Phosphorus Availability in Soils and Use Efficiency for Food and Environmental Sustainability

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Abstract

Phosphorus (P) is indispensable for all life forms and is known as ‘king-pin’ in world agriculture. In spite of its high P concentration in most soils of the world (~100–3000 mg P kg^{-1} soil), P is the most deficient nutrient in global agriculture. Its highly complex chemistry and occurrence of series of transformations on the soil colloidal complex make it the least soluble compound in soils. Phosphorus concentration in soil solution varied widely from very high (10^{-4} M) to a deficient (10^{-6} M), further extremely low in the least fertile soils of tropical regions. The minimum P concentration to which growing plant roots are exposed and P deficiency in rhizosphere occurred is ~1 μM. Aside from inherent behavior of the farmers to add more and more of the P-fertilizers being added to soils under different cropping systems, available P concentration in soil solution seldom exceeds ~5 μM L^{-1}. Phosphorus dynamics and availability in soils are significantly controlled by the soil’s properties including physical, chemical, and biological. About 90% variability in organic P (Po) and inorganic P (Pi) is related to soil texture with a negative correlation with a sand content of the soil. Due to calcium (Ca^{2+}) ion activity in the aqueous phase, there occurs a formation of insoluble Ca-P minerals (viz. hydroxyl apatite (HA), β-tricalcium phosphate

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(*β*-TCP), dicalcium phosphate dehydrate (DCPD), octacalcium phosphate (OCP)) in the calcareous soils. In acidic soils, aluminum (Al^{3+}) and iron (Fe^{3+}) get attached to SOM, leading to the formation of metal-OM complexes. The soil management and crop production practices that increase soil organic matter (SOM) levels had a significant influence on P availability and its dynamics in soils. The application of organic manures either alone or conjointly with fertilizers causes a significant change in P fractions (Po and Pi) due to reduction in P sorption, conversion of non-labile P to the labile P pool, and prevention of the formation of meta-stable compounds like *β*-TCP and HA in the soil, causing a large flush of available P in the equilibrium soil solution and increased P use efficiency (PUE).

Keywords

Phosphorus release kinetics · Mineral solubility · Reaction products · Integrated nutrient management · Soil properties

Abbreviations

ACP	Amorphous calcium phosphate
ANN	Artificial neural networks
$CaCO_3$	Calcium Carbonate.
CEC	Cation exchange capacity
CDB	Citrate dithinonite bicarbonate
DCP	Dicalcium phosphate
DEM	Digital elevation model
FYM	Farm yard manures
GRNN	General regression neural network.
HA	Hydroxyapatite
IFA	International Fertilizer Industry Association
MCP	Monocalcium phosphate
MSE	Mean square error
MLR	Multiple linear regression
OCP	Octa calcium phosphate
PDE	Phosphodiesterase
PME	Phospho-monoesterase
Q/I	Quantity-intensity relationship
RP	Rock phosphate
SOC	Soil organic carbon
SOM	Soil organic matter
SPR	Standard phosphate requirement
SVM	Support vector machine

12.1 Introduction

Being the second most important plant nutrient for crop growth, phosphorus is a very important plant nutrient. It is indispensable for all life forms and is known as 'king-pin' in world agriculture. Phosphorus plays a critical role in optimizing plant growth due to its involvement in different metabolic processes viz. production of adenosine tri-phosphate, enzyme regulation, and nucleic acid and phospholipids' structural element (Bünemann et al. 2006). Being next only to nitrogen (N), P is the most deficient nutrient in global agriculture, in spite of its high concentration in most soils in the world (~100–3000 mg P kg^{-1} soil), of which a significant amount exist in organic forms (Condron et al. 2005; Richardson et al. 2005; Menezes-Blackburn et al. 2016). It is because of its complex chemistry and occurrence of series of transformations on the soil colloidal complex, making its less soluble compound in soils (Halford 1997; Singh et al. 2010). Because of highly complex interactions and biogeochemical transformations in soils, the estimation of the P release potential of soils is difficult (Maassen and Balla 2010; Kumar et al. 2018). Phosphorus gets sorbed on oxides and hydroxides, forms insoluble compounds which are often not available to the plants, and got fixed in soils (Halajnia et al. 2009). Phosphorus concentration in soil solution varied widely from very high (10^{-4} M) to a deficient (10^{-6} M), to extremely low (10^{-8} M) in very low fertility tropical soils (Syres et al. 2008). The minimum P concentration to which growing plant roots are exposed and P deficiency in rhizosphere occurred is ~1 μM (Hendriks et al. 1981).

The most recent estimate revealed that globally ~5.7 billion ha of land has been suffering from P deficiency, a big hurdle for achievable optimal crop yields (Batjes 1997). Under most conditions, a significant portion of applied P gets fixed in soils as primary minerals, or as organically complexes form, and thereby, only ~1.5% to 11% remains available to growing plants for their requirement (Menezes-Blackburn et al. 2018). Even after the addition of higher inputs of P-fertilizers in texturally divergent soils, available P concentration in soil solution seldom exceeds ~5 μM L^{-1} (Wang et al. 2015). In addition, apatite mineral which is a basic input for the P industries are limited and may finish within~100 years, if used in the same extent (Stevenson and Cole 1999). Therefore, improving P use efficiency (PUE) has overwhelming significance as that of N use efficiency (Saini et al. 2019). The United States Geological Survey estimated the world rock phosphate (RP) reserves are ~18,000 million tons (Mt), while resources were ~ 50,000 Mt. (Jasinski 2006). The International Fertilizer Industry Association (IFA) estimated world RPuseof~171 Mt. in 2005 (Prud'homme 2006). With this rate of usage, the P reserve exploited between 600 and 1000 years (Isherwood 2003; Sattari et al. 2012).

Phosphorus dynamics is considered to be influenced by different mechanisms viz. dissolution-precipitation, sorption-desorption, and mineralization-immobilization reactions, etc. (Frossard et al. 2000; Manning et al. 2006) (Fig. 12.1), which is governed by various soil physicochemical properties of soils (Griffin and Jurinak 1973; Sharpley et al. 1984; Tunesi et al. 1999; Pant et al. 2002; Singh and Singh 2007a; Singh et al. 2020a; Kumar and Meena 2020). Soil P availability and use efficiency of applied fertilizer-P depends upon its dynamics in relation to soil

