil Sci.* 152, 463-471.
- Hunt, J.F., Ohno, T., He, Z., Honeycutt, C.W., Dail, D.B., 2007. Inhibition of phosphorus sorption to goethite, gibbsite, and kaolin by fresh and decomposed organic matter. *Biol. Fert. Soils* 44, 277-288.
- Ji, B., Hu, H., Zhao, Y., Mu, X., Liu, K., Li, C., 2014. Effects of deep tillage and straw returning on soil microorganism and enzyme activities. *The Scientific World J.* 2014, 451-493.
- Jia, W., Yan, Z., Chadwick, D.R., Kang, L., Duan, Z., Bai, Z., Chen, Q., 2015. Integrating soil testing phosphorus into environmentally based manure management in peri-urban regions: A case study in the Beijing area. *Agr. Ecosyst. Environ.* 209, 47-59.
- Jin, Y., Liang, X., He, M., Liu, Y., Tian, G., Shi, J., 2016. Manure biochar influence upon soil properties, phosphorus distribution and phosphatase activities: A microcosm incubation study. *Chemosphere* 142, 128-135.
- Jones, C.A., Jacobsen, J.S., Mugaas, A., 2007. Effect of low-rate commercial humic acid on phosphorus availability, micronutrient uptake, and spring wheat yield. *Commun. Soil Sci. Plant Anal.* 38, 921-933.
- Jones, D.L., 1998. Organic acids in the rhizosphere – a critical review. *Plant Soil* 205, 25-44.
- Jones, D.L., Oburger, E., 2011. Solubilization of Phosphorus by Soil Microorganisms, In: Bünemann, E., Oberson, A., Frossard, E. (Eds.), *Phosphorus in Action: Biological Processes in Soil Phosphorus Cycling*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 169-198.

- Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N., Smernik, R.J., Amonette, J.E., 2010. An investigation into the reactions of biochar in soil. *Soil Res.* 48, 501-515.
- Kalsi, H.K., Singh, R., Dhaliwal, H.S., Kumar, V., 2016. Phytases from *Enterobacter* and *Serratia* species with desirable characteristics for food and feed applications. *3 Biotech* 6, 64.
- Kandeler, E., Tscherko, D., Bruce, K.D., Stemmer, M., Hobbs, P.J., Bardgett, R.D., Amelung, W., 2000. Structure and function of the soil microbial community in microhabitats of a heavy metal polluted soil. *Biol. Fert. Soils* 32, 390-400.
- Karaca, A., Cetin, S.C., Turgay, O.C., Kizilkaya, R., 2010. Effects of Heavy Metals on Soil Enzyme Activities, *Soil Heavy Metals*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 237-262.
- Kaur, G., Reddy, M.S., 2015. Effects of phosphate-solubilizing bacteria, rock phosphate and chemical fertilizers on maize-wheat cropping cycle and economics. *Pedosphere* 25, 428-437.
- Khan, M.S., Zaidi, A., Ahemad, M., Oves, M., Wani, P.A., 2010. Plant growth promotion by phosphate solubilizing fungi – current perspective. *Arch. Agron. Soil Sci.* 56, 73-98.
- Khan, M.S., Zaidi, A., Ahmad, E., 2014. Mechanism of phosphate solubilization and physiological functions of phosphate-solubilizing microorganisms, In: Khan, M.S., Zaidi, A., Musarrat, J. (Eds.), *Phosphate Solubilizing Microorganisms: Principles and Application of Microphos Technology*. Springer International Publishing, Cham, pp. 31-62.
- Khan, M.S., Zaidi, A., Wani, P.A., 2007. Role of phosphate-solubilizing microorganisms in sustainable agriculture – A review. *Agron. Sustain. Dev.* 27, 29-43.
- Kim, Y.K., Jordan, D., McDonald, A.G., 1997. Effect of phosphate-solubilizing bacteria and vesicular-arbuscular mycorrhizae on tomato growth and soil microbial activity. *Biol. Fert. Soils* 26, 79-87.
- Koch, O., Tscherko, D., Kandeler, E., 2007. Temperature sensitivity of microbial respiration, nitrogen mineralization, and potential soil enzyme activities in organic alpine soils. *Global Biogeochem. Cy.* 21, 497-507.
- Lan, M., Comerford, N.B., Fox, T.R., 1995. Organic anions' effect on phosphorus release from spodic horizons. *Soil Sci. Soc. Am. J.* 59, 1745-1749.
- Li, B., Brett, M.T., 2013. The influence of dissolved phosphorus molecular form on recalcitrance and bioavailability. *Environ. Pollut.* 182, 37-44.
- Li, N., Qiao, Z.W., Hong, J.P., Xie, Y.H., Zhang, P., 2014. Effect of soluble phosphorus microbial mixed fertilizers on phosphorus nutrient and phosphorus adsorption-desorption characteristics in calcareous cinnamon soil. *Chin. J. Appl. Environ. Biol.* 20, 662-668.
- Li X, Luo L, Yang J, Li B, Yuan H., 2015. Mechanisms for solubilization of various insoluble phosphates and activation of immobilized phosphates in different soils by an efficient and salinity-tolerant *Aspergillus niger* strain An2. *Appl. Biochem. Biotech.* 175, 2755-2768.
- Liu, J., Hu, Y., Yang, J., Abdi, D., Cade-Menun, B.J., 2014a. Investigation of soil legacy phosphorus transformation in long-term agricultural fields using sequential fractionation, P K-edge XANES and solution P NMR spectroscopy. *Environ. Sci. Technol.* 49, 168-176.
- Liu, J., Yang, J., Liang, X., Zhao, Y., Cade-Menun, B.J., Hu, Y., 2014b. Molecular speciation of phosphorus present in readily dispersible colloids from agricultural soils. *Soil Sci. Soc. Am. J.* 78, 47-53.
- Liu, W., Zhang, Y., Jiang, S., Deng, Y., Christie, P., Murray, P.J., Li, X., Zhang, J., 2016. Arbuscular mycorrhizal fungi in soil and roots respond differently to phosphorus inputs in an intensively managed calcareous agricultural soil. *Sci. Rep.* 6, 24902.
- Liu, X.Z., Sun, L.Y., 2004. Effect of bentonite and phosphorus fertilizer on inorganic phosphorus transformation and their availabilities in calcareous soil. *Acta Agriculturae Nucleatae Sinica* 18, 59-62.
- Lone, A.H., Najar, G.R., Ganie, M.A., Sofi, J.A., Ali, T., 2015. Biochar for Sustainable Soil Health: A Review of Prospects

and Concerns. *Pedosphere* 25, 639-653.

