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*Review*

# Phosphorus management issues for crop production: A review

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**Phosphorus (P) is an essential element for plant growth. On account of its low solubility in soil, P is often a limiting factor to optimum crop growth and therefore P fertilisation is an important aspect of nutrient management plans to ensure profitable and sustainable crop production. Plant P availability is controlled by sorption, desorption and precipitation of P from P released during weathering of P minerals and applied P. Much research has been focused on the fate of P in soils, fertilisation practices and how to improve its use efficiency in cropped soils. The components, forms, availability and cycling of P in soils are summarized in this review taking into account the complex and interrelated processes which determine the amounts and availability of several inorganic and organic forms of soil P. The importance of plant and soil testing to assess plant nutrient status and some recent developments on microbial P solubilisation into classical knowledge on the subject are also covered. The review recommends the potential use of P as biofertilisers in an attempt to reduce reliance on expensive mineral fertilisers.**

**Key words:** Biofertilisers, crop productivity, phosphorus dynamics, phosphorus fertilisation, plant testing, soil testing.

## INTRODUCTION

Most soils have inherently very little capacity to supply sufficient phosphorus (P) for crop production. However, P is an essential nutrient for plant growth. It stimulates growth of young plants, giving them a good and vigorous start. Phosphorus stress early in the growing season will reduce crop productivity more than P restrictions later in the crop cycle (Grant et al., 2001). In the absence of adequate amounts of the element, plants fail to get off to a quick start, their root systems do not develop satisfactorily, the plants become dwarfed, and they tend to show a purplish discoloration of the stems and of the petioles and lower sides of the leaves (Mengel and Kirkby, 2001).

The dominant characteristics of soil P are very low solubility of the phosphate minerals and its strong binding on to particle surfaces results in small soil solution concentrations, thus making P a limiting factor to optimum crop growth. Phosphorus fertilisation is therefore a necessity to maintain profitable crop production and is an integral part of crop production systems in most countries (Haygarth et al., 2013). The majority of P for fertiliser manufacture is mined from

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sedimentary phosphorite deposits. However, in some instances igneous rocks rich in apatite are mined also for this purpose. These P sources are finite and it is believed to become exhausted in the next 40 to 400 years (Obersteiner et al., 2013). Global P scarcity is a pressing issue and the implementation of P management strategies to meet both agricultural and environmental challenges is more than timely.

When added to soil, P fertiliser undergoes several different reactions, including adsorption on soil particles and precipitation. Soil chemical properties, moisture and texture as well as fertiliser type and placement influence rate of fertiliser P transformations occurring in the soil. On account of the very low mobility of applied P, coupled with the fact that P is not subject to volatilisation losses, an accumulation of P occurred in soils with the continuous application of fertilisers. Recent studies have been done on the potential use of P solubilising microorganisms as biofertilisers to enhance the ability of plants to utilize P already present in the soil. While this build-up of P in soils is desirable from an agronomic perspective, it nonetheless represents a potential threat to fresh water quality (Sharpley, 2012).

Proper assessment of crops' P needs by either plant or soil testing is essential for crop production and environmental protection. This review focuses on the importance of P in crop production and strategies adopted to ensure a proper management of soil and fertiliser P, which also incorporates some recent developments on microbial P solubilisation into classical knowledge on the subject.

## PHOSPHORUS IN CROP PRODUCTION

### Importance of phosphorus in plant growth

Phosphorus is essential for plant growth by being involved in energy metabolisms, in cellular transfer mechanisms, in respiration, and in the photosynthesis of the crop. It is taken up by the plant as either $H_2PO_4^-$ or $HPO_4^{2-}$ (orthophosphate ions), depending on soil pH. Although it has been suggested that plants also absorb soluble low-molecular weight organic compounds (that is, nucleic acid and phytin), these compounds are likely converted to orthophosphate ions in the rhizosphere. Plant uptake of $HPO_4^{2-}$ is much slower than with $H_2PO_4^-$. However, P is incorporated into adenosine di- and tri-phosphate (ADP and ATP, respectively) required for the energy metabolism in the plant. Phosphorus is also an essential element in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) that contain the genetic code of the plant and which play a role in producing proteins, other compounds essential for plant structure, seed yield, and in genetic transfer (Havlin et al., 2014). Phosphate also occurs in phospholipids including those of membranes, in sugar phosphates, and in various nucleotides and co-enzymes. Phytic acid, the hexaphosphate ester of myo-inositol, or its calcium or magnesium salts (phytin), serves as a storage form of phosphate in seeds (Sanchez, 2007).

Phosphorus generally accounts for 0.1-0.5% of the dry weight of plants, in which it is always present in its highest oxidation forms, viz., ortho- and pyrophosphate. Several sources (Bergmann, 1992) gave adequate ranges of contents in dry matter of crop plants. A deficiency in P inhibits reactions in the citric acid cycle, thus leading to the accumulation of pyruvic acid. Since protein synthesis is also inhibited, concentrations of non-proteinaceous N compounds rise. The inhibition of starch and cellulose synthesis in P deficient plants leads to abnormally high sugar levels, and these in turn encourage the synthesis of anthocyanins. Severe P deficiencies, however, also inhibit sugar synthesis (Ozanne, 1980; Mengel and Kirkby, 2001; Sanchez, 2007; Fageria et al., 2011).

One of the first symptoms of P deficiency of many plant species includes darkening of the leaves resulting in blue-green foliage. As described by Epstein (1972), often red, purple, or brown pigments develop in the leaves, especially along the veins. With increasing P deficiency, the dark green colour changes to a grayish-green to bluish-green metallic lustre. The visual P deficiency symptoms usually appear on lower leaf tips and progress along leaf margins until the entire leaf turns purple. The purple colour is due to accumulation of sugars that enhances synthesis of anthocyanin (a purple pigment) in the leaf (Ozanne, 1980).

In the absence of adequate amounts of P, plants fail to get off to a quick start, their root systems do not develop satisfactorily, and the plants become dwarfed or become stunted, showing narrower and shorter leaves in the sugarcane plant (Korndörfer, 2005). Phosphorus deficiency may also reduce seed numbers, their viability and size (Ozanne, 1980). Other symptoms of P deficiency in small grain crops such as wheat include poor tillering, and delayed maturity (Prasad and Power, 1997). For a thorough discussion on nutritional disorders of plants consults *inter alia* Bergmann (1992).