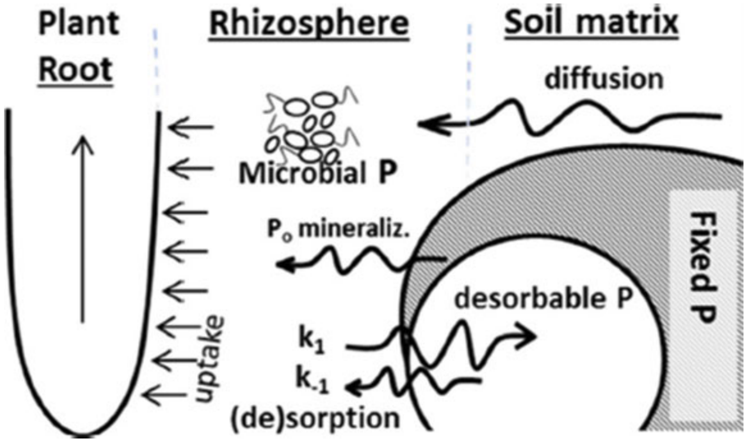

Fig. 12.1 Rhizosphere processes involved in soil phosphorus bioavailability and plant uptake different mechanisms

management and crop production practices (Reddy et al. 1999; Singh et al. 2020b; Saini et al. 2021). Practices responsible for a hike in inherent soil organic matter (SOM) levels had a significant influence on P availability and its dynamics in soils (Messiga et al. 2012). The application of organic manures increases soil organic carbon (SOC) concentration (Benbi et al. 2016), due to enhanced soil microbial biomass (Singh and Benbi 2018; Sharma et al. 2020a) and enzymatic activity (Sharma et al. 2020b) which significantly impacts the P availability (Chen et al. 2003a; Sigua et al. 2009; Sharma et al. 2020b; Singh et al. 2020b). Manure application to the soil along with inorganic P fertilizers causes a significant change in P fractions (viz. organic P and inorganic P) (Singh and Singh 2011; Ranatunga et al. 2013), reduction in sorption (Varinderpal-Singh et al. 2006; Song et al. 2007; Singh and Singh 2007b), P release kinetics (Singh and Singh, 2016; Saini et al. 2021), conversion of non-labile P to the labile P pool (Hundal et al. 1988) and prevention of the formation of meta-stable compounds like β-tricalcium phosphate and hydroxyapatite (HA) in the soil (Toor and Bahl 1999; Singh et al. 2010). Therefore, for compiling information on different soil management factors affecting the fate of applied fertilizer-P in the soils with special focus to improve its use efficiency in the global agriculture for the long-term sustainability of the agricultural production systems, the present chapter is compiled.

12.2 Crop Response to Fertilizer-P Application

Phosphatic fertilizers are generally applied in higher quantities than the plant requirement for increased land productivity and higher economic returns, which accumulate in the soils because of strong adsorptive forces, quicker precipitation, and immobilization into fixed forms from where it becomes unavailable to the plants.

Due to complex soil properties, most techniques to solubilize the recalcitrant P of soils become inefficient (Menezes-Blackburn et al. 2016). It got fixed in the soil along with slow diffusion and its availability to the roots is the most important area of interest nowadays (Ramaekers et al. 2010; Shen et al. 2011; Kumar et al. 2021). Due to low availability, P has been recognized as a major yield-limiting factor, more particularly for the developing or undeveloped countries which are facing a financial crisis and generally having lower grain yields (Lynch 2007; Richardson et al. 2011; Richardson and Simpson 2011; Meena et al. 2020). For that reason intensive cultivation in those regions, there is a need for judicious administration of phosphatic fertilizers for increased P availability and food security of projected ~9 billion human population by 2050 (Richardson et al. 2011).

From fertilizer-P application to P uptake by the plant roots, a significant portion is lost with environmental and ecological implications (Cordell et al. 2009a, 2011; Tirado and Allsopp 2012). About 1/3rd of applied P lost both due to poor management practices and by land degradation process including soil erosion (by water or wind), as only ~15–30% of applied P is used by the plants in their metabolic activities during the first growing season. The poor management practices viz. preparation of manures in open heaps might cause P loss up to the tune of ~50% to the environment (Tirado and Allsopp 2012). The mechanisms by which soil P becomes available to the plant's roots viz. diffusion, desorption, mineralization rate, etc. still required an abrupt mindset change of researchers (Menezes-Blackburn et al. 2016).

In general, its use efficiency in crop production is partitioned into PAE (P acquisition efficiency) and PUE (Manske et al. 2001; Veneklaas et al. 2012). The PAE is the capability of the agricultural crops to consumed P from the rhizosphere is referred to as PAE, while PUE is related to the ability to produce per unit of grains from every unit of P fertilizer (Hammond et al. 2009; Wang et al. 2010; Singh et al. 2020b). The dependency of PAE and PUE in improving the P availability to plants depends on several factors viz. soil, crop, and environmental (Wang et al. 2010). For sustainably reducing the P loss from the food chain and to improve the PUE, different response strategies are required in an integrated approach (Schroder et al. 2011). As per one estimate, up to ~70% of the global P demand could be met through enhanced PUE, while the remaining demand could be met through a higher resurgence and P use from its sources (Cordell et al. 2009b).

12.3 Factors Affecting P Availability

There are several factors affecting the availability of the soil P, which further affect the different metabolic activities and hence the growth and yields of the agricultural crops which are explained as below.

12.3.1 Soil pH and P Availability

The most important factor which affects the availability of P in the rhizosphere through soil solution is the pH of any soil. After extensive P uptake, mostly its concentration in soil solution was reduced, particularly under alkaline conditions (Chen and Barber 1990b). In calcareous soils, P gets precipitated as calcium phosphates (Ca-P) having extremely low solubility. Under low soil pH conditions, P gets precipitated as phosphates of Fe or Al (viz. Fe-P and Al-P, respectively) with lesser solubility. For better crop response of applied P, a pH range of 6.0–7.0 is considered important. The reclamation of the acidic or alkaline calcareous soils lead to increased P availability and therefore, crop response due to increased H_2PO^- ions in soil solution is related to easy absorption by the plants. The concentration of P in soil solution in ionic form decides its availability to plants roots. The $H_2PO_4{}^-$ and $HPO_4{}^{2-}$ ions in the soil solution constitute the main form absorbed by the plant roots (Shen et al. 2001). The predominance of $HPO_4{}^{2-}$ ions in a soil solution occurred between soil $pH = 7.5–8.2$, and preferential uptake of $H_2PO_4{}^-$ by plants compared to $HPO_4{}^{2-}$ results in its reduced availability in alkaline soils. The activity of $H_2PO_4{}^-$ plays a greater role in determining P uptake by the roots (Hagan and Hopkins 1955). Sentenac and Grignon (1985) reported that increasing pH above 5–7 gradually diminishes $H_2PO_4{}^-$, while increases the concentration of $HPO_4{}^{2-}$ ions. The $H_2PO_4{}^-$ is absorbed by the plants ~10-times more rapidly than the $HPO_4{}^{2-}$ form; therefore, P availability would be greater at low pH values unless other factors inhibited root growth (Chen and Barber 1990a). At pH >9.0, the release of more P would occur due to the effect of associated cations. Because at this pH, the proportion of $H_2PO_4{}^-$ ions would significantly decrease, while on the other hand the proportion of $HPO_4{}^{2-}$ ions would increase manifold (Tisdale and Nelson 1975). Tunesi et al. (1999) revealed that when increasing amounts of exchangeable cations such as Ca exceeds the solubility products for the P solid phase, which produces higher P removal from the solution is highly influenced by H^+ ion concentration in the soil solution. The lower phosphorus solubility in calcareous soils at near-neutral pH has been reported frequently (Gardner and Kelley 1940; Padmavathi-Devi and Narsimham 1978). Min-Zhang et al. (2001) delineated that increase in soil pH of Spodosols, Alfisols and Entisols leads to a shift in the P solubility reactions more particularly under the light-textured soils having sand fraction on the higher side. Quang et al. (1996) highlighted a negative correlation between P sorption capacity and pH of the soils. The PO_4–P sorption is increased under relatively acidic conditions, and $PO_4{}^-$–P precipitation as Ca-P under alkaline conditions due to higher pH largely affects its availability to the plant roots (Goldberg and Sposito 1984). The amorphous calcium phosphate, octa calcium phosphate, and apatite are important Ca-based phosphatic compounds formed in near-neutral calcareous and alkaline soils.

