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Phosphorus × Other Plant Nutrient Interactions, Reaction Products, Anion Exchange and Phosphate Fixation in Soil and Strategies to Increase Availability of the Native and Applied P to Crop Plants-A Mini Review and Critique

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ABSTRACT

Phosphorus is a major plant nutrient obtained from non-renewable phosphate rock, which is not much available in India. Over and above in this its recovery efficiency in crops hardly exceeds 15-20 per cent. Utmost care is therefore required in its use. Phosphorus applied to soil gets fixed by the formation of insoluble reaction products by reacting with Fe and Al in acid soils and with calcium in saline and alkaline soils. Two techniques used for identification of reaction products are X-ray diffraction and solubility product principle. In addition, phosphate ions are also held on Fe and Al hydroxides by anion exchange. The reaction products identified are variscite and strengite minerals in acid soils and dicalcium phosphate and hydroxy apatite in calcareous soils. Methods to increase phosphorus recovery by crops include: 1) addition of organic matter to soils; 2) addition of sulphur to compost or to ground rock phosphate or directly to soil and use of phosphorus solubilising organisms including VAM/AM along with ground rock phosphate.

Key words: Anion exchange, Phosphate fixation, Phosphorus, Reaction products.

Phosphorus is the costliest plant nutrient in crop production and is obtained from a non-renewable source, the phosphate rock, at present known stocks, which in the world may not last more than 350 years (Cordell *et al.*, 2009). Phosphate availability is more important for India, because it has no indigenous good quality phosphate rock deposits and has to depend mostly on imports. As a contrast the nutrient use efficiency of P is only 10-15 per cent in most crops, the remaining P is fixed in the soil and becomes lesser and lesser available to crop plants as the period from its application advances. Phosphorus use efficiency in crop production needs more attention than N, because N fertilizers are made from an infinite source, the atmospheric nitrogen. To make this possible a better understanding of interactions of P with other plant nutrients and other elements in soil is necessary.Of the fourteen essential plant nutrients taken up from soil, four (P, S, Cl and Mo) are absorbed by plants as anions ($H_2PO_4^-$, SO_4^{2-}, Cl^- and MoO_4^{2-}), eight as cations (K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, $Mn^{2+/3+}$, Zn^{2+}, Cu^+, Ni^+), one (N) both as a cation (NH_4^+) and an anion (NO_3^-) and one (B) anion (BO_3^-) and as boric acid molecule $[B(OH)_4)]^-$ (Prasad, 2007). The anionic nutrients react with cations in the soil. Nitrates, chlorides and most sulphates form water soluble compounds and application of the fertilizers containing these offer no problem in their absorption by plants. However, water soluble phosphate fertilizers single/ordinary superphosphate (SSP/OSP) and triple/concentrated superphosphate (TSP/CSP) containing monocalcium phosphate ($Ca(H_2PO_4)_2$) and mono ammonium (MAP) or diammonium phosphate (DAP), when applied to soils react with cations present in soil solution and form less water soluble compounds creating problems in the absorption of P and associated cation.

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Reactions with primary nutrients (N and K)

N, P and K are considered as primary nutrients, because they are removed by the crop in the largest amounts and have to be added during each crop season. Application of N along with P increases P uptake by wheat (Mehta *et al.*, 1963). One of the factors could be acid forming property of N fertilizers (Prasad and Power, 1997), which increases P availability in soils. Similarly an application of 60 kg K/ha increased P uptake in wheat to 24.5 kg P/ha from 16.6 kg P/ha in check plots (Jat *et al.*, 2013). A combined application of NPK at their optimum rates gives the highest yield and nutrient uptake and is the basis of balanced fertilization (Prasad *et al.*, 2004).

Reactions with secondary nutrients (Ca and Mg)

When ammonium phosphate is applied to soil, the following reactions take place, because in most cultivated soils calcium is the dominant cation present in large amounts.