Excess of P rarely has direct toxic effects on crop plants because phosphate ions are firmly sorbed and immobilized in soil. Heavy dressing of P fertilisers can, however, induce deficiencies of micronutrients such as Zn and Fe, but they can also prevent uptake of toxic trace elements. Uptake and metabolism of Zn in particular are disturbed by high concentrations of P in soils and plants, especially if accompanied by high pH values and iron oxide levels in soil. The Fe metabolism, and particularly the transport of Fe within the plant, is also impaired by excessive P levels. Phosphorus excess can also induce deficiencies of Ca, B, Cu and Mn. The effects of excessive P levels, which may appear particularly in soils with a poor sorption capacity, are therefore virtually always indirect (Ozanne, 1980; Bergmann, 1992; Mengel
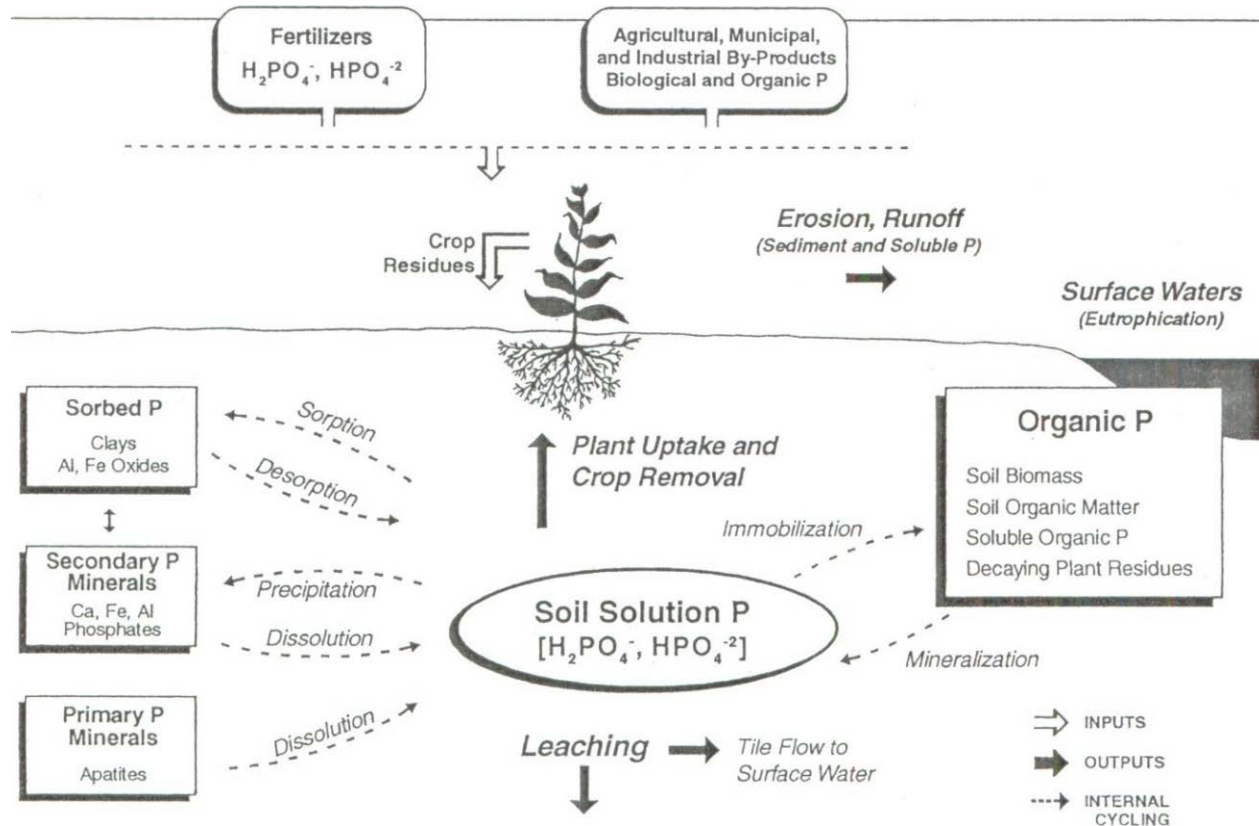
**Figure 1.** The soil P cycle as reproduced from Pierzynski et al. (2005).

and Kirkby, 2001; Fageria, 2009).

The total amount of P required by a crop to produce a ton of marketable product varies amongst field crops, e.g. 3.8, 4.8, 5.1, 5.2, 7.0 and 7.7 kg for maize, wheat, sunflower, groundnut, canola and soybean, respectively. Maize, wheat, sunflower, groundnut, canola and soybean remove, respectively, 3.1, 3.8, 3.7, 3.0, 5.1 and 6.7 kg P from fields in a ton of marketable product. Thus 0.7, 1.0, 1.4, 2.2, 1.9 and 1.0 kg P remain in the residues of maize, wheat, sunflower, groundnut, canola and soybean on fields, respectively (Hanway and Olson, 1980; Johnston, 2005; Fageria et al., 2011). Uptake of P by fruit (Tagliavini and Scandellari, 2013) and vegetable (Lorenz and Vittum, 1980) crops are dealt with in detail elsewhere.

**Phosphorus dynamics in the soil-plant system**

The dynamics of P in soils is best described by showing the soil P cycle such as the one proposed by Pierzynski et al. (2005) and reproduced in Figure 1. From the viewpoint of plant nutrition and availability to crops, the P in soil has most conveniently been categorized into three forms, namely solution P, labile P and non-labile P (Pierzynski et al., 2005). The relationship among these

three forms of P is often simplified to the following equilibrium equation (Havlin et al., 2014).
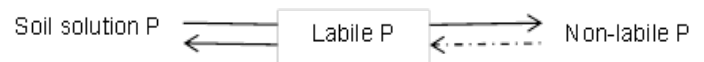


Phosphorus occurs in soil solution as orthophosphate ions, $H_2PO_4^-$ and $HPO_4^{2-}$, which are in fact the only forms of P that can be taken up by crops. At a pH 7.2, $H_2PO_4^- \sim HPO_4^{2-}$. Below this pH, $H_2PO_4^- > HPO_4^{2-}$, whereas $HPO_4^{2-} > H_2PO_4^-$ above pH 7.2. To maintain the concentration of P in soil solutions at an optimum value for plant growth (about 0.2 mg $L^{-1}$), all the chemical and biochemical processes of the soil P cycle must come into play to release P rapidly enough for crop uptake through dissolution-precipitation, sorption-desorption, mineralisation-immobilisation, and oxidation-reduction reactions (Pierzynski et al., 2005).

While the inorganic P in soils equilibrates with the soil solution P through adsorption-desorption reactions and through dissolution-precipitation, the organic P component influences the P concentration in the soil solution through mineralisation and immobilisation (Pierzynski et al., 2000). Both P mineralisation and immobilisation rates are affected by factors such as temperature, moisture, aeration, pH, cultivation intensity

and P fertilisation (Havlin et al., 2014). The extent of P mineralisation over immobilisation depends on the C:P ratio of the residues deposited in the soil (Stevenson and Cole, 1999). Mineralisation occurs rapidly if the C:P ratio of the organic matter is less than 200:1, while immobilisation will be predominant if the C:P ratio exceeds 300:1 (Pierzynski et al., 2000).

### *Transformations of phosphorus fertiliser in soil*

When soluble phosphatic fertilisers are applied to soils, they initially dissolve causing an immediate rise in the concentration of soil solution P, which then participates primarily in adsorption and precipitation processes (Prasad and Power, 1997). The reactions that occur among the phosphate ions present in the soil solution, the soil constituents, and the non-phosphatic components in the fertilisers, primarily remove the P from the solution phase and render the phosphate less soluble over time (Sample et al., 1980). This phenomenon is commonly referred to as P fixation, adsorption or retention. As a consequence of fixation, P becomes highly immobile in soils and generally stays near the point of application (Prasad and Power, 1997). In fact, at the beginning the sorption processes are easily reversible and the added P remains readily available for plant uptake, thereby imparting a high residual value to the phosphate fertilisers (Havlin et al., 2014).