12.3.2 Organic Matter of Soil and P Availability

Inherent organic matter of soil is the vital factor responsible for P availability and good soil health. The build-up of SOM improves the availability of essential plant nutrients, even under deficient conditions. The soils with higher SOM contents had a higher fraction of organic P in nature, which get mineralized to readily available P form in the soil solution for their uptake by the plant roots. Soil organic matter binds the Fe due to its chelating nature and prohibits the formation of insoluble Fe-P, which are unavailable to the plants even when fertilizer-P is applied. The frequent use of organic manures in alkaline soils not only improves P supply but also increased the availability of mineral forms of Pin the soil upon decomposition. Generally, the critical P concentration for optimum plant growth varies near to 0.2 μg P ml^{-1} (Fox and Kamprath 1970). In calcareous soils, SOM and orthophosphates compete for the exchange site on the highly reactive calcium carbonates ($CaCO_3$) surfaces (Halford and Mattingly 1975). The adsorption of organic materials on the sorption sites reduces the bonding energy of the adsorbed P, which reduces the plant P requirements for their optimum growth. The application of organics manures to soil leads to an increase in the soil macro-aggregate and mineral associated C (Benbi et al. 2016; Sharma et al. 2020a), which also influences P availability and related dynamics (Messiga et al. 2012; Singh et al. 2020b). The increase in inherent SOM with integrated nutrient management improves biomass and their activities (Sharma et al. 2020a, b), and improves P status in the soils (Chen et al. 2003a; Sigua et al. 2009). Organic manure application along with inorganic P fertilizers causes a significant improvement in organic (Po) and inorganic P (Pi) fractions (Ranatunga et al. 2013; Yadav et al. 2020) and reduction in P sorption (Prasad and Mathur 1997; Varinderpal-Singh et al. 2006; Song et al. 2007; Singh et al. 2010; Singh and Singh 2016). The soil management practices that involved higher addition of SOM thorough crop biomass like in agroforestry systems (Jalali and Ranjbar 2010), lead to relatively higher MBC in the soils under poplar-based agroforestry compared to intensive cereal-based cropping system (Benbi et al. 2012). The accumulation of leaf litter in soils under agroforestry affects the soil P availability by mineralization of Po (Prakash et al. 2018).

The improvement in soil microbial activity and the formation of Po occur with an increase in SOM content in soils (Dalal 1979). Increased P availability in the soils accelerates P cycling through enhanced biological quality due to increased microbial activity and associations with mycorrhiza with tree species. Inter-cropping as in agroforestry system helps release P from recalcitrant P pools, making it available to the crops. The higher availability of the available Po compared to the total P in soils under agroforestry systems was because of better land use and the addition of higher quantity of plant-mediated biomass (as litters, leaves, etc.) in soils as compared to any other conventional system. The increased microbial biomass plays a major role in P turnover by affecting its transformation and redistribution into different Po and Pi forms (Stewart and Tiessen 1987). A linear relationship between Po content and SOM in calcareous soils has been reported by Sharpley et al. (1989). Shaheen et al.

(2007) observed that Olsen-P was relatively higher in soils with greater SOM content, which was further strengthened by better relation between Olsen-P and SOM content (Trivedi et al. 2010). SOM controls the short-and long-term P availability in the soils and therefore to growing plant roots (Runyan and Dodorico 2012; Singh et al. 2020b).

Jiang et al. (2006) studied SOC and P interactions under seeded alfalfa fields in China and reported that number of growing years results increased SOC, total P, and available P. SOC was significantly positively correlated with total P, available P, and soil total N (r = 0.627**, 0.691**, and 0.546*, respectively). Zhang et al. (2012) observed that the amounts of P released from the soils showed a linear positive correlations with the Po content, indicated that Po can easily release P and thereby enhanced P availability in soil solution. Hadgu et al. (2014) reported negative trends between P availability in soils to the plant roots if SOC declined below critical levels as then SOM may compete with P for adsorption sites.

12.3.3 Dominant Clay Type, Soil Texture, and P Availability

In the different soil primary particles, only clay fraction has been chemically active which results in different reactions in the soils. For P availability, clay holds a special place as it fixed the P and reduces its availability to the plants. The soils with lesser clay content have better availability of P as compared to the soils with higher clay percentages. Among different clay types, 1:1type clay (Kaolinite) has a higher P fixation capacity relative to 2:1 type clays (montmorillonite, illite vermiculite, etc.). Due to prevailing harsh weather conditions of tropical regions, much of the P got fixed due to the dominance of the Kaolinite type of clays in the soils. It has been well established that differences in P content are accompanied by variation in soil texture, with total P varied inversely to grain size (Johnston et al. 1997). Soil with higher organic matter content has been reported to supply higher amounts of P. Generally, higher quantum of amorphous Fe and Al oxides in fine-textured soils with higher SOC leads to sorb soil P (Richardson 1985; Sah et al. 1989; Lockaby and Walbridge 1998). Fixation of applied fertilizer-P happens due to the presence of higher amounts of clay, Al, Fe, and sesqui-oxides (Doddamani and Seshagiri-Rao 1989). The higher adsorption capacity of the soils with higher clay content has been reported (Bahl et al. 1986). On average, the higher percentage of sand content in soils will lead to higher release of P as compared to the soils with lower sand content (Bahl 1990). The phosphate adsorption release curves for silt and clay fractions from black Chernozem and Solodized soils revealed that clay fractions adsorbed 1 to 1.5 and 2 to 10-times higher P than silt fractions, respectively at the same equilibrium P concentration (Goh et al. 1986). About 90% variability in Po and Pi has been reported to be related to soil texture with a negative correlation with soil inherent sand proportions (O′ Halloran et al. 1985). Clay content of the soil has a direct relationship with the fixation of applied P causing reduced availability of P to the plant roots but is not affected much due to silt and sand content of soils (Douli and Gangopadyay 1984). Clay content of the soil was reported to be significantly related to soil P sorption

(Samadi 2006). Therefore, it could be concluded that heavy textured soils have lower available P in soil solution as compared to the comparative light-textured soils.