- Mahajan, A., Gupta, R.D., 2009. Bio-fertilizers: Their kinds and requirement in India, Integrated Nutrient Management (INM) in a Sustainable Rice – Wheat Cropping System. Springer Netherlands, Dordrecht, pp. 75-100.
- Martens, D.A., Johanson, J.B., Frankenberger, W.T.J., 1992. Production and persistence of soil enzymes with repeated addition of organic residues. *Soil Sci.* 153, 53-61.
- Moradi, N., Sadaghiani, M.H.R., Sepehr, E., Mandoulakani, B.A., 2012. Effects of low-molecular-weight organic acids on phosphorus sorption characteristics in some calcareous soils. *Turk. J. Agric. For.* 36, 459-468.
- Mukherjee, S., Sen, S.K., 2015. Exploration of novel rhizospheric yeast isolate as fertilizing soil inoculant for improvement of maize cultivation. *J. Sci. Food Agric.* 95, 1491-1499.
- Noack, S.R., McBeath, T.M., McLaughlin, M.J., Smernik, R.J., Armstrong, R.D., 2014. Management of crop residues affects the transfer of phosphorus to plant and soil pools: Results from a dual-labelling experiment. *Soil Biol. Biochem.* 71, 31-39.
- Osorio, N.W., Habte, M., 2015. Effect of a phosphate-solubilizing fungus and an arbuscular mycorrhizal fungus on leucaena seedlings in tropical soils with contrasting phosphate sorption capacity. *Plant Soil* 389, 375-385.
- Othieno, C.O., 1973. The effect of organic mulches on yields and phosphorus utilization by plants in acid soils. *Plant Soil* 38, 17-32.
- Othman, R., Panhwar, Q.A., 2014. Phosphate-Solubilizing Bacteria Improves Nutrient Uptake in Aerobic Rice, In: Khan, M.S., Zaidi, A., Musarrat, J. (Eds.), *Phosphate Solubilizing Microorganisms: Principles and Application of Microphos Technology*. Springer International Publishing, Cham, pp. 207-224.
- Owen, D., Williams, A.P., Griffith, G.W., Withers, P.J.A., 2015. Use of commercial bio-inoculants to increase agricultural production through improved phosphorus acquisition. *Appl. Soil Ecol.* 86, 41-54.
- Pabalan, R.T., Bertetti, F.P., 2001. Cation-exchange properties of natural zeolites. *Rev. Mineral. Geochem.* 45, 453-518.
- Parab, N., Sinha, S., Mishra, S., 2015. Coal fly ash amendment in acidic field: Effect on soil microbial activity and onion yield. *Appl. Soil Ecol.* 96, 211-216.
- Patel, K.J., Singh, A.K., Nareshkumar, G., Archana, G., 2010. Organic-acid-producing, phytate-mineralizing rhizobacteria and their effect on growth of pigeon pea (*Cajanus cajan*). *Appl. Soil Ecol.* 44, 252-261.
- Pickering, H.W., Menzies, N.W., Hunter, M.N., 2002. Zeolite/rock phosphate – a novel slow release phosphorus fertilizer for potted plant production. *Sci. Hortic.* 94, 333-343.
- Quin, L.D., Borbaruah, M., Quin, G.S., Dickinson, L.C., Jankowski, S., 1998. Reaction of the hydroxy groups of zeolites with phosphorylating agents. *Heteroat. Chem* 9, 691-698.
- Randriamanantsoa, L., Frossard, E., Oberson, A., Bünemann, E.K., 2015. Gross organic phosphorus mineralization rates can be assessed in a Ferralsol using an isotopic dilution method. *Geoderma* 257-258, 86-93.
- Regelink, I.C., Weng, L., Lair, G.J., Comans, R.N.J., 2015. Adsorption of phosphate and organic matter on metal (hydr)oxides in arable and forest soil: a mechanistic modelling study. *Eur. J. Soil Sci.* 66, 867-875.
- Rietz, D.N., Haynes, R.J., 2003. Effects of irrigation-induced salinity and sodicity on soil microbial activity. *Soil Biol. Biochem.* 35, 845-854.
- Roberts, T.L., Johnston, A.E., 2015. Phosphorus use efficiency and management in agriculture. *Resour. Conserv. Recycl.* 105, Part B, 275-281.
- Sahay, R., Patra, D.D., 2014. Identification and performance of sodicity tolerant phosphate solubilizing bacterial isolates on *Ocimum basilicum* in sodic soil. *Ecol. Eng.* 71, 639-643.
- Salih, H.M., Yahya, A.I., Abdul-Rahem, A.M., Munam, B.H., 1989. Availability of phosphorus in a calcareous soil treated with rock phosphate or superphosphate as affected by phosphate-dissolving fungi. *Plant Soil* 120, 181-185.
- Santini, A., Ghelardini, L., De Pace, C., Desprez-Loustau, M.L., Capretti, P., Chandelier, A., Cech, T., Chira, D., Diamandis, S., Gaitniekis, T., Hantula, J., Holdenrieder, O., Jankovsky, L., Jung, T., Jurc, D., Kirisits, T., Kunca, A., Lygis, V., Malecka, M., Marcais, B., Schmitz, S., Schumacher, J., Solheim, H., Solla, A., Szabò, I., Tsopelas, P., Vannini, A.,