The solid labile phases which are formed initially however gradually revert to less soluble P forms (non-labile) and adsorption continues to decrease soil solution P concentration with time and to cause a reduction in plant available P (Pierzynski et al., 2005). Fixation of P by soils thus plays an important role in determining the ultimate availability of fertiliser P to crops and its mobility in soils. On account of its significant role in affecting the availability and mobility of P, an understanding of the different reactions underlying P fixation in soils is a first step towards obtaining optimum P nutrition and towards achieving efficient management of the fertiliser P to protect freshwater sources.

### *Fixation of applied phosphorus in soil*

The most active soil constituents involved in the retention of applied P in the soils are the hydrous oxides of iron and aluminium.

These oxides occur either as discrete compounds in soils or as coatings on soil particles or as amorphous Al hydroxyl-compounds between the layers of expanding Al silicates. Studies carried out (Sample et al., 1980) have shown that these hydrous oxides of Fe and Al retained large amounts of P from soil solution, the amount of P sorbed by hydrous oxides of iron and aluminium being dependent upon the time of reaction, the temperature, pH

and the P concentration in the soil solution. Bache (1964) studied P sorption by gibbsite and hydrous ferric oxide and showed that the mechanism of P retention in soils by the Al and Fe oxides followed three distinct stages which occur at different P concentrations in the solution: (i) a high energy chemisorption, (ii) precipitation of a separate phosphate phase, and (iii) a low energy sorption of P onto the precipitate.

In acid soils, the predominance of positive charges on Al and Fe oxides/ hydroxides facilitates the attraction of negatively charged orthophosphate $H_2PO_4^-$ and $HPO_4^{2-}$ ions (Havlin et al., 2014). The mechanism of P adsorption on Al/Fe oxide surface involves the exchange of phosphate for OH groups as shown in Figure 2. When the orthophosphate ion is bonded through one Al-O-P bond, the $H_2PO_4^-$ is considered as labile as it can readily be desorbed from the mineral surface to soil solution. But when the $H_2PO_4^-$ is bonded to the Fe/Al hydroxides through two Al-O bonds, a stable six-membered ring is formed and the $H_2PO_4^-$ is regarded as non-labile and unavailable for plant uptake.

As reviewed by Sample et al. (1980), at low solution P concentrations hydrous oxides retain P through sorption-type reactions but at higher P concentrations, that is when the concentration of P and associated cations in the soil solution exceeds that of the solubility product ($K_{sp}$) of the mineral, precipitation reactions are favoured. In neutral and calcareous soils, Ca being the dominant cation, the addition of soluble P initially results in the precipitation of di-calcium phosphate dihydrate {$CaHPO_4.2H_2O$} which, with time slowly reverts to other more stable but less soluble Ca phosphates (Pierzynski et al., 2000). The precipitates in Ca systems as described by Sharpley (2000), usually occur in the following sequence: mono-calcium phosphate {$Ca(H_2PO_4)_2$}, di-calcium phosphate dihydrate {$CaHPO_4.2H_2O$}, octa-calcium phosphate {$Ca_8H_2(PO_4)_6.5H_2O$} and finally hydroxy-apatite {$Ca_{10}(PO_4)_6(OH)_2$} or fluoro-apatite {$Ca_{10}(PO_4)_6F_2$}.

In acid soils, the chemical equation given below summarises the precipitation reactions involving soluble Fe or Al with $H_2PO_4^-$ to form Al or Fe hydroxyl-phosphates (Weil and Brady, 2017).

$$Al^{3+} + H_2PO_4^- + 2H_2O \rightleftharpoons 2H^+ + Al(OH)_2H_2PO_4$$
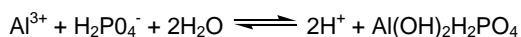
As reviewed by Sharpley (2012), P in the soil solution generally reacts with Al oxides to form amorphous Al-P organized phases such as sterretite {$Al(OH_2)_3.HPO_4.H_2PO_4$}; and with Fe oxides to precipitates such as tinticite {$Fe_6(PO_4)_4(OH)_6.7H_2O$} or griphite {$Fe_3Mn_2(PO_4)_2.5H_2O$}. Alumino-silicate minerals, such as kaolinite, montmorillonite and illite also play a significant role in P fixation (Weil and Brady, 2017). Phosphorus is adsorbed to a larger extent by 1:1 clays (e.g. kaolinite) than by 2:1 clays (e.g. montmorillonite). This can be explained by the presence of higher amounts
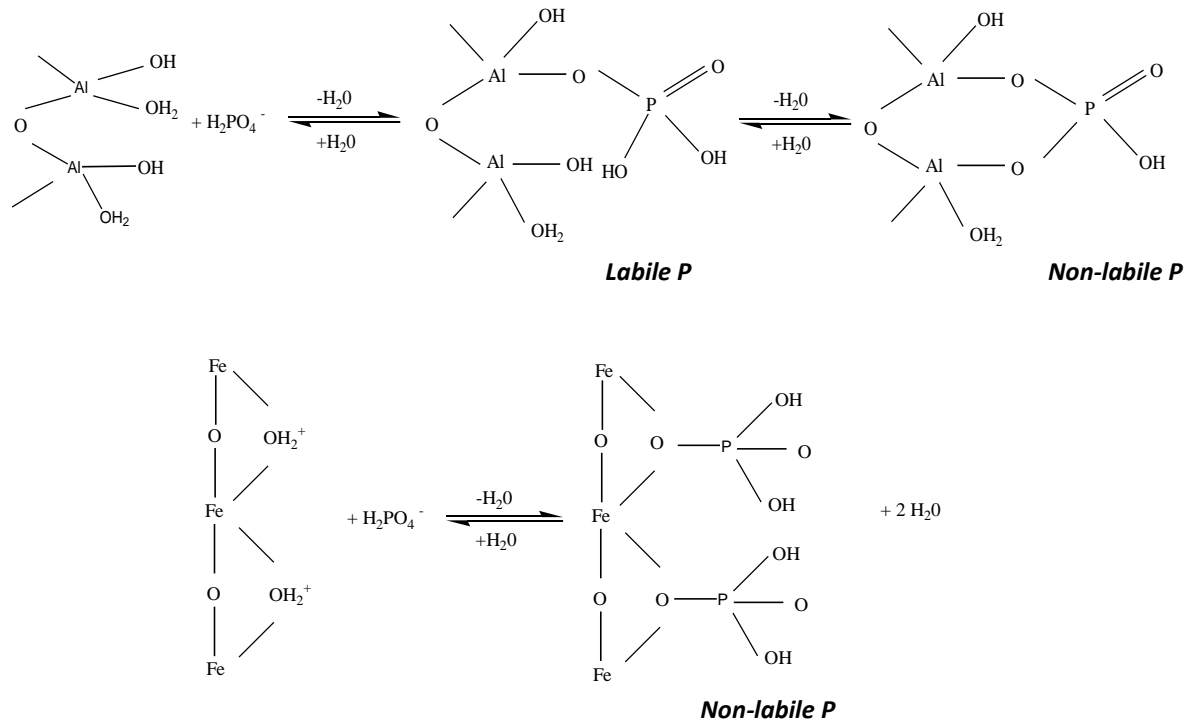
**Figure 2.** Mechanism of P adsorption to Fe/Al oxide surface.
Source: Adapted from Havlin et al. (2014).

of Fe/Al oxides associated with kaolinitic clays. Moreover in the kaolinitic clays, a larger number of OH groups are exposed in the Al layer to exchange with P (Havlin et al., 2014). In addition, the presence of pH-dependent charges on kaolinitic clays also contributes to P adsorption. The mechanisms of P adsorption by alumino-silicate minerals are in fact the same as described above for the oxides of Al and Fe. Thus at low P concentrations, the P is adsorbed onto the silicate clays with the replacement of surface hydroxyl groups as illustrated in Figure 2. High P concentrations, such as soon after application of soluble mineral P fertilisers, favour the release of Si and Al with the subsequent precipitation of Al-P compounds (Sample et al., 1980).