12.3.4 Calcium Carbonate and P Availability

Calcium carbonate ($CaCO_3$) exerts a dominant effect on the nature and properties of P in calcareous soils. It accumulates under calcareous soils and governs the P reactions in soil (Lindsay 1979) due to its adsorption and precipitation on the reactive surface of $CaCO_3$ (Cole et al. 1953; Griffin and Jurinak 1973; Freeman and Rowell 1981; Amer et al. 1955). Availability of P in the soil, to large extent depends upon the presence of $CaCO_3$ both in amorphous and crystalline forms. Generally, in the calcareous soils with highly reactive $CaCO_3$ surfaces, P reactions such as precipitation and adsorption affect the availability of the applied P-fertilizers (Cole et al. 1953; Griffin and Jurinak 1973; Freeman and Rowell 1981; Amer et al. 1955). In the soil solution of calcareous soils, activity of the Ca^{2+} ions leads to the formation of insoluble Ca-phosphate minerals (Tunesi et al. 1999). However, higher involvement of exchangeable Ca ions to P sorption than $CaCO_3$ has already been reported by Akinremi and Cho (1991). The adsorption process has been seen to be predominant at lower P ($<10^{-4}$ M) concentrations in solution (Halford and Mattingly 1975; Freeman and Rowell1981; Solis and Torrent 1989; Hamad et al. 1992), while the precipitation reaction dominates at higher P concentration (Matar et al. 1992). The P sorption capacity of calcite is apparently <0.3 μ mol P m^{-2} (Griffin and Jurinak 1973; Freeman and Rowell 1981; Borrero et al. 1988), which is about 1/tenth of natural Fe oxides (Torrent et al. 1992; Torrent et al. 1994). Freeman and Rowell (1981) observed that only ~25% of P sorbed by calcite was isotopically exchangeable within 14-days and by the time Ca-P had precipitated on the surface. By contrast, isotopic exchangeability at a similar time and equilibrium concentration was usually >40–50% for PO_4^-adsorbed on geothite and on non-calcareous soils containing high-affinity PO_4^- adsorbents like geothite, haemetite, gibbsite, kaolinite, etc. (Torrent et al. 1992; Torrent et al. 1994). Soper and El-Bagouri (1964) reported that the availability of added PO_4^- was not related to the carbonate content of the soil, but $CaCO_3$ had a very large effect on the movement of applied P. The extent of PO_4^-movement in non-calcareous soil was greater than in the calcareous soil regardless of the source of P added. The movement of P from applied fertilizer decreased with an increase in $CaCO_3$ contents in soil (Bell and Black 1970). Similarly, Sharpley et al. (1984, 1989) highlighted a reverse trend between fertilizer-P availability and fertilizer-P availability index due to accumulation of P on the surface of $CaCO_3$ in soil. Borrero et al. (1988) reported that in calcareous soil both the total apparent surface area of $CaCO_3$ and P sorption by $CaCO_3$ are relatively lower than clay, which played an important role in the P sorption. Halajnia et al. (2009) through a study on eight soils treated with two levels of inorganic P and manure reported that Olsen-P and NH_4OAc extractable Al and active $CaCO_3$ had a positive relationship with each other in P applied soils. In the floodplain calcareous soils of Indian Punjab, Singh and Singh (2007a) reported that for soils with comparatively higher $CaCO_3$ content, inflection point of isotherm that revealed that only at high equilibrium solution P concentration, the P deposition in soil was distinct. On the contrary, Ryan et al. (1985) reported negative relationship between loss of P from solution to both total and active $CaCO_3$ and observed no effect of $CaCO_3$ particle size on P retention from solution. The studies (Ryan et al. 1985; Solis and Torrent 1989) revealed that in the calcareous soils, P sorption was even more closely related to Fe and Al oxide and clay content than to $CaCO_3$ content (Castro and Torrent 1998).

12.3.5 Free and Amorphous Fe and Al Oxides and P Availability

Amorphous Al hydroxide formed as result of the weathering of clay minerals has a profound influence on P availability and sorption reactions. The activity of these free oxides and their ability to absorb PO_4^-ion decreased in due course of weathering (Araki et al. 1986). According to Bloom (1981) and Gerke (1992, 1993) Al^{3+} and Fe^{3+}gets bound to SOM to form metal-OM complexes which are considered responsible for the P fixation. Vo Dinh Quang et al. (1996) reported that the sites responsible for the high energy P sorption sites on Al oxi-hydroxides and to a lesser extent on poorly ordered Fe oxi-hydroxides (Solan et al. 1995; Wang et al. 1991; Zhang and Karathanasis 1997). Borling et al. (2001) and Niskansen (1990) reported that Al was more strongly correlated with P sorption than Fe. Similarly, Pant et al. (2002) observed that the P sorption maxima were positively linked with oxalate extractable Al and citrate dithionate-bicarbonate (CDB) extractable Al under anaerobic conditions and there was no significant relation with them. Borggaard et al. (1990) revealed that poorly crystalline Fe and Al oxides affect P sorption maximum significantly than from well crystalline Fe oxides. Brennon et al. (1994); Saini and MacLean (1965) reported that amounts of Al oxide in the soil were more important than that of Fe in assessing the PO_4^- ions adsorption capacity of the soils. Milap-Chand et al. (1995) reported a direct relation between P adsorption and cation exchange capacity (CEC), amorphous forms of Fe and Al, clay content, and SOC content in soils of north-western India. Adetunji (1997) conducted laboratory experiments in low activity clay soils of Ogun State (Nigeria) to develop the relationships between P sorption capacity and reported that CDB extractable-Fe was the most important variable accounting for ~99% of the variation in adsorption capacity. Likewise, Halajnia et al. (2009) reported increased recovery of CBD-P and found that Fe oxides play an important role in P sorption. In the recent floodplain soils of Indian Punjab, Singh and Singh (2007b) reported that in a majority of non-calcareous soils, the P fixation is generally regulated by strong attraction of non-carbonated clays The redox-sensitive Fe^{+3}oxides during anoxic conditions are subjected to reductive dissolution which could change the sorption behavior and release of Fe^{2+} and dissolved P (Heiberg et al. 2010). Several other studied also highlighted increased Fe and P concentrations in soils in relation to reduction in redox potential (Meissner et al. 2008).

12.3.6 Application of Organic Manures and P Availability

Among different sources of organic manures, farmyard manure (FYM) has a special role to play in increasing soil and water productivity through the improvement in soils' properties pertaining to physical, chemical, and biological aspects and making the nutrient available to the plants. The role of FYM on increased P availability in the P deficient soils has not been well understood particularly under tropical environments and under anaerobic conditions, though P fertilization is skipped due to prevailing anaerobic (reduced) conditions. On-farm trials carried out at the central highland of Madagascar reported high variations in the performance of FYM in terms of land productivity and P consumptive use patterns of rice where soils mostly remained under anaerobic conditions (Andriamananjara et al. 2016; Bhatt et al. 2021). The higher response of applied FYM in the inherently P deficient soils helps in maintaining soil pH and oxalate extractable P contents due to improved soil properties. Rabeharisoa et al. (2012) reported that in the anaerobic conditions, pH of soils becomes a critical indicator for P availability from the soil solution as it improves anion exchange membrane extractable P content in soils, particularly in low SOC soils. Extended microbial Fe-oxide reduction might be responsible for increased labile P with SOM application in soils with higher P fixation capacity. The isotope dilution principles generally preferred to study the soil P which was isotopically exchangeable (ratio of radioactive P to non-radioactive P in plants) and which, reflects increased amounts of labile P pools in soils labeled with radioactive $^{32}PO_4^-$ ions after FYM additions (Larsen 1952). Mineral P enhanced the above-ground biomass and P uptake by 0.35–1.62 g pot^{-1} and 1.59–5.71 mg pot^{-1}, respectively as compared to the control plots (Fig. 12.2) (Rakotoson and Tsujimoto 2020). However, the increase in biomass occurred to the tune of 0.11–0.77 g pot^{-1} with the addition of FYM. Plant P uptake increased with FYM additions relative to the control, which was related to the additive effect of FYM application to the mineral P application.