- Vettrairao, A.M., Webber, J., Woodward, S., Stenlid, J., 2013. Biogeographical patterns and determinants of invasion by forest pathogens in Europe. *New Phytol.* 197, 238-250.
- Sanyal, S.K., De Datta, S.K., 1991. Chemistry of Phosphorus Transformations in Soil, In: Stewart, B.A. (Eds.), *Advances in Soil Science*. Springer New York, New York, NY, pp. 1-120.
- Sattari, S.Z., Bouwman, A.F., Giller, K.E., van Ittersum, M.K., 2012. Residual soil phosphorus as the missing piece in the global phosphorus crisis puzzle. *P. Natl. Acad. of Sci.* 109, 6348-6353.
- Sharma, S.B., Sayyed, R.Z., Trivedi, M.H., Gobi, T.A., 2013. Phosphate solubilizing microbes: sustainable approach for managing phosphorus deficiency in agricultural soils. *SpringerPlus* 2, 587.
- Sharpley, A.N., 1985. Phosphorus cycling in unfertilized and fertilized agricultural soils. *Soil Sci. Soc. Am. J.* 49, 905-911.
- Silva, C.A.R., Sampaio, L.S., 1998. Speciation of phosphorus in a tidal floodplain forest in the Amazon estuary. *Mangroves Salt Marshes* 2, 51-57.
- Simpson, R.J., Oberson, A., Culvenor, R.A., Ryan, M.H., Veneklaas, E.J., Lambers, H., Lynch, J.P., Ryan, P.R., Delhaize, E., Smith, F.A., Smith, S.E., Harvey, P.R., Richardson, A.E., 2011. Strategies and agronomic interventions to improve the phosphorus-use efficiency of farming systems. *Plant Soil* 349, 89-120.
- Sims, J.T., Simard, R.R., Joern, B.C., 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. *J. Environ. Qual.* 27, 277-293.
- Singh, H., Reddy, M.S., 2011. Effect of inoculation with phosphate solubilizing fungus on growth and nutrient uptake of wheat and maize plants fertilized with rock phosphate in alkaline soils. *Eur. J. Soil Biol.* 47, 30-34.
- Skraly, F.A., Cameron, D.C., 1998. Purification and characterization of a *Bacillus licheniformis* phosphatase specific for D- α -Glycerophosphate. *Arch. Biochem. Biophys.* 349, 27-35.
- Someshwar, A.V., 1996. Wood and combination wood-fired boiler ash characterization. *J. Environ. Qual.* 25, 962-972.
- Song, J.F., Cui, X.Y., 2003. Analysis of organic acids in selected forest litters of Northeast China. *Int. Rev. Cytol.* 14, 285-289.
- Ström, L., Owen, A.G., Godbold, D.L., Jones, D.L., 2005. Organic acid behaviour in a calcareous soil implications for rhizosphere nutrient cycling. *Soil Biol. Biochem.* 37, 2046-2054.
- Strobel, B.W., 2001. Influence of vegetation on low-molecular-weight carboxylic acids in soil solution – a review. *Geoderma* 99, 169-198.
- Štursová, M., Baldrian, P., 2011. Effects of soil properties and management on the activity of soil organic matter transforming enzymes and the quantification of soil-bound and free activity. *Plant Soil* 338, 99-110.
- Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S.A., Dixon, L., Bol, R., MacKay, R.L., Richardson, A.E., Condon, L.M., Haygarth, P.M., 2015. Land use and soil factors affecting accumulation of phosphorus species in temperate soils. *Geoderma* 257, 29-39.
- Sun, G.F., Jin, J.Y., Shi, Y.L., 2011. Advances in the effect of humic acid and modified lignin on availability to crops. *Chin. J. Soil Sci.* 42, 1003-1009.
- Sundara, B., Natarajan, V., Hari, K., 2002. Influence of phosphorus solubilizing bacteria on the changes in soil available phosphorus and sugarcane and sugar yields. *Field Crops Res.* 77, 43-49.
- Suri, V.K., Choudhary, A.K., Chander, G., Verma, T.S., Gupta, M.K., Dutt, N., 2011. Improving phosphorus use through co-inoculation of vesicular arbuscular mycorrhizal fungi and phosphate-solubilizing bacteria in maize in an acidic alfisol. *Commun. Soil Sci. Plant Anal.* 42, 2265-2273.
- Sutton, A.L., Nelson, D.W., Hoff, J.D., Mayrose, V.B., 1982. Effects of injection and surface applications of liquid swine manure on corn yield and soil composition. *J. Environ. Qual.* 11, 468-472.
- Taghipour, M., Jalali, M., 2013. Effect of low-molecular-weight organic acids on kinetics release and fractionation of phosphorus in some calcareous soils of western Iran. *Environ. Monit. Assess.* 185, 5471-5482.
- Tahir, M.M., Khurshid, M., Khan, M.Z., Abbasi, M.K., Kazmi, M.H., 2011. Lignite-derived humic acid effect on growth of wheat plants in different soils. *Pedosphere* 21, 124-131.
- Thibaud, M.C., Morel, C., Fardeau, J.C., 1988. Contribution of phosphorus issued from crop residues to plant nutrition. *Soil*

- Sci. Plant Nutr. 34, 481-491.
- Thingstrup, I., Kahiluoto, H., Jakobsen, I., 2000. Phosphate transport by hyphae of field communities of arbuscular mycorrhizal fungi at two levels of P fertilization. *Plant Soil* 221, 181-187.
- Tian, Z., Zong, L., Niu, R., Wang, X., Li, Y., Ai, S., 2015. Recovery and characterization of lignin from alkaline straw pulping black liquor: As feedstock for bio-oil research. *J. Appl. Polym. Sci.* 132, 1-9.
- Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., Schindler, D., Schlesinger, W.H., Simberloff, D., Swackhamer, D., 2001. Forecasting agriculturally driven global environmental change. *Science (New York, N.Y.)* 292, 281-284.
- Tripathi, K.P., 2005. Effect of organic acid on phosphorus-use efficiency by clusterbean (*Cyamopsis tetragonoloba*) in arid soil of Rajasthan. *Indian J. Agric. Sci.* 75, 651-653.
- Turner, B.L., 2008. Resource partitioning for soil phosphorus: a hypothesis. *J. Ecol.* 96, 698-702.
- van Hees, P.A.W., Dahlén, J., Lundström, U.S., Borén, H., Allard, B., 1999. Determination of low molecular weight organic acids in soil solution by HPLC. *Talanta* 48, 173-179.
- Wang, Y., Chen, X., Whalen, J.K., Cao, Y., Quan, Z., Lu, C., Shi, Y., 2015. Kinetics of inorganic and organic phosphorus release influenced by low molecular weight organic acids in calcareous, neutral and acidic soils. *J. Plant Nutr. Soil Sci.* 178, 555-566.
- Wanner, B.L., 1996. Phosphorus assimilation and control of the phosphate regulon. *Escherichia coli and Salmonella* 41, 1357-1381.
- Weber, O., Delince, J., Duan, Y., Maene, L., McDaniels, T., Mew, M., Schneidewind, U., Steiner, G., 2014. Trade and Finance as Cross-Cutting Issues in the Global Phosphate and Fertilizer Market, In: Scholz, R.W., Roy, A.H., Brand, F.S., Hellums, D.T., Ulrich, A.E. (Eds.), *Sustainable Phosphorus Management: A Global Transdisciplinary Roadmap*. Springer Netherlands, Dordrecht, pp. 275-299.
- Wei, L.L., Chen, C.R., Xu, Z.H., 2010. Citric acid enhances the mobilization of organic phosphorus in subtropical and tropical forest soils. *Biol. Fert. Soils* 46, 765-769.
- Wisniewski, A.V., Liu, Q., Liu, J., Redlich, C.A., 2005. Glutathione protects human airway proteins and epithelial cells from isocyanates. *Clin. Exp. Allergy* 35, 352-357.
- Withers, P.J.A., Edwards, A.C., Foy, R.H., 2001. Phosphorus cycling in UK agriculture and implications for phosphorus loss from soil. *Soil Use and Manage.* 17, 139-149.
- Wyngaard, N., Cabrera, M.L., Jarosch, K.A., Bunemann, E.K., 2016. Phosphorus in the coarse soil fraction is related to soil organic phosphorus mineralization measured by isotopic dilution. *Soil Biol. Biochem.* 96, 107-118.
- Xiang, C.Y., Ma, Y.M., Tian, X.P., 2005. Effects of long-term culture and fertilization on the contents of forms of phosphorus and their availability in albic soil. *Acta Agronomica Sinica* 31, 48-52.
- Xu, G., Sun, J., Shao, H., Chang, S.X., 2014. Biochar had effects on phosphorus sorption and desorption in three soils with differing acidity. *Ecol. Eng.* 62, 54-60.
- Xu, G., Zhang, Y., Sun, J., Shao, H., 2016. Negative interactive effects between biochar and phosphorus fertilization on phosphorus availability and plant yield in saline sodic soil. *Sci. Total Environ.* 568, 910-915.
- Yadav, B., Verma, A., 2012. Phosphate solubilization and mobilization in soil through microorganisms under arid ecosystems, In: Alí, M. (Eds.), *The functioning of ecosystems*. Intech, Rijeka, Croatia, pp. 93-108.
- Yan, Y.P., Liu, F., Li, W., Liu, F., Feng, X.H., Sparks, D.L., 2014. Sorption and desorption characteristics of organic phosphates of different structures on aluminium (oxyhydr)oxides. *Eur. J. Soil Sci.* 65, 308-317.
- Yang, M., Lin, J., Zhan, Y., Zhu, Z., Zhang, H., 2015. Immobilization of phosphorus from water and sediment using zirconium-modified zeolites. *Environ. Sci. Pollut. Res. Int.* 22, 3606-3619.
- Yu, X., Liu, X., Zhu, T.H., Liu, G.H., Mao, C., 2011. Isolation and characterization of phosphate-solubilizing bacteria from walnut and their effect on growth and phosphorus mobilization. *Biol. Fert. Soils* 47, 437-446.
- Yuan, H.M., Blackwell, M., McGrath, S., George, T.S., Granger, S.J., Hawkins, J.M.B., Dunham, S., Shen, J.B., 2016.