In calcareous soils, P adsorption may also occur on the carbonates ($CaCO_3$) present. As reviewed by Prasad and Power (1997), the interaction of P with the $CaCO_3$ involves two reactions: the first reaction occurs at low P concentration and consists of adsorption of P on $CaCO_3$ surfaces, while the second reaction is a nucleation process to form phosphate crystals. The different above-mentioned reactions of added P in soils, explain the high residual values of P fertilisers that are often reported in the literature (Havlin et al., 2014). As reviewed by Morel and Fardeau (1989), 80-99% of P applied as fertilisers remains in the soil. In fact as summarised by Barrow (1980), the literature available on the residual value of P fertilisers has two contrasting strands. First, a reported decline in effectiveness of the P fertilisers during the first few months (or years) after their application implying that repeated applications of P is required and second, mention is frequently made about the continuing uptake of P by the crops over several years after its application, which is particularly beneficial for crops with long growing seasons such as sugarcane. Thus as observed by Cavalot et al. (1988), a single application of P fertilisers at planting was sufficient to meet the needs of a sugarcane crop cycle for six to seven years. The data in the literature in effect support the conclusion of Havlin et al. (2014) that the residual availability potential for immobile nutrients such as P could only be assessed through soil testing.

**Factors and reactions affecting phosphorus availability and mobility**

It follows from the preceding sections that in general, P retention or fixation in soils is a continuous process involving precipitation, chemisorption and adsorption (Prasad and Power, 1997). At low solution P concentrations, P retention follows mainly an adsorption mechanism while at high P concentrations in solution, precipitation predominantly occurs following solubility product principles. As the availability and mobility of P in soils are highly influenced by P retention, the soil properties

influencing P retention and solubility need to be known and are discussed subsequently.

## Soil mineralogy and clay content

Adsorption and desorption reactions are affected by the type of mineral surfaces in contact with P in the soil solution (Havlin et al., 2014). Phosphorus is adsorbed most extensively by Al and Fe oxides and to a greater extent by 1:1 clays (such as kaolinite) as compared to 2:1 clays (e.g. montmorillonite) due to the presence of higher Fe/Al oxides content in the 1:1 clay minerals (Havlin et al., 2014). Apart from the nature of the minerals, the clay content of soils also affects the degree of P fixation. Among soils of similar clay mineralogy, P fixation will obviously increase with rising clay content (Kamprath and Watson, 1980). Thus soils with a sandy texture have low P adsorption capacities with the P more susceptible to leaching than soils of a clayey texture (Pierzynski et al., 2000).

In calcareous soils, the presence of $CaCO_3$ with large surface area also shows a high adsorption and a rapid precipitation of Ca-P minerals (Havlin et al., 2014). Calcareous soils with highly reactive $CaCO_3$ and a high Ca-saturated clay content have in this context been shown to exhibit low solution P levels, since the P in the soil solution is instantaneously precipitated or adsorbed (Havlin et al., 2014).

In addition, the type of cations on the cation exchange sites of the clays has an influence on P adsorption (Havlin et al., 2014). Ca-saturated clays have been shown in this context to exhibit greater P adsorption than their Na-saturated counterparts. As reviewed by Kurtz (1953), even at pH levels below neutrality, where calcium precipitation would not be expected, calcium clays retain more phosphate than sodium, ammonium or potassium clays. This observation was explained by a possible precipitation of calcium phosphate at the colloid surface or a binding of phosphate to the soil colloid through $Ca^{2+}$ on the exchange complex (Kurtz, 1953).

## Soil pH

Phosphorus fixation in acidic soils is more pronounced than in calcareous/alkaline soils and the P adsorbed is held more strongly. In fact, in most soils, maximum P retention occurs at the low pH values of 3.0 to 4.0 because of adsorption by Fe/Al oxides. As the pH increases, P adsorption decreases resulting in a higher concentration of P in soil solution (Havlin et al., 2014). In general, P availability to plants in most soils will be at its maximum when the soil pH is maintained in the range of 6.0 to 7.0 (Weil and Brady, 2017). Above pH values of 7, the presence of $CaCO_3$ accounts for P fixation, resulting in a decline of soil solution P.

## Soil organic matter

Soil organic matter in association with cations such as Fe, Al and Ca is capable of retaining significant amounts of P (Prasad and Power, 1997). Humic acid dissolves Al from soil minerals to form complexes which give rise to new surfaces for P adsorption by ligand exchange of the phosphate ions for the hydroxyl groups (Sample et al., 1980). Hence the overall effect of an increase in organic matter content of the soil would be an increase in P adsorption. On the other hand, in calcareous soils, organic matter and P compete for the same adsorption sites on $CaCO_3$, thereby decreasing the ability of the calcareous soils to adsorb P (Sample et al., 1980).

The presence of organic compounds in soils has also been reported to increase P availability by maintaining the P in solution through the formation of stable complexes with Fe and Al (Prasad and Power, 1997). The organic anions known to be most effective in competing and replacing $H_2PO_4^-$ are citrate, oxalate, tartrate and malate (Havlin et al., 2014). In soils with very high organic matter, P mobility is further enhanced by the organic matter forming a coating on the colloidal surfaces responsible for P adsorption (Pierzynski et al., 2000). This explains why organic compounds tend to move P to a greater depth than would inorganic P alone in soil solution. In this context, the continuous application of manure has been found to result in elevated P levels at 0.6 to 1.2 m soil depths while the application of the same amount of P as inorganic fertilisers resulted in much less downward movement of P (Havlin et al., 2014).

## Phosphorus management for crop production

### Management of phosphorus fertilisers

The efficiency with which P fertilisers are used by crops depends not only on the extent of P deficiency in soils and on crop P requirements but also on factors such as the time of application, placement, rate and frequency of the fertiliser P applications (Havlin et al., 2014). In that context, the 4R nutrient stewardship was advocated by the fertilizer industry worldwide aiming towards efficient on-farm P management practices focused on four central components, which are the application of the right fertilizer source at the right rate, at the right time and in the right place. All of these factors, by influencing P fixation reactions in the soil, eventually determine P availability and uptake by crops.