Toor and Bahl (1997) reported a gradual increase in $NaHCO_3$-P in soils amended with poultry manure (at 2×10^3 mg kg^{-1}) and incubated for 16 weeks at aerobic moisture regime (Table 12.1). In the acidic soil, $NaHCO_3$-P accumulation increased from 4.5 to 7.0 mg kg^{-1} during the initial 8 weeks of aerobic incubation. In the calcareous soil, $NaHCO_3$ concentration increased from initial 7.5 and 11.2 mg kg^{-1} during the initial 8 weeks of incubation. However, in the non-calcareous soil, $NaHCO_3$-P varied between 9.5 and 12.5 mg kg^{-1}, during the period followed by a gradual decrease with aging. However, Singh et al. (2010) reported the floodplain calcareous soils incubated with press mud application (@ 1.0%) exhibited increased $NaHCO_3$-P concentration from 9.4 to 14.3 mg kg^{-1} under aerobic (60% water-filled pore space) moisture regime during the 16 weeks of incubation. The extent of increase in P concentration in press mud amended soils was higher at nearly saturated (90% water-filled pore space), compared with the soils incubated under aerobic moisture regime (Table 12.1). Regardless of the moisture regime and press mud application, $NaHCO_3$-P concentration was higher in non-calcareous soils, compared to calcareous soils.

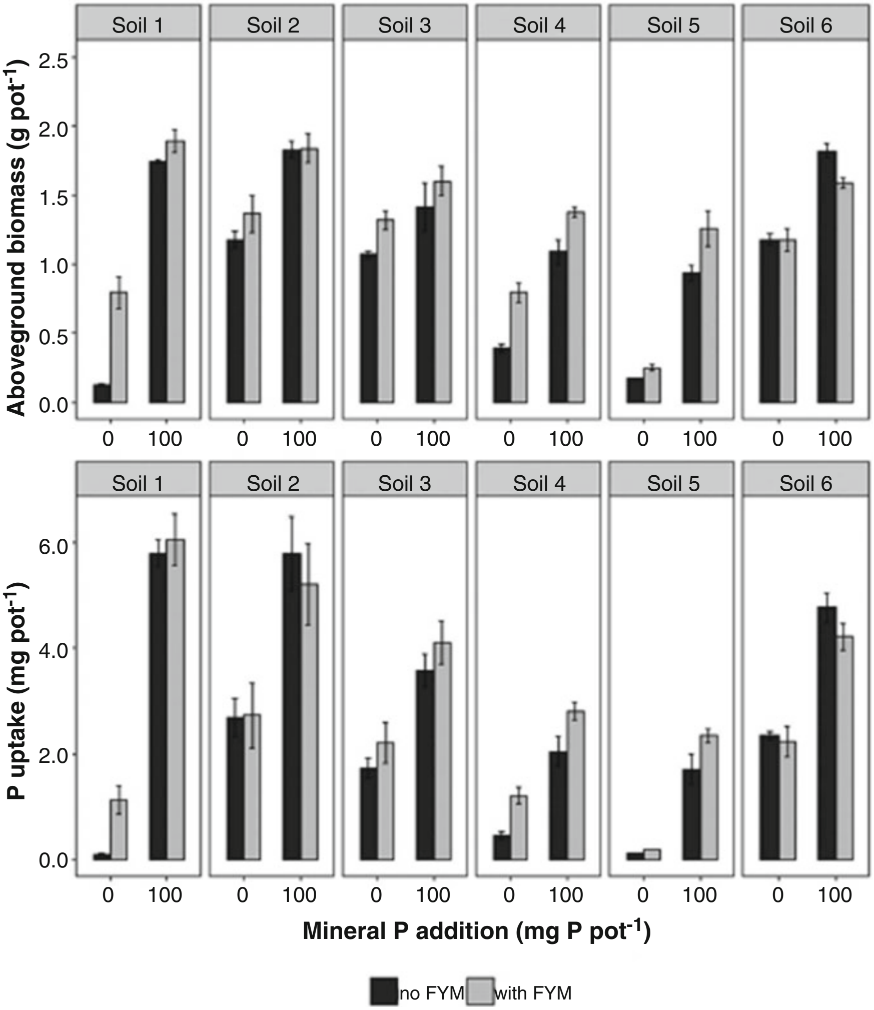

Fig. 12.2 Rice above-ground biomass and P uptake patterns under different mineral P and FYM applications (Source: Rakotoson and Tsujimoto 2020)

Organic manure application improves soil health by improving its physic-chemical properties and certainly improved the P concentration in the soil solution and ultimately has higher P use efficiencies. Vaneeckhaute et al. (2014) reported that that the sandy soil had significantly higher biomass yield and dry weight biomass yield with manure application as compared to the triple superphosphate (TSP), while the dry weight content and P content of the biomass was significantly higher than from the TSP treatment. P uptake (mg P) in the TSP treatment showed significant results as compared to the control. The PUE (dry weight yield) in the sandy soil was mostly negative as the yield of the reference TSP was lower than the control

Table 12.1 Change in $NaHCO_3$-P concentration in soils amended with organic manures under aerobic and nearly saturated soil moisture regimes

	Incubation period (weeks)						
Soil	1	2	4	8	12	16	References
Acidic (aerobic)	4.5	5.3	6.0	7.0	6.3	5.5	Toor and Bahl (1997)
Calcareous (aerobic)	7.5	8.4	9.7	11.2	9.8	8.5	
Non-calcareous (aerobic)	9.5	10.7	11.5	12.5	12.1	10.8	
Calcareous (aerobic)	9.4	12.0	12.3	12.7	13.4	14.3	Singh et al. (2010)
Calcareous (nearly saturated)	11.9	12.9	13.6	15.0	16.0	16.9	
Non-calcareous (aerobic)	12.5	16.0	16.3	16.6	17.3	18.9	
Non-calcareous (nearly saturated)	13.8	17.3	17.9	19.6	20.8	22.4	

Table 12.2 Average phosphorus use efficiency (PUE) based on the plant reaction in time (%) for the different bio-based fertilizers; PUE(control); PUE(TSP) = 100%, Fw Fresh weight; DW dry weight ([a]TSP < control; [b]bio-fertilizer < control) (Source: Vaneeckhaute et al. 2015)

PUE (%)	PUE (FWyield) Sand	PUE (FWyield) Rheinsand	PUE (DWyield) Sand	PUE (DWyield) Rheinsand	PUE (uptake) Sand	PUE (uptake) Rheinsand
Struvite	—21[a]	75	10[a]	67	22	42
$FePO_4$-sludge	—68[a]	159	—16[a]	233	16	3.3
Animal manure	—46[a]	—8.9	—8.5[a]	—67[b]	37	80
Digestate	—67[a]	—45[b]	—90[a]	—100[b]	80	63

(Table 12.2). Therefore, application of the organic amendments viz. farmyard manure, compost, poultry manure, etc. is reported to be best for increased average PUE based on the crop yield.