- Morphological responses of wheat (*Triticum aestivum* L.) roots to phosphorus supply in two contrasting soils. J. Agric. Sci. 154, 98-108.
- Zeng, X., Ma, Y., Ma, L., 2007. Utilization of straw in biomass energy in China. Renew. Sust. Energ. Rev. 11, 976-987.
- Zhang, F., Römheld, V., Marschner, H., 1989. Effect of zinc deficiency in wheat on the release of zinc and iron mobilizing root exudates. Z. Pflanzenernahr. Bodenk. 152, 205-210.
- Zhang, Z.Y., Fu, F.L., Gou, L., Wang, H.G., Li, W.C., 2010. RNA interference-based transgenic maize resistant to maize dwarf mosaic virus. J. Plant Biol. 53, 297-305.
- Zhou, X.B., Hong, J.P., Xie, Y.H., 2005. Effects of phosphorous bacteria fertilizer on phosphorus validity of calcareous soil. J. Soil Water Conserv. 19, 70-73.

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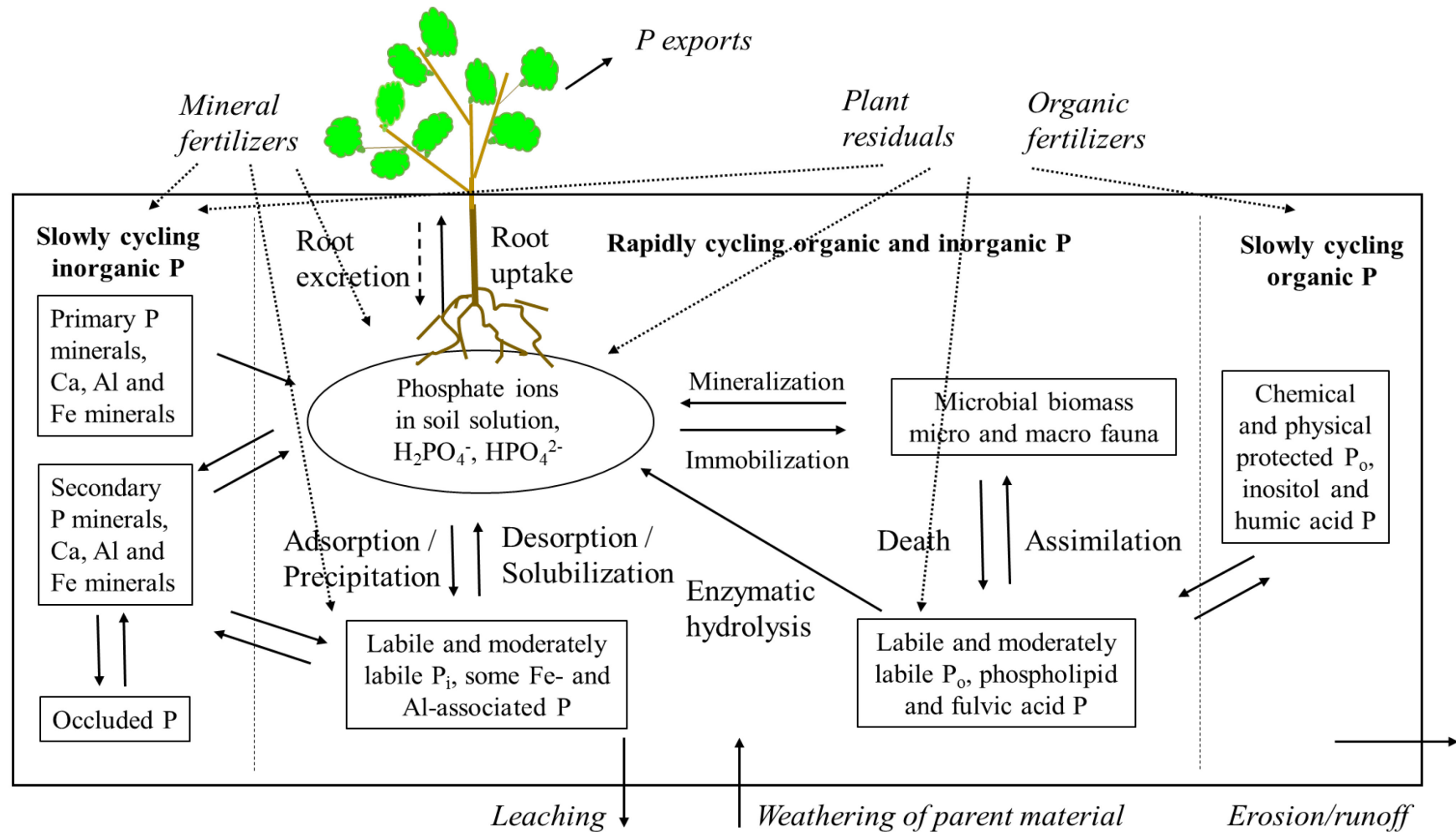
2 **Table 1**

3 Common phosphorus minerals found in acid, neutral and calcareous soils and their equilibrium dissolution reactions. Modified from Gustafsson et al. (2012) and Yadav and Verma (2012).

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Soil type	Minerals	Chemical formula	Equilibrium dissolution reaction
Acid soils	Strengite	$\text{FePO}_4 \cdot 2 \text{H}_2\text{O}$	$\text{FePO}_4 \cdot 2 \text{H}_2\text{O}(\text{s}) \leftrightarrow \text{Fe}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$
	Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}(\text{s}) \leftrightarrow 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$
	Variscite	$\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$	$\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}(\text{s}) \leftrightarrow \text{Al}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$
Neutral and calcareous soils	B-tricalcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2(\text{s}) \leftrightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$
	Dicalcium phosphate	CaHPO_4	$\text{CaHPO}_4(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{PO}_4^{3-} + \text{H}^+$
	Dicalcium phosphate dihydrate	$\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{PO}_4^{3-} + \text{H}^+ + 2\text{H}_2\text{O}$
	Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3 \text{F}$	$\text{Ca}_5(\text{PO}_4)_3 \text{F}(\text{s}) \leftrightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{F}^-$
	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3 \text{OH}$	$\text{Ca}_5(\text{PO}_4)_3 \text{OH} \leftrightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$
	Octacalcium phosphate	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}$	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O} \leftrightarrow 8\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 6\text{H}_2\text{O}$

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Fig. 1. The physicochemical and biological transformations of P in soil-plant and soil-solution systems (modified after Frossard et al., 2011). P_o: organic P; P_i: inorganic P. The dotted arrow

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indicates external phosphorus input and the solid arrow shows the internal phosphorus transformations.