Rock phosphate (PR) is the primary raw material used in the manufacturing of P fertilizers. The RP materials are sedimentary deposits found in Morocco, China, United States and Russia, representing nearly 72% of total world production. Igneous P containing rocks are also used in P fertilizer manufacturing like in South Africa (Havlin et al., 2014). None of the P in RP is water soluble, although the

citrate solubility varies between 3 and 20% of the total P. Finely ground sedimentary RP can be applied as P fertilizer to very acidic soils in warm, moist climates characteristic of tropical regions. In such conditions could RP beneficial for especially perennial crops due to residual P availability over several years (Hayworth et al., 2013).

Fertilisers produced from RP include inter alia single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) and ammonium polyphosphate (APP). Once SSP and TSP were the most important P fertilisers but their use have decreased relative to MAP, DAP and APP. However, SSP, TSP, MAP, DAP and APP contain 16-22, 44-52, 48-62. 48-53 and 35-62% $P_2O_5$, respectively (Mordtvedt et al., 1999). Compared to TSP, MAP, DAP and APP, contain SSP 11-12% S which could be an advantage for cropping. From this viewpoint, contain MAP (11-13%), DAP (18-21%) and APP (10-13%) N which is not the case with SSP and TSP. Soil reaction pH around a dissolving granule of MAP is 3.5 compared to a pH of 8.5 with DAP. This high dissolution pH of DAP resulted in the conversion of $NH_4^+$ to $NH_3$ which favours volatilization losses and seedling injuries (Havlin et al., 2014).

The timing of P fertilisation from an agronomic perspective is optimised if adequate amounts of P are available at all times to meet plant requirements (Bundy et al., 2005). Phosphorus is needed as from the earliest stages of crop growth since it is important in nearly all energy-requiring processes in the plant. As indicated by Bundy et al. (2005) the use of starter P fertilisers is known to promote early plant growth and development. As P stress early in the growing season reduces crop productivity more than P restrictions later during the crop season, P fertilisation is usually best carried out just before or at planting.

The placement of starter P fertiliser also plays an important role in its effectiveness to crops (Bundy et al., 2005). Phosphorus is relatively immobile in the soil and so remains near the site of fertiliser placement (Grant et al., 2001). Surface application after the crop has been planted will not place the P near the root zone and will thus be of little value to annual crops in the year of application (Havlin et al., 2014). For optimum P management, the question of band placement over broadcast application is an important consideration. As pointed out by Havlin et al. (2014), band placement of P reduces fertiliser-soil contact, resulting in less fixation than broadcast P. This implies that P is maintained in a plant-available form for a longer period of time.

In fact to ensure maximum P efficiency, a compromise has to be found between reducing the volume of soil fertilised so as to minimise fixation and providing a large enough fertilised soil volume to encourage root-fertiliser contact (Grant et al., 2001). Being immobile and moving mostly by diffusion which occurs over short distances in the soil, the P must be placed in a position where the plant roots can take it up early in the season. Therefore, soluble fertiliser P is most efficient when seed-placed or placed in a band close to the seed, especially for crops having poorly developed root systems (Grant et al., 2001).

The question of frequency of fertiliser P application in crop rotations or in permanent pastures is pertinent throughout the range of P-deficiency levels encountered in soils. Frequent P applications are likely to be more important in soils of high P fixation capacities than in soils with low P fixing properties (Stanford and Pierre, 1953). In general the repeated application of large amounts of P fertiliser to crops eventually result in a point where a single application at the time of planting will suffice to give optimum crop yields. Recent studies on the response to P fertilisation by ratoon sugarcane have even shown that on some sugarcane farms the application of P to ratoon sugarcane can be reduced during several years without a decline in productivity (Korndörfer, 2005).

The utilisation of water-insoluble rock phosphate to supply plant-available P in strongly weathered and P deficient acidic soils has been found to be agronomically responsive (Bolland et al., 2001). The efficacy of the rock phosphate depends upon its dissolution which is influenced by many factors, including soil pH (Yusdar et al., 2007) and fineness of grinding of the phosphate rock. From an agronomic point of view, while water-soluble fertilisers should be applied in bands as explained above, rock phosphates on the contrary will be most effective when broadcast throughout the field (Gilkes and Bolland, 1990). This is so because the dissolution of the rock phosphate will be enhanced when its degree of contact with the soil $H^+$ ions is increased (Gilkes and Bolland, 1990).

Organic wastes are excellent sources of plant available P when mineralized. Manure accounting for 98% of organic P applied to croplands. The form and content of P in fresh organic materials varied widely, depending on the source and handling thereof. With animal wastes, inorganic P ranges from 0.3 to 2% of the dry weight, while organic P ranges from 0.1 to 1%. Usually, animal waste application is based on the N requirements of crops and this results in P application in excess of crop requirements. Regular monitoring of extractable soil P content is therefore required to avoid over P fertilization and hence water pollution (Condron et al., 2005; Sharpley, 2012).

## Use of microbial biofertilisers

In general, biofertilizers increase availability of nutrients through the natural processes of nitrogen fixation, solubilizing P, and stimulating plant growth through the synthesis of growth-promoting substances. The use of microbial biofertilisers to enhance nutrient plant- availability

has indeed received much interest during the past decade in view of its potential contribution in sustaining crop growth and development. The agricultural sector is faced with escalating fertilizer prices and pressures to protect the environment that it has become imperative to evaluate alternative nutrient sources such as microbial fertilizer, so as to reduce reliance on expensive mineral fertilisers. Several studies (Indi et al., 2014; Viruel et al., 2014; Thongponkaew et al., 2016) have reported the ability of soil bacteria to transform soil P to forms available to plants by mineralizing organic P in soil and by solubilizing precipitated phosphates. As reviewed by Mohammadi (2012), the beneficial effects of P solubilising bacteria (PSB) in soybean have been observed through enhanced number of nodules, dry weight of nodules, yield components, grain yield, nutrient availability and crop P uptake. Studies done by Sundara et al. (2002) have shown that the utilisation of PSB in sugarcane cultivation enhanced tillering, stalk population, stalk weight and cane yield while reducing the required P fertilizer rates by 25%.

## Phosphorus solubilising microorganisms

Evidence of naturally occurring rhizospheric P solubilizing microorganism (PSM) dates back to 1903 (Khan et al., 2007). PSM are a group of microorganisms that can solubilise the fixed forms of organic and inorganic P, and make P more available to plants. As reviewed by Khan et al. (2009), bacteria are more effective in P solubilisation than fungi and among the whole microbial population in soil, PSB constitute 1 to 50%, while P solubilising fungi are only 0.1 to 0.5% in P solubilization potential. However, fungi in soils are able to traverse long distances more easily than bacteria and hence, may be more important to P solubilization in soils (Ingle and Padole, 2017). The phosphate solubilizing ability of PSM also depends on the nature of the N source used in the media with greater solubilization in the presence of ammonium salts than when nitrate is used as N source. In addition, PSB have an ability to promote plant growth by synthesis of phytohormones (indole-3-acetic acid, gibberellins and cytokinins) and various plant growth promoting substances.