12.3.7 Soil Moisture Status and P Availability

Soil moisture content significantly impacts the P availability, mineral dissolution, and sorption and release kinetics. The soils moisture content during the rice and wheat seasons appeared totally different, which affects the P availability. But over flooded soil conditions even negatively affects the P availability (Patric and Mahapatra 1968), due to Fe oxides' reductive dissolution (Huguenin-Elie et al. 2003). Due to the re-fixation of soil P in lesser available forms under a reduced environment, P availability is reduced to a large extent (Kirk et al. 1990). In the upland crops (viz. wheat, barley, maize, etc.), the already reduced P compounds are oxidized to lesser available forms and under prolonged oxidized conditions, thereby, soil P regains its pre-flooded conditions over a period of time (Willet 1991). Under the submerged conditions, the availability of P seems to be better than the aerobic conditions. This is why P application is generally recommended in aerobic crops (viz. wheat, gram, oilseeds, barley, etc.) than the anaerobic crops viz. paddy rice. Under the submerged condition, the unavailable and fixed forms of P become available to the plants under the reduced conditions (Broeshart et al. 1965, Mahapatra and Patrick 1969; Patrick et al. 1974; Ponnamperuma 1972). This has been the reason why the response of applied P to the paddy crop appeared lesser than when applied to wheat in a rice-wheat cropping system.

Some other factors also affect P absorption by the plant roots; among them, the degree and extent of waterlogged conditions, soil properties, inherent P status of soil under consideration, and fertilizer application method (Patrick et al. 1974). Under the flooded or reduced conditions, the availability of P enhanced to some extent as the case with Fe^{+3}inositol-P which reduced to Fe^{+2} inositol-P. Being an organic substrate, cellulose after combining with inorganic P, had profound effects on improving the availability of Po. Therefore, integrated nutrient use viz. use of organic manures along with inorganic manures is always advocated to improve the availability of the soil P to the plant roots which is further reflected in its growth and yield parameters (Zhang et al. 1994).

12.3.8 Soil Enzymatic Activity and P Availability

Soil enzymatic activity has a profound influence on the P availability to the plant roots. Plant species and soil microorganisms enhance phosphatase enzymes to mineralize Po compounds. Enzymatic activity has bimodal complementary action. The phosphodiesterase (PDE) has the capability to hydrolyze complex Po compounds viz. nucleic acids and phospholipids into much simpler compounds such as phosphor-monoesters which had the capabilities to mineralize Po into the forms readily available to the plants (orthophosphate, $H_2PO_4^-$) (Rejmánková et al. 2011; Stone and Plante 2014). Through P mineralization action, these enzymes played a critical role in the plant response under the limited P status of the soils (Dakora and Phillips 2002; Burns et al. 2013; Dalling et al. 2016). For modeling P cycling, phosphatase activity is considered crucial in different models pertaining to different ecosystems (Reed et al. 2015).

Phosphorus availability might be surplus when the composts are applied as N source for partial to complete supplementation of fertilizer-N. In the phospho-compost, both organic and inorganic pools of P get solubilize through organic acids during microbial activities. The cation bound chelate to phosphatic rock by hydroxyl and carboxyl groups and finally results in soluble-P. This process is triggered by soil microbial population which produces large amounts of organic acids and humic substances, including extracellular enzymes to promote SOM degradation. Enzymatic activities during the process of decomposition are vital and provide useful information on nutrient transformations and their release kinetics. Therefore, the quantification of soil enzymatic activities is considered a useful indicator for evaluating mass turnover in composts, which affects its stability and quality (Dalling et al. 2016). Among different enzymes, phosphatase being the most important which played a crucial role in P cycling and could be used as an indicator of microbial activities which further affect the P availability to the plant roots. Phospho-diesterase (PDE) and phospho-monoesterase (PME) are the two complementary enzymes; PDE hydrolyzes the nucleic acids and phospholipids complex compounds into simple phosphor-monoesters, while PME further mineralized Po into the orthophosphate that is absorbed within the rhizosphere by soil microbes (Rejmánková et al. 2011; Stone and Plante 2014). Therefore, these enzymes played a significant role in the mineralization of Po and thus in the crop response particularly under limited P availability (Dakora and Phillips 2002; Burns et al. 2013; Reed et al. 2015; Dalling et al. 2016).

It is well established that CO_2 uptake of tropical forests is affected by phosphatase activity (Goll et al. 2012; Yang et al. 2016). Therefore, critically understanding the P mineralization process, root behavior and the bacterial community interaction, and factors affecting it are important. Only agricultural experiments provide necessary insight on the role of bacteria in P possession which needs to be extended to the tropical forests with respect to their rhizosphere (Richardson and Simpson 2011; Pii et al. 2015). The interaction of plants roots and their bacterial community enables plants to prosper in soils under P deficient conditions either by enhancing PUE or P acquisition or even both (White and Hammond 2008). Under tropical conditions, plants could efficiently be using P through metabolic nucleic acid compounds produced through P re-sorption, recycling, and reduction (Vitousek and Sanford 1984; Hidaka and Kitayama 2011). The root and bacterial function are regulated by the inherent P availability and plant species (Treseder and Vitousek 2001; Costa et al. 2006; Lambers et al. 2009; Haichar et al. 2008; Bardgett et al. 2014; Hinsinger et al. 2015). Under grasslands, the activity of phosphor-monoesterase and phosphor-diesterase are reported to be significantly higher in comparison to the adjacent forest stand (Chen et al. 2000; Chen et al. 2003b). Chen et al. (2004) reported higher activities of acid and alkaline phosphor-monoesterase and phosphor-diesterase under ryegrass in comparison to the pine seedlings.

12.4 Phosphorus Movement and Environmental Degradation

Of the total applied fertilizer-P to the plants, a major part is lost either through erosion, and/or leaching. Intensive cropping intensity and tillage frequency have been adversely impacting the environmental quality along with biodiversity due to reactive N and P (Correll 1998). For meeting the P requirements of the crop plants, ~19 Mt. year^{-1} of P from RP is being used in P fertilizer manufacture industry (Heffer and Prud'homme 2008). Soil erosion and P loss to water bodies could be decreased by using the appropriated soil conservation measures as both erosion agents viz. water and wind-affected ~12 and 4% of the total European land area, respectively (Louwagie et al. 2009). It is estimated that soil erosion in Europe has caused a loss ranged from 5–40 t ha^{-1} year^{-1} (Verheijen et al. 2009) to 10 Mg t^{-1} year^{-1} (Louwagie et al. 2009). The higher part of P fixed with the clay fraction of soil gets eroded quickly with flowing water (Quinton 2002), and about

20–30 Mg year^{-1} of P is lost worldwide wide which is equivalent to15–20 kg P ha^{-1} year^{-1} (Ruttenberg 2003). Both soluble and particulate forms of P are moved with water moving across the surface, and eventually to have higher bio-available P concentration in surface waters (Schroder et al. 2011). Runoff water from the catchments results in the 'Eutrophication' which started in water at a P concentration of 0.10 g P m^{-3} (Correll 1998). Normally with surface runoff, P loss is considered more important than the leaching loss of soil P; therefore, more efforts are required made to arrest the surface runoff water to lakes or other water bodies.