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10 **Table 2**

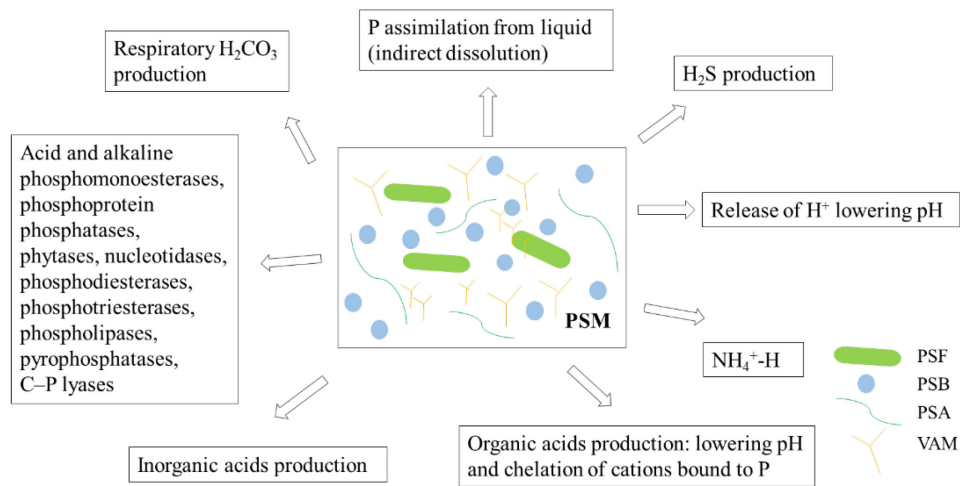
11 Examples of common phosphate solubilizing microorganisms in agricultural soils (Behera et al., 2014; Bolan, 1991;
12 Thingstrup et al., 2000).

Microorganism	Biological taxa
PSB	<i>Achromobacter, Aereobacter, Agrobacterium, Alcaligenes, Arthrobacter, Aspergillus, Azotobacter, Bacillus, Bradyrhizobium, Burkholderia, Chromobacterium, Enterbacter, Erwinia, Escherichia, Flavobacterium, Klebsiella, Micrococcus, Pantoea agglomerans, Pseudomonas, Rhizobium, Salmonella, Serratia, Thiobacillus,</i>
PSF	<i>Alternaria, Arbuscular mycorrhiza, Aspergillus, Fusarium, Helminthosparium, Penicillium, Rhizopus, Sclerotium</i>
PSA	<i>Streptomyces, Nocardia</i>

13 PSF: phosphate solubilizing fungi; PSB: phosphate solubilizing bacteria; PSA: phosphate solubilizing actinomycetes.

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18 **Fig. 2** Potential mechanisms for the solubilization of insoluble P by phosphate solubilizing microorganisms (PSMs). PSF:
19 phosphate solubilizing fungi; PSB: phosphate solubilizing bacteria; PSA: phosphate solubilizing actinomycete; VAM:
20 vesicular-arbuscular mycorrhizae (modified after Khan et al., 2010).

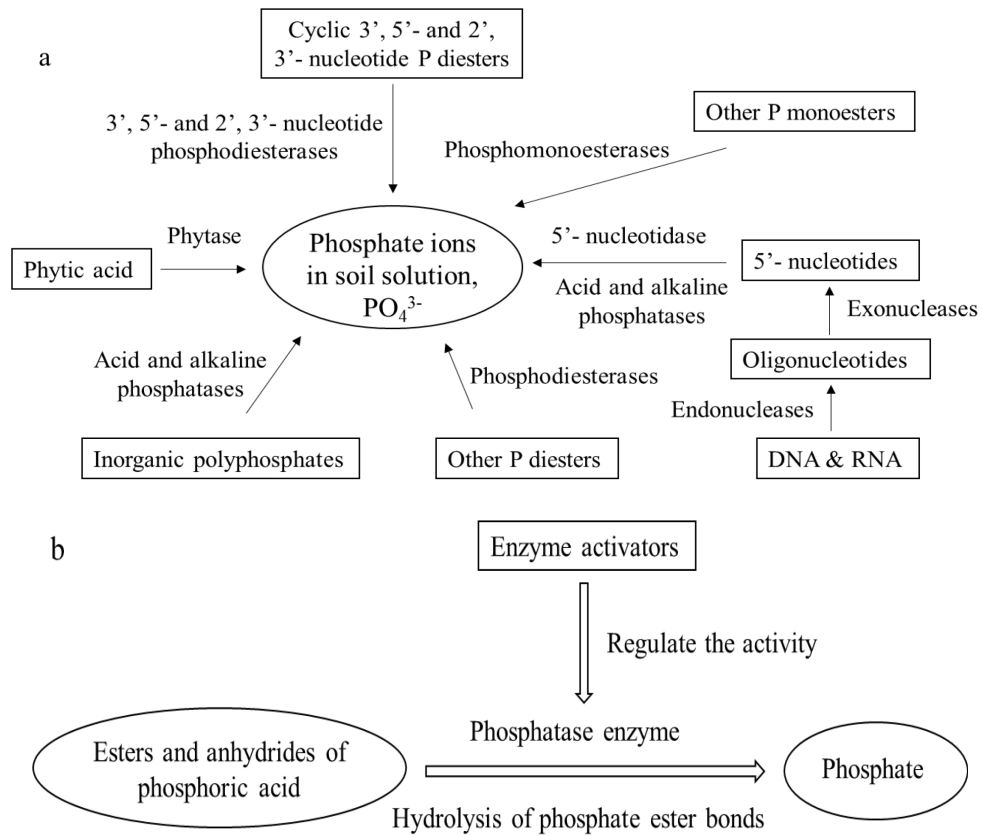
21 **Table 3**

22 PSM isolated from different soils and their effects on soil available phosphorus (AP) and the equivalent application rate of phosphate fertilizers (PF) when PSM and PSM fertilizers are applied.
 23 PSMF: phosphate solubilizing microbial mixed fertilizers; RP: rock phosphate; PBF: phosphate solubilizing bacteria fertilizers; VAM: vesicular arbuscular mycorrhizae; PSB: phosphate
 24 solubilizing bacteria; PSF: phosphate solubilizing fungi; AMF: arbuscular mycorrhizal fungi; CGMCC: hina General Microbiological Culture Collection Center of China Administration
 25 Committee for Culture Collection of Microorganisms.