	+Ca, H_2PO_4	+Ca	+2Ca, PO_4	+ 7Ca, 4 PO_4, 2OH
$NH_4H_2PO_4 \rightarrow$	$Ca(H_2PO_4)_2 \rightarrow$	$CaHPO_4 \rightarrow$	$Ca_3(PO_4)_2 \rightarrow$	$3Ca_3(PO_4)_2.Ca(OH)_2$
$-NH_4$	$-HPO_4$	$-H$		
Mono-ammonium Phosphate (MAP)	Mono-calcium Phosphate (MCP)	Diclacium Phosphate (DCP)	Tricalcium Phosphate (TCP)	Hydroxy appatite (HA)

MAP is first changed to MCP, which with more Ca changes to DCP and then TCP and ultimately to HA. MAP and MCP are water soluble, while DCP is ammonium citrate soluble. TCP and HA are not water or citrate soluble. As per the convention the water + citrate soluble P in a fertilizer is considered available P. Water soluble P is the one extracted by distilled water. The residue left is then extracted by 1 N ammonium acetate adjusted to pH 7.0 to extract citrate soluble P (AOAC, 1960; Prasad and Power, 1997). In India nitrophosphates have been evaluated for their water solubility (WS) in large number of experiments. The results indicated that 50 per cent WS is desirable for upland crops, such as wheat, maize etc, on neutral or above neutral soils, but fertilizers containing less than 50 per cent WSPC can be used in rice and sugarcane and for all crops in acid soils (Mahapatra *et al.*, 1973).

Magnesium is present in much lesser amounts than Ca, but Sample *et al.* (1986) have suggested the formation of $Mg_3(PO_4)_2$, $MgNH_4PO_4$ (struvite), $Mg(NH_4)_2(HPO_4)_2.4H_2O$ (Schertelite) and $Mg_3(NH_4)_2(HPO_4)_4$ (Hannayite) and some unidentified reaction products.

Reaction with micronutrients other than Fe

Of the micronutrients other than Fe, Zn has received the most attention and there are many reports on negative interaction of Zn and P (Adriano *et al.*, 1971; Bukowic *et al.*, 2003; Christensen and Jackson, 1981; Haldar and Mandal, 1981; Mousavi, 2011; Prasad *et al.*, 2014). Dwivedi *et al* (1975) were the first to induce zinc deficiency in a pot experiment with Hybrid maize Ganga 5 and a significant reduction in yield was recorded at a high level of P application. In the zinc-deficient plants, the concentration of zinc significantly increased in the roots and the nodes and decreased in the leaves and the internodes. Haldar and Mandal (1981) reported that application of phosphorus caused a decrease in the concentration of zinc, copper, iron and manganese both in shoots and roots. Application of zinc also similarly lowered the concentration of phosphorus, copper and iron, but increased that of manganese in shoots and roots. Phosphate × zinc interaction has since then received considerable attention in India, particularly with the development of high productive multiple cropping systems involving high yielding varieties and hybrids leading to continued large P applications resulting in an increase in Zn deficient areas and the subject has been extensively reviewed by Subba Rao and Rupa (2003). Singh *et al.* (1986) reported that applied P increased soil P levels and tissue P concentration, but resulted in a significant decrease of tissue Zn levels. The current global thrust is on identification of genes important for interactions between Pi, Zn and/or Fe transport and signaling is a useful target for breeders for improvement in plant nutrient acquisition (Xie *et al.*, 2019). However, this recognition of the negative interaction has gone too far and farmers are not applying enough P and Zn in their fields, despite majority of soils testing low to medium in available P (Tandon, 1987) and about 50 per cent of the soils in India testing low in available Zn (Singh, 2009) and good responses of most crops to P (Blaise *et al.*, 2014) and Zn (Rattan *et al.*, 2008; Patel, 2011) have been reported. Shukla and Behera (2012) predicted that additional production due to Zn application alone in India could be 11.86, 3.58 and 1.3 million tonnes in rice, wheat and maize, respectively. Not many studies have reported the effect of Zn application on P uptake; however, in general an increase in grain and straw yield of a crop is associated with an increase in P uptake. Shivay *et al.* (2015) from on-farm trials in Aligarh and Meerut districts in Uttar Pradesh reported a significant increase in grain and straw yield of rice by soil application of 5 kg Zn/ha and total P uptake increased from 20.47 kg P/ha in check plots to 27.08 kg P/ha in Zn applied plots in Aligarh and from 34.02 kg P/ha in check plots to 43.34 kg P/ha in P applied plots in Meerut. However, Zn application reduced Zn translocation to rice kernels from vegetative matter from 75.04 per cent in check plots to 70 per cent in Zn applied plots in Aligarh and from 45.15 per cent in check plots to 44.30 per cent in Zn applied plots in Meerut. This decrease in P concentration should be welcomed, because most P is stored as phytates, which interfere with Zn uptake by humans (Prasad *et al.*, 2016). Sprouting grains reduces phytates (Malleshri and Desikachar, 1986) and efforts are underway to develop low phytate mutants in cereal grains (Gutteri *et al.,* 2006).

