



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

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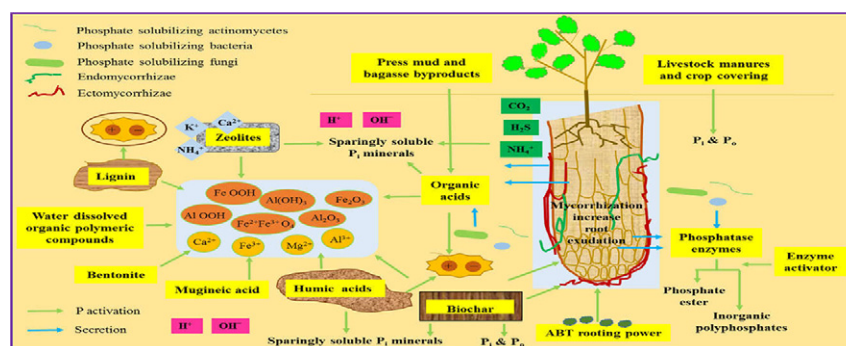
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HIGHLIGHTS

- Legacy phosphorus accumulated in soils is a large secondary global phosphorus source.
- Phosphorus activators accelerate and strengthen the phosphorus transformation process.
- Phosphorus activators can activate inorganic and organic phosphorus.
- Extensive research is needed to understand the interactions of phosphorus activators with natural soil.

GRAPHICAL ABSTRACT



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ABSTRACT

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

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1. Introduction

Phosphorus (P) is a major limiting nutrient for crop growth in many agroecosystems and is indispensable in several physiological and biochemical processes (Simpson et al., 2011). Consequently, the availability of P controls the growth and development of all crops (Wyngaard

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et al., 2016). Plants assimilate P (predominantly as negatively charged primary and secondary orthophosphate ions) from the soil solution. Although most soils contain considerable total P stocks, only a small fraction (<1%) of the total inorganic P (P_i) and organic P (P_o) is dissolved at any given time (Bünemann, 2015). The concentration of P in soil solution remains really low, about 0.05–0.30 $\mu\text{g P mL}^{-1}$ (Bolan, 1991). It is estimated that crop productivity is limited by P deficiency on >40% of the world's arable land (Balemi and Negisho, 2012). P limitations are also a major productivity constraint in many natural (Augustine et al., 2003) and managed (Bünemann et al., 2011) grassland systems. Although other constraints may also limit productivity, soil P often needs to be replenished repeatedly to satisfy plant demand, in part because it is quickly removed from the dissolved (plant available) form by sorption, precipitation and microbial immobilization (Roberts and Johnston, 2015) or is lost through surface runoff (in particulate and dissolved forms), subsurface flow (leaching and throughflow via the soil matrix and macropores), drain flow and even groundwater which may accelerate the eutrophication of P sensitive waters (Heathwaite and Dils, 2000; Hively et al., 2006; Holman et al., 2008; Sims et al., 1998).

Historically, chemical fertilizers, such as manufactured water-soluble phosphate have played a significant role in replenishing this P pool. However, these fertilizers are derived from mined rock-phosphate which has a finite (and rapidly diminishing) supply (Gilbert, 2009). Some studies claim that, at current rates of extraction, global commercial phosphate reserves will be depleted in 50–100 years (Abelson, 1999; Sattari et al., 2012). Opinions vary about the reliability of these data because they are principally based on second and third hand information and the figures change all the time (Gilbert, 2009). However, it is likely that remaining reserves will have increasingly lower quality and will be increasingly more costly to extract, which means that the supply of high quality phosphate fertilizer will also become progressively more restricted (Cordell et al., 2009). The rising demand for agricultural commodities in developing countries has put increasing pressure on land resources for higher yields, with associated growth in the demand for phosphate fertilizers (Weber et al., 2014). This realization (sometimes described as a “potential phosphate crisis”) is pushing global fertilizer prices up (Chowdhury et al., 2017).

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

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

Unfortunately, most legacy P is not available for plants to absorb easily. However, it may be possible to manipulate soils to increase the availability of this P for crops. The aims of this review are to clarify our current understanding of the cycling and transformation of legacy P in agricultural soils and to present findings from the published literature

about so-called “P activators”. Furthermore, we evaluate the contribution of P activators to soil legacy P availability, assess the advantages and disadvantages of different P activator classes and summarize the key mechanisms involved.

2. The forms and mobility of soil P

More than 80% of P applied as fertilizer can become unavailable for plant uptake shortly after application via sorption, precipitation (typically by reaction with Al^{3+} and Fe^{3+} in acidic soils and Ca^{2+} in calcareous soils: Table 1) or microbial immobilization (Gustafsson et al., 2012; Roberts and Johnston, 2015; Yadav and Verma, 2012). To take full advantage of legacy P, it is necessary to understand the long-term dynamics of this P in soil (Liu et al., 2014a).

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

The total P in top soils (0–15 cm) typically ranges from 50 to 3000 mg P kg^{-1} , depending on parent material, soil texture, vegetation cover and soil management history (Sanyal and De Datta, 1991). According to Stutter et al. (2015), based on 32 soils from the United Kingdom, arable soils tend to be dominated by ortho- P_i with orthophosphate monoester species associated with strongly sorbing Al and Fe soil surfaces. Intensive grasslands tend to be dominated by orthophosphate monoesters and as grazing becomes more extensive labile orthophosphate diesters, associated with labile soil organic matter and microbial turnover, dominate. The diversity of P species in less intensively managed soils can be viewed as a positive indicator of ecosystem function and diversity.

P_i generally accounts for 60–80% of total P in agricultural soils (predominantly in minerals). The total P content is usually at least one order of magnitude larger than the amount of P that rapidly cycles through the soil-plant system and two to three orders of magnitude larger than the amount of P present as plant-available P_i in the soil solution (HPO_4^{2-} or H_2PO_4^-) (Frossard et al., 1995). The dominant form of orthophosphate ion present in the soil is pH dependent. At pH 4–5, orthophosphate usually exists as H_2PO_4^- ions but as pH increases, first HPO_4^{2-} ions and then PO_4^{3-} ions become more dominant (Yadav and Verma, 2012).

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

The concentration of P in the soil solution is primarily controlled by adsorption/desorption equilibria between labile P_i in the solid phase

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