Microorganism	Strains	Isolated area	Experiment soil	Crop	P activation response on soil	References
PSB	<i>Enterobacter agglomerans</i> <i>Glomus etunicatum</i>	Purchased	Silt loam (pH=5.6), Mexico	Tomato	P concentration increased by 10.5-31.6%; mixed higher	(Kim et al., 1997)
	<i>Fusarium oxysporum</i> <i>Alternaria solani</i>	Obtained from the culture collection of University of Mysore, India	Sandy loam soil (pH=6.9), India	Tomato	AP increased by 26.7-183.3%	(Hariprasad and Niranjana, 2009)
	<i>Pseudomonas chlororaphis</i> <i>Bacillus cereus</i> <i>Pseudomonas fluorescens</i>	Walnut production areas from Sichuan, China	Sandy loam soil (pH=7.1), China	Walnut	AP increased by 9.7-50.7%; mixed higher; <i>B. cereus</i> had no effect	(Yu et al., 2011)
PSF	<i>Pseudomonas synxantha</i> <i>Burkholderia gladioli</i> <i>Enterobacter hormaechei</i> <i>Serratia marcescens</i>	Rhizosphere of <i>Aloe</i> <i>barbadensis</i> from Indian	Unsterile loamy soil (pH=7.8), India	<i>Aloe barbadensis</i>	AP increased by 230-403%	(Gupta et al., 2012)
	<i>Ocimum basilicum</i>	Sodic soil sites from Sultanpur, India	Sodic soils (pH=9.3), India	Sweet basil (<i>O. basilicum</i>)	Residual fertility P conversion rate increased by 17.2-32.1%	(Sahay and Patra, 2014)
PSF	<i>Penicillium oxalicum</i>	Mine landfills of RP from Udaipur, India	Sandy loam soil (pH=8.1), India	Wheat and maize	AP increased by 35.1-85.3% for wheat and 106.3-127.7% for maize	(Singh and Reddy, 2011)
	<i>Candida tropicalis</i>	Crops rhizospheric soil in Birbhum, West Bengal, India.	Silty clay soil (pH=5.2), India	Maize	PF application rate reduced by 34.9-467.4%	(Mukherjee and Sen, 2015)

PSB & VAM	<i>Aspergillus niger</i> <i>A. fumigatus</i> <i>Penicillium pinophilum</i>	Plant rhizosphere in soils from Ismailia and South Sinai Governorates	Sandy soil (pH=8.4), Egypt	Wheat and faba bean	AP increased by 12.1-194.2% for wheat and 15.9-208.3% for faba bean	(Abdul Wahid and Mehana, 2000)
PSB & PSF	<i>Pantoea cyripedii</i> <i>Pseudomonas plecoglossicida</i>	Rhizospheric soil of <i>Stevia rebaudiana</i> from Pojewa, India	Sandy loam (pH=8.3), India	Maize-wheat Cropping	P absorption increased by 41.2-117.6% for maize and 41.05-41.8% for wheat	(Kaur and Reddy, 2015)
PSB & PSF	<i>Bacillus subtilis</i> QST713 <i>Trichoderma asperellum</i> T34	Purchased	Siliceous and calcareous growing media (pH=7.8)	Cucumber	AP increased by 16.8% (Fungi T34) and 39.85 (Bacteria QST713) in siliceous soil; 6.6% (T34) and 60.7% (QST713) in calcareous soil	(García-López et al., 2016)
PSB & AMF	<i>Mortierella</i> sp. <i>Claroideoglomerus claroideum</i>	Andisol from Hawai'i, America	Sandy loam (pH=5.4), Clay loam (pH=4.9), America	<i>Leucaena leucocephala</i>	Varied from soil type; Mixed higher	(Osorio and Habte, 2015)
PBF	<i>Penicillium</i> sp. <i>Aspergillus foetidus</i>	Rhizospheric soil of tomato, eggplant and cucumber, Iraq	Silt clay soil (pH=8.2), Iraq	Typical torrifuvent	AP increased by 24.2-138.6%	(Salih et al., 1989)
	AB-233	Purchased	Loamy soil, (pH=7.4), China	Soybean	AP increased by 11.8-57.1%	(Zhou et al., 2005)
PSMF	<i>Pseudomonas</i> <i>Rahnella</i> <i>Aspergillus niger</i> <i>Penicillium</i>	Purchased	Clay soil (pH=8.1), China	Rape	AP increased by 1.84-15.44%; Mix PSB > mixed PSF, both higher than mixed PSB with PSF	(Li et al., 2014)
PSB & PSMF	<i>Bacillus subtilis</i> <i>Bacillus licheniformis</i>	Depository in CGMCC	Silt clay soil (pH was not	Corn Rice	P absorption increased by 25.93-50.56% for corn and	(Ho et al., 2013)

	<i>Streptomyces cellulosae</i>		mentioned),		18.58-44.09% for rice	
	<i>Aspergillus versicolor</i>		India			
PSF & PSMF	<i>Bacillus megatherium</i> var <i>Phosphaticum</i>	Purchased	Clay soil (pH was not mentioned), India	Sugarcane	PF application rate reduced by 25%	(Sundara et al., 2002)



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30 **Fig. 3.** (a) Phosphate regeneration through enzymatic decomposition of various P compounds in soil (modified after Burns &

31 Dick, 2002); (b) The role of phosphatase enzymes in mineralizing P_o to phosphate and enzyme activators activating

32 phosphatase enzymes.

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36 **Table 4**

37 The main low molecular weight organic acids identified in agricultural soils (Gerke, 2015; Jones, 1998; Song and Cui, 2003;

38 Strobel, 2001; van Hees et al., 1999).

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Classification	Carboxylate	Organic acid	Molecular formula	Molecular mass	Organic acid	Molecular formula	Molecular mass
Aliphatic	Monobasic	Formic	HCOOH	46.03	Lauric	C ₁₁ H ₂₃ COOH	200.32
		Acetic	CH ₃ COOH	60.05	Palmitic	C ₁₅ H ₃₁ COOH	256.42
		Propionic	C ₂ H ₅ COOH	74.08	Linolenic	C ₁₇ H ₂₉ COOH	278.44
		Butyric	C ₃ H ₇ COOH	88.11	Linoleic	C ₁₇ H ₃₃ COOH	282.47
		Valeric	C ₄ H ₉ COOH	102.14	Oleic	C ₁₇ H ₃₃ COOH	282.47
		Pyruvate	CH ₃ COCO ₂ H	88.06	Arachidic	C ₁₉ H ₃₉ COOH	312.53
		Glycolic	CH ₂ OHCOOH	76.05	Carnaubic	C ₂₃ H ₄₇ COOH	368.62
		Lactic	CH ₃ CH(OH)COOH	90.08			
	Dicarboxylic	Oxalic	HOOC ₂ COOH	90.04	Maleic	C ₄ H ₄ O ₄	116.08
		Malonic	HOOCCH ₂ COOH	104.06	Fumaric	C ₄ H ₄ O ₄	116.08
		Succinic	HOOC(CH ₂) ₂ COOH	118.09	Ketoglutaric	C ₅ H ₆ O ₅	146.11
		Tartaric	HOOC(CHOH) ₂ COOH	150.09	Aconitic	C ₆ H ₆ O ₆	174.11
		Malic	HOOCCHOHCH ₂ COOH	134.09			
	Tribasic	Oxalacetic	C ₄ H ₄ O ₅	132.07	Citric	C ₆ H ₈ O ₇	192.43
	Aromatic	Monobasic	Benzoic	C ₆ H ₅ -COOH	122.12	Sinapic	C ₁₁ H ₁₂ O ₅
Phenylacetic			C ₆ H ₅ -CH ₂ COOH	136.15	Phthalic	C ₈ H ₆ O ₄	166.13
Cinnamic			C ₆ H ₅ -CH=CH-COOH	148.16	P-coumaric	C ₉ H ₈ O ₃	164.16
Ferulic			C ₁₀ H ₁₀ O ₄	194.19	Salicylic	C ₇ H ₆ O ₃	138.12
2-Naphthoic			C ₁₁ H ₈ O ₂	172.18	Gallic	C ₇ H ₆ O ₅	170.10
Indole-3-acetic			C ₁₀ H ₉ NO ₂	175.18	Vanillic	C ₈ H ₈ O ₄	168.15
P-phenylcinnamic			C ₁₅ H ₁₂ O ₂	224.25	Syringic	C ₉ H ₁₀ O ₅	198.18
P-hydroxybenzoic			C ₇ H ₆ O ₃	138.12	Shikimic	C ₇ H ₁₀ O ₅	174.16
3-Phenylpropanoic	C ₉ H ₁₀ O ₂	150.17					
Amino acid		NH ₂ -CH(R)-COOH*					

40 *R indicates R-groups in amino acids. The R-groups give the amino acids their physical-chemical characteristics such as

41 polarity (hydrophobic or hydrophilic) and charge (acidic or positive versus basic or negative).