Reactions with aluminium (Al) and iron (Fe)

Al and Fe are third and fourth elements, respectively in abundance in the earth's crust after O_2 and Si and mineral soils are made up of mostly aluminosilicate minerals. Al is not a plant nutrient but is actively involved in reactions with phosphates. Mukherjee *et al.* (1947) were the first to point out that acid soils contained a lot of exchangeable Al, which was mainly responsible for soil acidity and Foy (1992) pointed out that it was highly toxic to crop plants. Reaction products between Al/Fe and P including minerals have been identified by using two techniques, namely, X-ray diffraction (Ghosh *et al.*, 1996) and solubility product principle (Wright and Peach, 1960). The most frequently reported Al and Fe-phosphate minerals formed as a reaction product are: variscite [$Al(OH)_2H_2PO_4$] with a pK_{sp} value of 30.5 and

strengite [$Fe(OH)_2 H_2PO_4$] with a pK_{sp} value of 33.6-35.0 (Lindsay and Moreno, 1960). Sometimes K and NH_4^+ substitute part of Al and give minerals like taranakite (Sample *et al.*, 1986).

In India Bhujbal and Mistry (1986) carried out studies on the isolation and identification of reaction products of ammonium nitrate phosphate (ANP) fertilizers containing 30, 50 and 70 per cent water-soluble phosphorus (WSP) of total phosphorus in representative soils of the Vertisol, Oxisol, Alfisol, Entisol, Mollisol and Aridisol groups. ANP fertilizers were applied in solid form to soil and reaction products formed at and around the site of ANP fertilizer placement were identified after six weeks incubation in moist soils by X-ray diffraction technique. DCP was detected with ANP of 30 and 50 per cent WSP in all soils. Bruschite (dicalcium phosphate dihydrate- $Ca HPO_4 \cdot 2H_2O$) was the major reaction product of ANP fertilizers containing 30 and 50 per cent WSP in Vertisols, Entisols, Aridisols, Mollisols, Oxisols and Alfisols and of ANP containing 70 per cent WSP in Vertisols, Entisols, Alfisols, Aridisols and Mollisols. In addition to DCP, $FePO_4 \cdot 2H_2O$ (metastrengite) and $AlPO_4 \cdot 2H_2O$-monoclinic (metavariscite) were formed in Alfisols and Oxisols with ANP of 30 and 50 per cent WSP. $FePO_4 \cdot 2H_2O$ and $AlPO_4 \cdot 2H_2O$ (metavariscite) were identified in Alfisol and Oxisols, while $AlPO_4 \cdot 2H_2O$-orthorhombic (Variscite) was formed in Alfisols with ANP of 70 per cent WSP (Roncal-Herrero *et al.*, 2009). In another laboratory study on the characterization of soil-fertilizer P reaction products carried out by Ghosh *et al.* (1996) reacting three-soils occurring in a topo-sequence in the plateau region of Bihar (India) with saturated solutions of DAP, TSP and ammonium polyphosphate (APP) for 1 hour and 24 hour and the reaction products (precipitates) formed in the solutions after 120 days of incubation were isolated and identified through X-ray diffraction technique, Brushite ($CaHPO_4 \cdot 2H_2O$), Strengite ($FePO_4 \cdot 2H_2O$), Variscite ($AlPO_4 \cdot 2H_2O$) and $Fe_4(P_2O_7)_3$ were identified as major soil-fertilizer P reaction products.