Phosphorus solubilising bacteria are present in rhizosphere and non-rhizosphere soils and as highlighted by Khan et al. (2009), usually one gram of fertile soil contains $10^1$ to $10^{10}$ bacteria, and their live weight may exceed 2,000 kg ha$^{-1}$. Among the soil bacterial communities, ectorhi-zospheric strains from *Pseudomonas* and *Bacilli*, and endo-symbiotic rhizobia have been described as effective phosphate solubilizers (Mohammadi, 2012). Many PSB have been isolated from various groups, e.g. *Bacillus*, *Pseudomonas*, *Erwinia*, *Agrobacterium*, *Serratia*, *Flavobacterium*, *Enterobacter*,

*Micrococcus*, *Azotobacter*, *Bradyrhizobium*, *Salmonella*, *Alcaligenes*, *Chromobacterium*, *Arthrobacter*, *Streptomyces*, *Thiobacillus* and *Escherichia* (Zhao and Lin, 2001). Strains from bacterial genera *Pseudomonas*, *Bacillus*, *Rhizobium* and *Enterobacter* along with *Penicillium* and *Aspergillus* fungi are the most powerful P solubilizers (Whitelaw, 2000). Populations fluctuate according to physicochemical and biological properties of soils.

## Mechanisms of phosphorus solubilization

A vast range of microbial P solubilisation mechanisms exists in nature, and much of the global cycling of insoluble organic and inorganic soil phosphates is attributed to bacteria and fungi. The mechanism of P solubilization employed by soil microorganisms are generally categorized into either the release of complex compounds, the liberation of extracellular enzymes (also referred as biochemical P mineralization) or the release of P during the degradation of substrate (Ingle and Padole, 2017). The P solubilizing activity is determined by the ability of microbes to release metabolites such as organic acids, which through their hydroxyl and carboxyl groups chelate the cation bound to phosphate, the latter being then converted to soluble forms (Khan et al., 2007). Phosphate solubilization also takes place through microbial mechanisms such as organic acid production and proton extrusion. A simplified sketch of P solubilization in soil is shown in Figure 3.

Numerous studies (Indi et al., 2014; Viruel et al., 2014; Thongponkaew et al., 2016) have reported the potential of soil bacteria to enhance plant P-availability through increased solubility of Ca-phosphates present in soils. Calcium phosphate (Ca-P) release results from the combined effects of pH decrease and carboxylic acids synthesis, but proton release is not the single mechanism (Deubel et al., 2000). As reviewed by Khan et al. (2009), microorganisms through secretion of different types of organic acids e.g. carboxylic acid and rhizospheric pH lowering mechanisms dissociate the bound forms of phosphate like $Ca_3(PO_4)_2$. In fact, acidification of the microbial cell surroundings releases P from apatite by proton substitution (that is, excretion of $H^+$) or release of $Ca^{2+}$ (Goldstein, 1994). Moreover, carboxylic anions produced by PSB, have high affinity to calcium and solubilize more P than acidification alone (Staunton and Leprince, 1996). Organic anions and associated protons are effective in solubilizing precipitated forms of soil P (e.g. Fe-P and Al-P in acid soils, Ca-P in alkaline soils), chelating metal ions that may be associated with complexed forms of P or facilitating the release of adsorbed P through ligand exchange reactions (Jones, 1998).

Solubilization of Fe and Al occurs via proton release by PSB by decreasing the negative charge of adsorbing
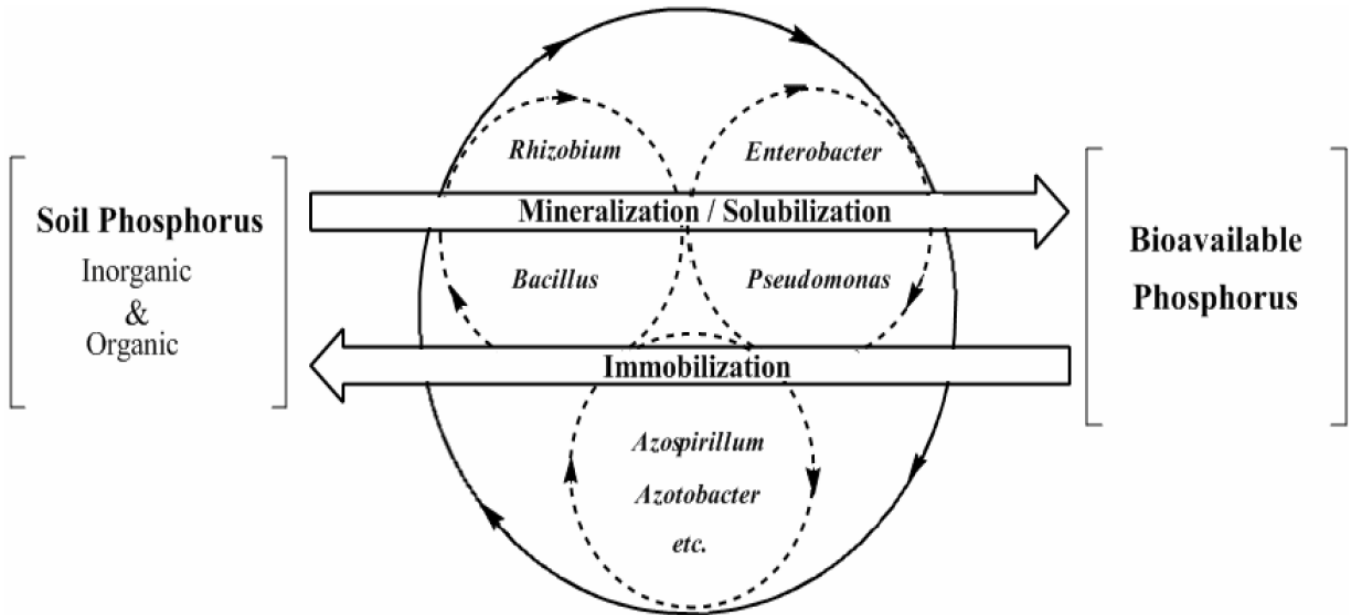
**Figure 3.** Schematic diagram of soil P mobilization and immobilization by bacteria with vesicular arbuscular mycorrhizae. Source: Reproduced from Kim et al. (1997).

surfaces to facilitate the sorption of negatively charged P ions. Carboxylic acids mainly solubilize Al-P and Fe-P through direct dissolution of mineral phosphate as a result of anion exchange of $PO_4^{3-}$ by acid anion or by chelation of both Fe and Al ions associated with phosphate (Omar, 1998). In addition, carboxylic anions replace phosphate from sorption complexes by ligand exchange (Whitelaw, 2000) and chelate both Fe and Al ions associated with phosphate, releasing phosphate available for plant uptake after transformation. The ability of organic acids to chelate metal cations is greatly influenced by its molecular structure, particularly by the number of carboxyl and hydroxyl groups.Mineralization of soil organic P plays an imperative role in P cycling of an agricultural system. Organic P may constitute 4-90% of the total soil P. As highlighted by Cosgrove (1967), almost half of the microorganisms in soil and plant roots possess P mineralization potential under the action of enzymes. Phosphorus can be released in the soil from organic compounds by three groups of enzymes, notably non-specific phosphatases, phytases and phosphonatases (Ingle and Padole, 2017). Alkaline and acid phosphatases use organic phosphate as a substrate to convert it into inorganic form (Beech et al., 2001). Generally, the phosphatases hydrolyze the soil organic P or split P from organic residues. It has been reported that mixed cultures of PSMs are most effective in mineralizing organic phosphate (Molla et al., 1984). Moreover as highlighted by Khan et al. (2007), mixed cultures or co-inoculation with other micro-organisms such as N fixers are generally preferred over single inoculation treatments since they benefit crops better that either group of

organisms alone.