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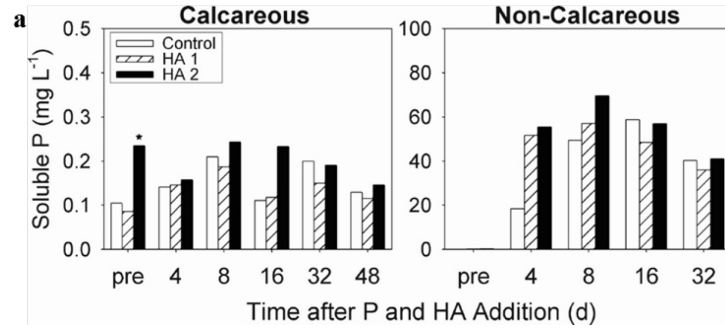
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Table 5

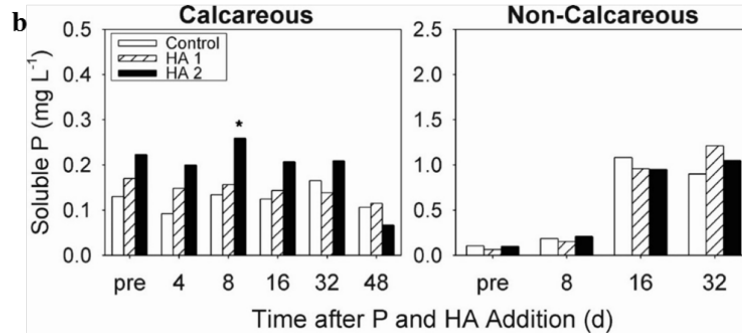
The type and concentration of low molecular weight organic acids added to different types of agricultural soil and their effects on P transformation.

LMWOAs	Concentration	Soil type	Soil area	Effects	References
Citrate and Tartrate acid	0.1-0.5 mmol L ⁻¹	Black loam and gravelly clay soil	Egmont, Okaihau in New Zealand	Fe and Al sorb P _i : citrate (50% reduction), tartrate (20% reduction).	(Earl et al., 1979)
Acetic, formic, lactic, citric, malic, oxalic, tartaric acid	10 mmol kg ⁻¹	Silt loam derived from volcanic ash and clay loam from loess	Patua, Italy; Tokomaru, New Zealand	Decrease the adsorption of P by soils: tricarboxylic acid > dicarboxylic acid > monocarboxylic acid.	(Bolan et al., 1994)
Acetic acid	0.2, 2 mmol kg ⁻¹	Arid soil	Rajasthan, India	No effect of acetic acid application alone on the Olsen-P. Having an effect when applied along with fertilizers P.	(Tripathi, 2005)
Oxalic, citric acid Malic acid	10 mmol kg ⁻¹	Plantation and natural forest soils	Subtropical and tropical areas in Australia	Solubilizing of P _i : citric acid, 34.7%, malic and oxalic, no significant differences.	(Wei et al., 2010)
		Vegetable, garlic, and potato land use calcareous soils	Hamedan, Iran	Malic and citric acids had no effect on Fe-Al oxide fraction, but oxalic acid significantly reduced this fraction.	(Taghipour and Jalali, 2013)
		Calcareous clay soil, neutral silty clay loam, and acidic silty clay soil	Luancheng (wheat), Shenyang (corn), and Taoyuan (rice), China	P _o release induced by low molecular weight organic acids is ascribed to their ability to mobilize NaHCO ₃ -P _o rather than to chelate cations (i.e., Fe ³⁺ , Al ³⁺) bound to P _o in soil.	(Wang et al., 2015)
α-naphthaleneacetic acid	10 ⁻⁴ , 10 ⁻⁵ , 10 ⁻⁶ mmol L ⁻¹	Nutrient solution	Spain	The secretion of common organic acid increased by proteoid roots of white lupin.	(Gomez and Carpena, 2014)

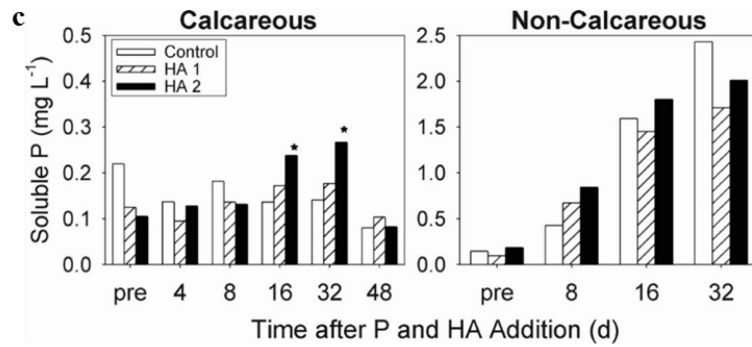
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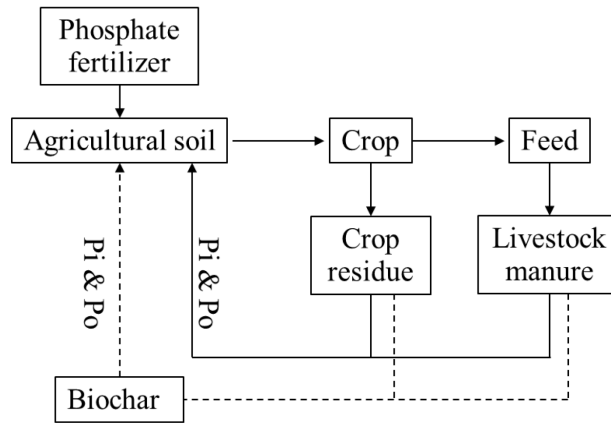
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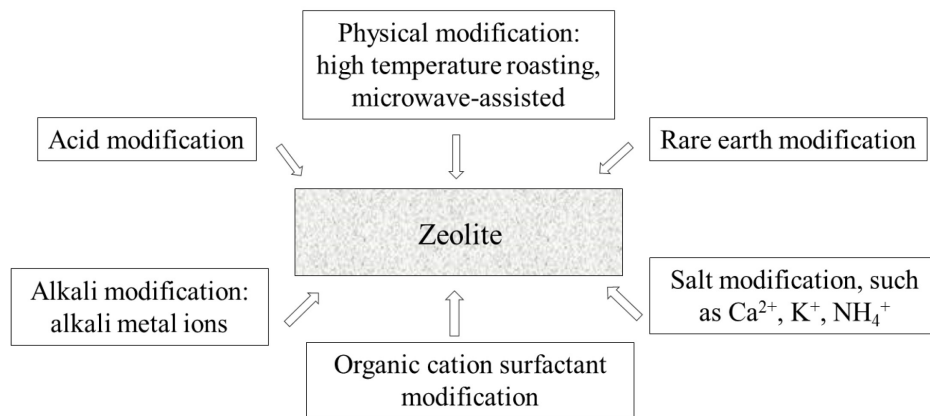
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Fig. 4. (a) Water-soluble P concentrations 1.9 cm to the side of a mono-ammonium phosphate (MAP) fertilizer band, uncoated (control) or coated with a humic acid (HA) product (HA 1 or HA 2). The pre-fertilization sample (pre) was collected less than 1 h prior to fertilization; (b) Water-soluble P concentrations 3.8 cm to the side of a MAP band; (c) Water-soluble P concentrations 3.8 cm below a MAP band. *Significant difference from control $p < 0.05$ (Jones et al., 2007, original images with permission from Taylor & Francis Group).