In addition to the formation of less soluble reaction products, phosphorus is also fixed by anion exchange with OH in Al and Fe hydroxides and on broken edges of kaolinite (Hingston *et al.* 1972, 1974) and with CO_3 (Griffin and Jurinak 1973, 1974) with calcite in calcareous soils. Kanwar and Grewal (1960) reported from Punjab that in acid soils 72 per cent P was fixed by Al/Fe oxides, while in calcareous and alkaline soils 70 per cent P was fixed by carbonates. Chatterjee *et al.* (2014) reported higher P fixation in an Alfisol containing more kaolinite than a Vertisol. It explains high P-fixation in tropical acid soils, which are rich in Al/Fe oxides (Nakaru and Uehara, 1972).

Strategies to increase P availability to crop plants

Placement of phosphorus: Phosphorus is mostly absorbed by diffusion by root tips and root hairs and for better absorption it has to be deep placed in the rhizosphere. Phosphorus is never top dressed on the surface of the soil as nitrogen.

Application of organic manures

Organic manures produce a lot of organic acids that increases phosphorus solubility in soils and other organic molecules, which chelate the cations holding phosphates and make it available to crop plants. Organic manures also produce enzyme phosphatase that dissolves organically bound P in soils. Garg and Bahl (2008) reported that the differential phosphatase activity in the organic manures was reflected in dynamic P availability. The highest amount of Olsen extractable P was in poultry manure (PM)-treated soil followed by farm yard manure, green manure and field pea crop residue (CR). In their study organic manure addition along with inorganic P, irrespective of the source, increased the Olsen extractable P throughout the incubation period and P uptake by maize increased with the increasing level of inorganic P in both soils. The highest uptake was obtained in PM-treated soil and lowest in the CR-amended soil. This is the basis of composting with rock phosphate (Mishra *et al.,* 1984).

Phosphate solubilizing organisms (PSO)

PSOs have recently received considerable importance in solubilizing inherent soil P and applied P (Gaur, 1990; Richardson, 2007; Sharma *et al.*, 2013; Prasanna *et al.*, 2014; Shahane *et al.*, 2017; Liang *et al.*, 2020). Quite a group of organisms are involved in the process, mainly fungi (*Aspergillus*, *Penicillium, Rhizoctonia* and *Trichoderma* species) and bacteria (*Bacillus* and *Pseudomonas* sp.). Cultures of VAM/AM have also been successfully used in increasing the native and applied P (Kim *et al.*, 1997; Prasanna *et al.*, 2014). The main mechanism of solublization is secretion of acid organic molecules (Sharma *et al.*, 2013). PSOs have been used for direct use of finely ground rock phosphate (Motsara *et al.*, 1995; Park *et al.*, 2011).

Addition of sulphur to rock phosphate

Swaby (1975) used sulphur-oxidizing bacteria (*Thiobacillus thio-oxidans* and *Thiobacillus thioparus)* for increasing the solubility of phosphorus in rock phosphate + sulphur mixtures. This mixture was called as *biosuper*. Application of elemental sulphur or any other acid forming fertilizers, such as nitrogen fertilizers are likely to increase the solubility of phosphate in soil.

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