### *Crop response to microbial phosphorus solubilisation*

Although total P may be high in soils, only 0.1% of it is actually available to crops. The application of the PSB as bioinoculants through mechanisms explain above can enhance solubilisation of fixed soil P and/or applied fertilizer P, resulting in increased crop yields. This helps to minimize the P fertilizer application, reduces risks of environmental pollution and promotes sustainable agriculture (Chen et al., 2006). Following inoculation with *Pseudomonas* spp., it was observed that the number of nodules, dry weight of nodules, yield components, grain yield, nutrient availability and uptake in soybean crop increased (Son et al., 2006). Pot experiments undertaken by Sadiq et al. (2013) demonstrated that PSB enhanced growth rate of the sugarcane significantly over the non-inoculated control. Studies under field conditions showed that the utilization of PSB with 75% recommended P rate improved sugarcane growth and yields (Indi et al., 2014). Pot experiments carried out by Niazi et al. (2015) showed that when PSB are applied in combination with organic amendments such as pressmud, both the organic and inorganic pool of soil P are mobilized more efficiently which was translated into enhanced growth and yield of mash bean. The use of PSB in combination with mineral P fertilisers in maize cultivation stimulated seedling emergence, shoot length, grain yield, grain weight, total dry biomass and P uptake of maize plants (Viruel et al., 2014).

As reviewed above, the use of microbial inoculants (commonly referred to as biofertilizers) in agriculture represents an environment friendly alternative to expensive mineral fertilisers. Despite the promising results, PSM-based biofertilisers have not witnessed a rapid widespread application in agriculture, mainly because of the inconsistent performance over a range of environments and variable response of plant species or genotypes to inoculation, depending on the bacterial strain used. Indeed, doubts have been raised about the ability of PSM to liberate phosphate under field conditions. As reviewed by Khan et al. (2007), variations in the effectiveness of PSM inoculations have been attributed to the following: (1) survival and colonisation of inoculated PSM in the rhizosphere; (2) competition with native microorganisms; (3) nature and properties of soils and plant varieties; (4) insufficient nutrients in the rhizosphere to produce enough organic acids to solubilise phosphorus; and (5) inability of PSM to solubilise soil P.

## ASSESSMENT OF PHOSPHORUS NEEDS OF CROPS

The quantity of soil P available to crops depends on many interacting factors such as the environment (water, temperature) and the soil management practices (Havlin et al., 2014). The quantity of P necessary to optimise crop yield further depends on both the plant P requirements and on the P-supplying capacity of the soil. Diagnostic techniques commonly employed to assess the P status of a soil include the identification of plant P-deficiency symptoms (Importance of phosphorus in plant growth), plant testing and soil analysis (Sumner, 2006). The following sections outline how plant testing and soil analysis techniques are utilized to evaluate the nutrient status of soils. Though visual deficiency symptoms provide an indication of P deficiency, they are seldom conclusive. Consequently accurate diagnosis typically requires a plant tissue test (Sanchez, 2007). In conjunction with soil tests, plant testing may also aid in determining the P-supplying capacity of a soil.

### Plant testing

Plant testing in a narrow sense can be described as the determination of the concentration of an element such as P or of an extractable fraction of the element in a particular part of a crop when the latter is sampled at a certain time or stage of morphological development (Walsh and Beaton, 1973). Plant testing involves either field tests which are performed on fresh tissue or laboratory-based analysis of the plant tissue. It is based on the premise that the amount of a given nutrient in a plant is related to the availability of that nutrient in the soil (Havlin et al., 2014). In essence plant testing helps to identify deficiency symptoms or to determine nutrient shortages before they appear.

Diagnostic standards with respect to plant testing involve the utilisation of critical levels or sufficiency ranges (Sanchez, 2007). These levels or ranges are usually determined by developing a response curve relationship as shown in Figure 4. As reviewed by Westermann (2005), the critical nutrient range is the range of concentrations above which the crop is amply supplied and below which the crop is deficient in the nutrient investigated. Usually the diagnosis of a nutrient deficiency, including P deficiency, by tissue analysis is a post-mortem of the current fertilisation practices (Sanchez, 2007) and is used to correct impending shortages of the nutrient in future crops.

### Soil testing

Soil testing is an essential and integrated part of crop management in present-day agricultural systems (Fageria et al., 2011). Crop response is poorly related to the total amount of P in a soil and therefore a successful soil test should represent some index of P availability (Sanchez, 2007). Agronomic soil tests to indicate available P have been designed such that (i) they are simple for routine application, (ii) they extract sufficient P to be easily measurable, (iii) they extract sufficient P to represent a significant portion of the soil P potentially available for plant uptake, and (iv) they do not extract significant amounts of P that are not available to plants (Tiessen and Moir, 1993).

To assess the soil P available to crops, several extracting agents are being used, with the most commonly utilised ones listed in Table 1. The principles, methodology and usage of these soil tests are dealt with in detail elsewhere (Olsen and Sommers, 1982; Sims and McGrath, 2012). However, the Bray, Citric acid, Colwell, Olsen and Truog soil tests were developed exclusively for P extraction while the AB-DTPA, Mehlich, Morgan and Egner soil tests were developed for multinutrient extraction. These extractants cover a broad range of soil conditions, from acid to alkaline, from low to high cation exchange capacity (CEC), and from arid to humid soil conditions (Fageria et al., 2011). Many of the soil test extractants employ acids to dissolve the Ca, Al, and Fe phosphates, which have been shown to be the main inorganic sources of labile P (Beegle, 2005). Extractants such as the Bray-1 and -2, and Mehlich-1, -2 and -3, are dilute solutions of the strong acids, namely HCl, $HNO_3$, and $H_2SO_4$. As discussed by Holford (1997), a soil test should extract a quantity of P that is positively related to extractable P and negatively related to the P buffering capacity of the soil but in practice the selection of the extractant is based on the degree of correlation between the soil P extracted and a measure of crop growth (Fageria et al., 2011). The preferred extractant is normally the one giving the best correlation between the
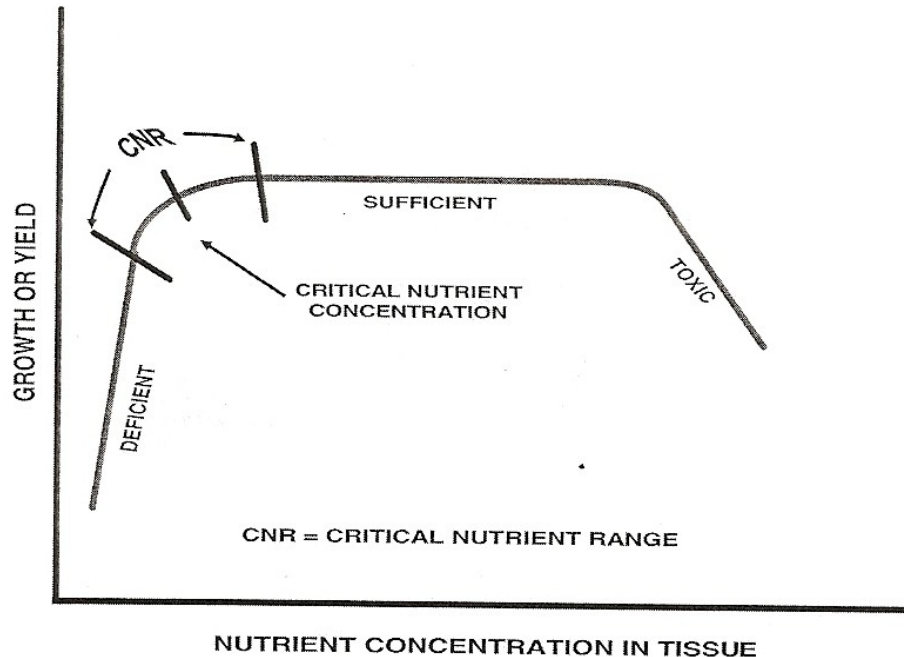
**Figure 4.** Growth or yield of plants in relation to nutrient concentration in plant tissue. Source: Reproduced from Westermann (2005).