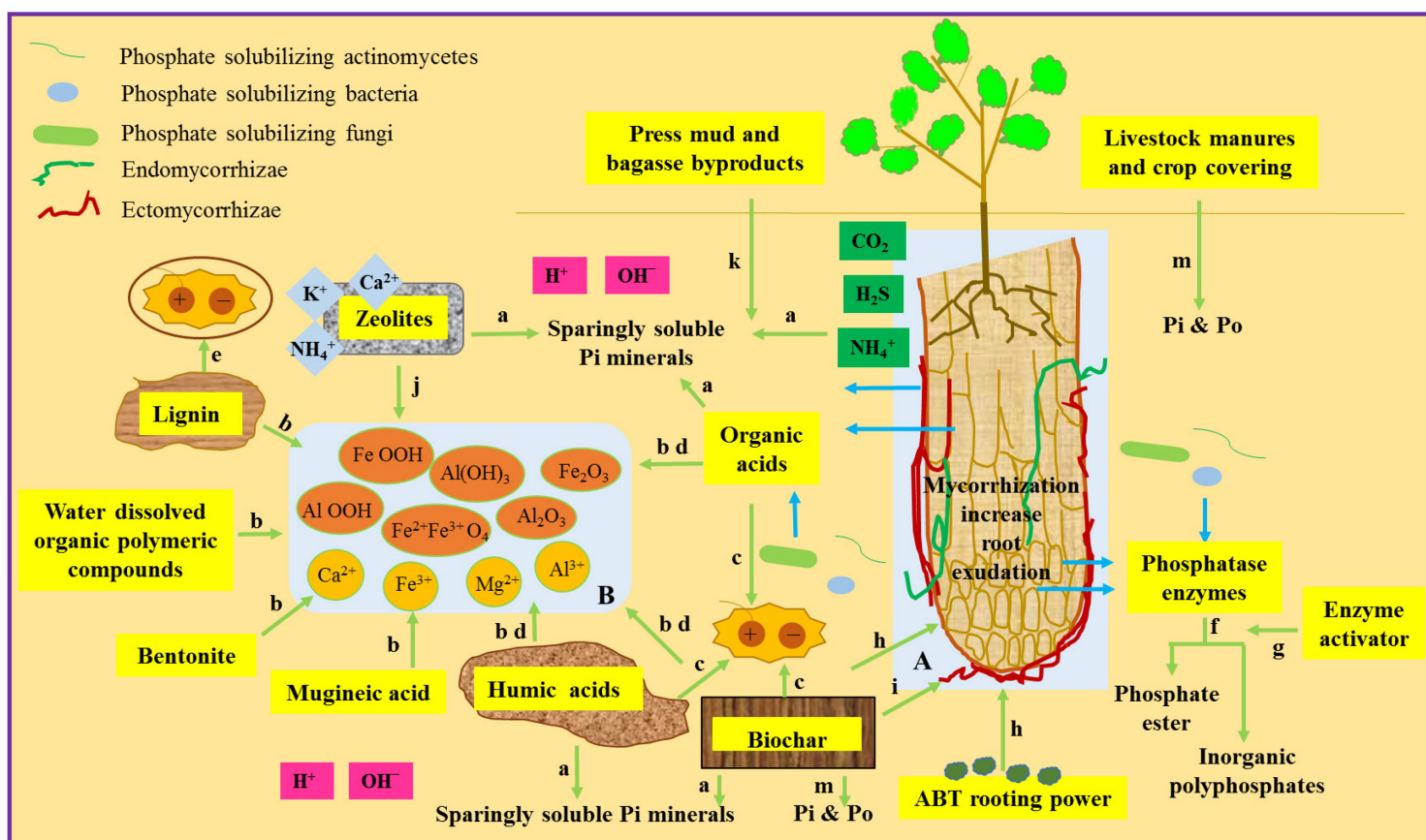
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Fig. 5. Schematic illustration of the recycling of phosphorus between agricultural residues and soil, including the application of biochar. P_i is inorganic phosphorus, P_o is organic phosphorus.



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Fig. 6 Schematic summary of different approaches to modify zeolite.



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Fig. 7. Illustration of different mechanisms involved in the solubilization and mineralization of insoluble P by P activators in soils. (A) Enlarged drawing of root; (B) Metal ions and metal oxides which easily form P-O-M compounds in soil. (a) Effect of soil pH on sparingly soluble P_i (inorganic phosphorus) minerals; (b) Formation of complexes with (B) to release phosphate; (c) Competition for sorption sites with phosphate in soil; (d) Adsorption of metal and metal oxides to release phosphate; (e) Sheltering sorption sites in soil; (f) Hydrolysis of P_o (organic phosphorus) and P_i; (g) Strengthening of phosphatase enzyme activity; (h) Promotion of root growth; (i) Biochar increasing mycorrhizal-plant associations; (j) Exchange-induced dissolution; (k) Production of organic acids by microbial processes; (m) P_o & P_i retention and release. ABT rooting powder: have the ability to promote rooting and to increase the survival rate of plants under abiotic stress.

Table 6

Summary of the advantages and disadvantages of the P activators described in this review.

P activators	Advantages	Disadvantages
Phosphate solubilizing microorganisms	Economically feasible; Activate both P_o and P_i ; High activation effect	Complex screening and domesticating process; Easily affected by environment; Time consuming; Potential invasions
Phosphatase enzyme and enzyme activators	Mineralize complex P_o compounds	High specificity; Easy to be inactive
Low molecular weight organic acid	Fast responding speed; High activation effect; Amend soil salinization	Cause soil acidification
Humic acid and lignin	Increase soil organic matter; Improve soil conditions	May sorb phosphate itself
Crop residue and manure	Biodegradable, abundant resources found in nature; Low processing costs; Release both P_i and P_o ; Secondary nutrient supply	Bring soil pests; Contain microbial populations; Easily lost in runoff
Biochar	Improve soil conditions; Release P_i and P_o ; Good for microorganisms	Preparation process is complex; Mixed reports on activation effect
Zeolites and others	Reuse and recycle waste resources	Seldom used in soil; Non-indigenous in soil; May bring heavy metal to soil