Reduced tillage with residue retention helps to arrest the runoff water, sloping land terracing, planting along the contour, agroforestry are some of the key soil conservation technologies recommended in sloppy landscape (Schroder et al. 2011). One best practice is to apply the P fertilizer when the soil required it under deficient conditions. The frozen or snow-covered land or dry and hard soil or waterlogged should not be applied with P fertilizer (Schroder et al. 2011). Another aspect for harvesting better PUE is to apply it where it is required, and that too near to the plant roots as it moved slowly in the field (Schroder et al. 2011). For sustainably improving the soil health, one best and effective way is to enhance the inherent SOM levels through integrated approaches. Manure P must be used to the extent possible as it not only improved the soil health but also reduces the P losses in the ecosystem. Besides, improved the PUE has a key role in maintaining ecosystems' functioning and long-term sustainability (Tirado and Allsopp 2012).

12.5 Phosphorus Fractions in Soils

Under natural conditions, soils P constituted by both Po and Pi forms, mostly unavailable to the plants (Murphy and Sims 2012). Soil P fractions are considered important for studying soil P dynamics (Chang and Jackson 1957; Hedley et al. 1982; Aulakh et al. 2003). The calcareous soils had the dominance of Pi pool which ranges from ~75–85% of total P (Jiang and Gu 1989). In the calcareous floodplain soils, Pi comprised ~92–94 of total P concentration (Singh and Singh 2007b) (Table 12.3). The Pi pool is further partitioned as Ca-P (HCl-extractable P), Fe- and Al-P (non-occluded Fe- and Al-bound P), and occluded P (Chang and Jackson 1957; Solis and Torrent 1989). Majority of Pi exists as Ca-bound forms in the calcareous soils. Jun et al. (2010) reported that Pi comprised ~52–68% of total P in calcareous soils under wheat mono-cropping. Jalali and Tabar (2011) reported that the soils under garlic, orchard, pasture, potato, leafy vegetables, and wheat cultivation had dominance of Ca-P, constituting ~61–78% of total P, while labile P was the least in abundance (<2% of total P). In barley–soybean cropping system, Zheng and MacLeod (2005) reported that plant P uptake, labile, and moderately labile Pi increased with additions of fertilizer-P. The fertilized-P is mainly retained as soil labile Pi (~43–69% of total P) followed by the other fractions viz. ~20–30% of moderately labile Pi, and ~ 7–29% of sparingly soluble-P (HCl-P + H_2SO_4-P). As clay content in the soil increased, the recovery of labile P is reduced. Wager et al. (1986) reported that recovery of applied P fertilizer as labile Pi (~48% of total P) is

Table 12.3 Literature reports on effects of different cropping systems on soil P fractions in surface layer

Cropping system	Soil type	Total P (mg kg^{-1})	Inorganic P (Pi) (mg kg^{-1})	Organic P (Po) (mg kg^{-1})	Olsen-P (mg kg^{-1})	Reference(s)
Rice-wheat	Floodplain soils, Punjab, India	242–771	170–722	9.8–55.7	5.3–13.9	Singh and Singh (2007b)
Wheat monoculture	Calcarid Regosol	753–1127	422–738		2.3–22.9	Jun et al. (2010)
Groundnut-wheat	Tolewal sandy loam soil (*Typic Ustochrepts*)	390.2	343.2	47.1	10.4	Aulakh et al. (2003)

higher, compared with the moderately labile Pi (~43% of total P) and the sparingly soluble Pi pools (~9% of total P). Aulakh et al. (2003) reported that crops removed ~21–54% of applied fertilizer-P, with rest for accumulation and for other losses which account up to ~33–64% and ~ 12–32%, respectively. Beck and Sanchez (1996) studied soils' Pi and Po pools in a highly weathered soil and reported that NaOH-Pi acts as a sink for fertilizer-P, while later pool (Po) was the source of P availability in controlled systems (with no-P fertilizer application). Beck and Sanchez (1996) reported a direct relationship with the grain yields and the P availability to the plant roots, particularly under deficient conditions. Integrated nutrient management has always proved best for improving the $NaHCO_3$, better PUE, and P uptake (Motavalli and Miles 2002). Under the integrated nutrient management, particularly under the deficient conditions, moderately labile and non-labile P pool was increased and decreased by 3-and 6-times and by ~14% and ~ 18%, respectively, compared to the control plots, where no fertilizer-P was applied (Ahmed et al. 2019).

During mineralization of SOM, the Po compounds become available to the plants which leads to higher concentration of Pi (Noack et al. 2012; Wang et al. 2012). Zhongqi et al. (2006) studied P distribution in soils with manure application as Pi forms, enzymatically hydrolysable-Po and non-hydrolyzable-Po, and reported that water soluble-P, $NaHCO_3$-P, and enzymatically hydrolysable-P_o were directly associated with applied P, while NaOH-extractable P was not closely related to the manure applied P. Application of the organic acids with lower molecular weights (@ 10 m mol kg^{-1} soil) increased the Pi and Po availability. Soil Po released by low molecular weight organic acids is derived from the soil labile Po fractions. In contrast, Pi released by low molecular weight organic acids resulted from the mobilization of the moderately labile NaOH-Pi (Fe/Al-P) and HCl-Pi (Ca-Pi) fractions in the order of citric acid (4.83 mg kg^{-1}) > oxalic acid (2.40 mg kg^{-1}) > malic acid (2.04 mg kg^{-1}). Po release by low molecular weight organic acids occurred primarily due to the dissolution of soil labile Po ($NaHCO_3$-Po) (Wang et al. 2017). Regardless of the soil textural class, the application of low molecular weight organic acids followed an order of oxalic acid (0.63–-3.17 mg kg^{-1}) > citric acid (0.61–2.82 mg kg^{-1}) > maleic acid (0.52–1.76 mg kg^{-1}), results in cumulative Po and mainly labile Po ($NaHCO_3$-Po) release. Under the calcareous soil, Pi release enhanced from the HCl-Pi (Ca-Pi) fraction, where oxalic acid was most effective while in neutral and acidic soils, citric acid was most effective in releasing Pi from the NaOH-Pi (Fe/Al-Pi). Mechanism for the kinetics of Po release ascribed tothe ability of low molecular weight organic acids to mobilize the labile Po ($NaHCO_3$-Po) rather than their ability to chelate cations (i.e. Fe^{3+} and Al^{3+}) bound to Po in soil (Zhang et al. 2012). Soil texture, organic matter, and P status of soils significantly affect the P mineralization/immobilization pattern in soils (Gang et al. 2012).

12.6 Phosphorus Sorption and Release Kinetics

Phosphorus release kinetics has great significance for plant nutrition and environmental pollution because it predicts how quickly reaction approaches quasi-equilibrium (Amer et al. 1955). Under the P deficient conditions, the rate with which plants used P through roots also reduced due to the sorbed-P, which as such cannot be utilized (Nagarajah et al. 1968). The time-dependent P release from soils requires an understanding of mechanisms involved in the P reactions on soil colloidal complex (Singh and Singh 2016). The release and transport of PO_4^- ions from the manure applied soil has an unfavorable impact on the quality of surface water bodies due to P enrichment called 'eutrophication' (Jeremy and Daniel 2003). Under acidic conditions, inorganic orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) are the dominated P forms, which are absorbed by the plants (Mozaffari and Sims 1994).