soil P extracted and the measure of crop growth used.

The test based on Bray-1 extractant, which is a mild-acid solution, has been found to be reliable for predicting crop response to P fertilisation on neutral to acidic soils but it has been less effective on alkaline soils, where the acid from the extractant is neutralised quickly by the bases present while the fluoride ions are precipitated by Ca (Sanchez, 2007). The Bray-2 extractant has the same concentration of $NH_4F$ (0.03M) as Bray-1, but the HCl concentration has been raised to 0.1 M to give it an increased capacity to extract the less soluble Ca-P (Fageria et al., 2011). The Mehlich-1 extractant has the advantage of simultaneously extracting P, K, Ca, Mg, Cu, Mn, Fe, and Zn (Sanchez, 2007). The Mehlich-2 extractant was developed to allow simultaneous determination of the same nutrients over a still wider range of soil properties (Sanchez, 2007). However, the corrosive nature of the Mehlich-2 extractant discouraged its use and its composition was ultimately slightly modified to become Mehlich-3 which has been found to be reliable across a wide range of soil and crop production circumstances (Sanchez, 2007).

Whichever extractant or method is selected for the available soil P analyses, the P soil-test levels need to be converted into P fertiliser recommendations. A useful starting point for that conversion is the determination of critical soil test P levels, which refer to the soil P value above which there will be no response to P fertiliser (Sanchez, 2007). In fact, to convert soil test P values into fertiliser P recommendations, two sets of calibration information for each combination of crop-soil type-climate are required, namely: (i) the soil P test level that produces the maximum yield, and (ii) the quantity of fertiliser P that is required to reach that test level (Thomas and Peaslee, 1973). Thus, in situations where the soil test P levels are below the critical P value, fertilisation is required and the rate of P fertiliser will depend on the soil test P level.

Other critical aspects of soil testing are to follow an acceptable strategy of systematic soil sampling (Pennock et al., 2006). After sampling an informed decision on the appropriate soil P test by a laboratory of choice is of great importance. The selected laboratory must be reliable, implying that its analyses are repeatable over the long term, and comparable with those of other laboratories of this nature (Swyngedouw and Lessard, 2008).

**Phosphorus buffering capacity**

The soil P buffering capacity is an important soil property providing a suitable indication of available P in the soil (Holford, 1997). McDowell et al. (2001) explained that since soil P buffering capacity is a function of sorption capacity and sorption strength, it controls the rate of desorption and diffusion of P from soil to solution. The higher the soil P buffering capacity, the slower but the longer P will be replenished in the soil solution following its absorption by plant roots. As explained by Holford (1997), this replenishment capacity depends on the

**Table 1.** Common soil tests for estimating available soil phosphorus.

| Extractant | Extracting reagents |
|---|---|
| AB-DTPA | 1M $NH_4HCO_3$+ 0.005M DTPA, pH 5 |
| Bray-1 | 0.025N HCl + 0.03N $NH_4$ F |
| Bray-2 | 0.1N HCl + 0.03N $NH_4$ F |
| Citric acid | 1% citric acid |
| Colwell | 0.5M $NaHCO_3$, pH 8.5 |
| Egner | 0.02N Ca-lactate + 0.02NHCl |
| Mehlich-1 | 0.05N HCl + 0.025N $H_2SO_4$ |
| Mehlich-2 | 0.2N $CH_3COOH$ + 0.25N $NH_4Cl$ + 0.015N $NH_4F$ + 0.012N HCl |
| Mehlich -3 | 0.2N $CH_3COOH$ + 0.25N $NH_4Cl$ + 0.015N $NH_4F$ + 0.013N $HN0_3$ + 0.001M EDTA |
| Modified Morgan | 0.62N $NH_4OH$ + 1.25 N $CH_3COOH$, pH 4.8 |
| Morgan | 0.54N HOAc + 0.7 NaOAc, pH 4.8 |
| Olsen | 0.5M $NaHCO_3$, pH 8.5 |
| Truog | 0.002N $H_2SO_4$ buffered at pH 3 with $(NH_4)_2S0_4$ |

Source: Adapted from Sanchez (2007).

quantity of P in the labile pool and the ease with which this P is released into solution.

Phosphate is continuously taken up by plant roots throughout the growing season and the amount of P removed from the soil therefore depends upon two factors: (1) the amount of soil phosphate available to the roots at any one time that is, the intensity factor, and (2) the ability of the soil to maintain the intensity factor throughout the whole absorption period i.e. the capacity/quantity factor. It is obvious that for crops with long growing seasons (e.g. sugar cane) quantity measurements are of more significance than intensity measurements. As explained in previous section, fertilizer recommendations have traditionally been based on an estimate of available P in the soil using extraction procedures (Table 1). Recommendations based on direct determinations of the quantity of P required to raise the status of a soil to a desirable level are likely to be more reliable than those based on an estimate of the amount of available P in the soil as such (Meyer, 1974). Increasing awareness of the unsuitability of soil P tests to reliably predict the agronomic P status of soils (especially high P fixing soils), has led to investigations related to quantity/intensity (Q/I) concept. The soil buffer capacity is in fact a Q/I ratio given by the slope of the adsorption curve. Sorption tests provide a new approach whereby the importance of sorptive properties of soils are taken into consideration in the development of efficient and more precise fertilizer programme, particularly aimed at recommending fertilizer for an entire crop cycle on the basis of a single pre-plant soil analysis.

## CONCLUSION

Although P is present in the soil, it is not readily available for crop uptake. In general, crops require an adequate P supply during the early stages of growth to ensure profitable crop production. Hence, it is a common practice to apply P to fields during plantation. Phosphorus fertiliser use efficiency in cropped soils can be enhanced or reduced by fertiliser choice, placement, timing and rate. Moreover, the amount and availability of soil and applied P are determined by physical, chemical and biological processes, which as discussed in this review can be managed in attempts to optimize crop uptake of P for profitable yields. Cognisance should be taken also of biofertilisers' potential to solubilise soil P for plant uptake. Plant and especially soil testing are essential for proper fertilisation programmes to ensure optimal crop production with minimal surface water pollution.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

## ACKNOWLEGMENT

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