After about 24 h of fertilizer-P application, almost ~80% of soluble-P is released into the soil solution, followed by the second phase of slow-release which continues up to 504 h (Jeremy and Daniel 2003). Total P released from the manure amended soils was ~29% in the top 10 cm soil layer, followed by ~8% from the sub-surface (45–65 cm) soil layer. The P release is rapid initially, followed by a slower release of 2160 h, and the Elovich equation was the best fitted kinetic model to determine the fate of P released into the soil solution (Yang et al. 2019). The amount of Pi (P_i-solubilized by oxalic and citric acids) increased with increasing organic acid concentrations. The oxalic acid exhibited a lower P_i solubility capability, compared with citric acid at a concentration of ≤ 1 m mol L^{-1}, whereas citric acid was higher at ≥ 1.5 m mol L^{-1}. Hosseinpur and Pashamokhtari (2008) reported that P release reached ~73% within the initial 15 days following bio-solid application in calcareous soil. Singh and Singh (2016) reported that cumulative P release was significantly ($p < 0.05$) higher after 12 weeks compared to that of 1 week after incubation. At aerobic and nearly saturated moisture regimes, non-calcareous soil had much higher cumulative P release compared to the calcareous soil. Phosphorus release from floodplain calcareous and non-calcareous soils proceeded in two phases. It increased rapidly with increasing equilibration time and gradually leveled off with shaking time enhancement. The Pi (at 25 mg kg^{-1}) and press mud (PM, 0.5%) application ($P_{25}PM_{0.5}$ and $P_{25}PM_{1.0}$) accelerated the P release from soils, and the reaction completed fast within 6–12 h of equilibration, indicating the dissolution of native P and conversion of non-labile to labile P pools. They compared nine different empirical models of varying complexity fitted to time-dependent P release data showed higher coefficient of determination for Elovich equation ($R^2 = 0.961–0.996^{**}$) followed closely by modified Crank's equation ($R^2 = 0.961–0.980^{**}$), power function equation ($R^2 = 0.946–0.995^{**}$) and differential rate equation ($R^2 = 0.903–0.997^{**}$).

The cumulative amount of P released in the inorganic fertilized plots was higher, and the rate of P release was much faster with fertilizer-P application than that of the biosolids amended soil (Derek et al. 2012). Parabolic diffusion equation best described the P release kinetics data, which showed that P desorption was mass-transfer limited process. The X-ray absorption trends near to edge structure revealed dissolution of Ca-P and Fe-P minerals occurs from the exchangeable sites. Under P deficient conditions or due to excessive P uptake, there is a rapid redistribution between the aqueous, adsorbed, and precipitated phosphate (PO_4^{3-}) species.

12.7 Mineral Solubility and Phosphorus Chemistry

Mostly mineral P forms of soils are found as insoluble forms viz. apatite, HA and oxy-apatite and Fe, Al, and Mn hydrated oxides (Grant et al. 2005). Phosphate reaction products are specific and specifically identifiable compounds, which are produced due to the application of fertilizer-P and its reaction with soil constituents. Phosphorus occurs in the soil in inorganic combinations, as it forms compounds with a variety of metals. Being chemically reactive, P exists in around 170 minerals (Halford 1997), however, organic forms constitute around ~15–80% of the total P in surface soils (Magid et al. 1996). Immediately after fertilizer-P application to soils, P undergoes fast transformations and changed into insoluble forms. During the start of the reaction, these are meta-stable and with time are converted to more stable P compounds. For the plants, meta-stable forms of P acts as a source for longer period of time (Black 1967). These reaction products primarily govern the availability of P to plants by controlling soil solution P concentration.

Bhujbal et al. (1986) recognized dicalcium phosphate (DCP) as a major reaction product after 2 weeks of incubation of ammonium nitro-phosphate fertilizer in vertisols, oxisols, alfisols, entisols, mollisols, and aridisols. Hasan and Bajaj (1982) reported the predominance of octacalcium phosphate (OCP) as a major reaction product of monocalcium phosphate (MCP) after 4 months of incubation in alluvial soils of Delhi. Black (1967) reported that in alkaline soils, OCP or apatite was the major reaction products, where monobasic calcium phosphate has been added. While studying the solubility and capacity relationship for residual available P in near-neutral and alkaline soils, Fixen and Ludwick (1982) reported that OCP was not likely an important residue in 27 out of 28 soils but TCP or a mineral similar to TCP in composition and solubility may have accompanied for at least a portion of fertilizer residue. Singh and Bahl (1993) in an experiment on ten soils varying in pH and $CaCO_3$ reported significant lowering of phosphate potential following combined application of 36 mg P kg^{-1} and *Sesbania.* Phosphorus solubility isotherms indicated an undersaturation with respect to OCP in most the neutral and alkaline soils. Sarkar et al.(1977) studied the reaction products formed in red soils of West Bengal following the application of MAP and MCP. They reported the formation of ammonium tarankite and variscite in soils of MAP application whereas reaction products of MCP caused the progressive dissolution of soil constituents and resulted in the formation of mainly colloidal amorphous Fe-Al phosphate compounds. While characterizing fertilizer-P reaction products in three texturally divergent soils, Ghosh et al. (1996) concluded that after 120 days of incubation followed by X-ray diffraction results in brushite, strengite, variscite as major soil fertilizer-P reaction products with ortho and polyphates as sources of P.

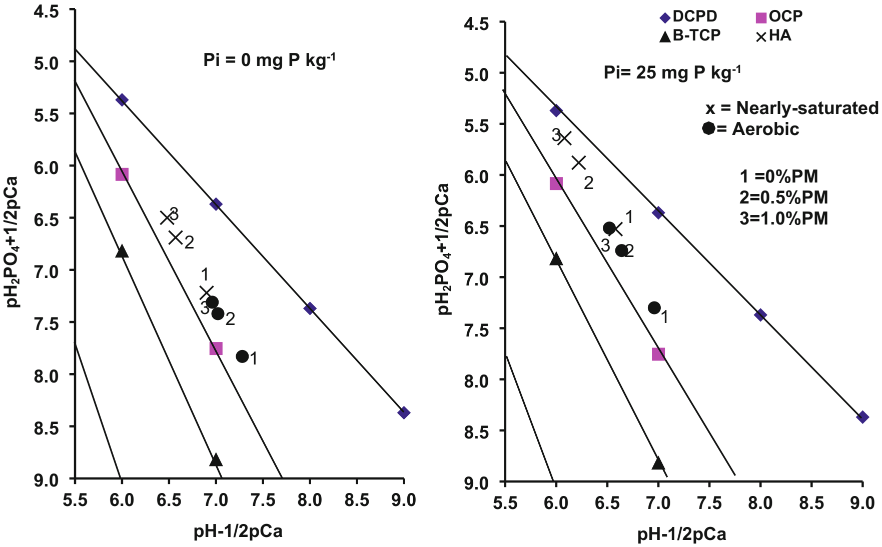

Fig. 12.3 Reaction products of P in sub-tropical calcareous soils (0—15 cm) without and with press mud (PM) and inorganic-P addition after 12 weeks of aerobic and nearly- saturated incubation (Source: Singh et al., 2010)

Integrated nutrient management as press mud (PM) and Pi application cause super-saturation with respect to dicalcium phosphate dihydrate (DCPD), delineating higher P availability in calcareous (Fig. 12.3) and non-calcareous soils (Fig. 12.4) (Singh et al. 2010). In the non-calcareous soils, solubility points shifted above DCPD, due to the lowering of phosphate potential, (Fig. 12.4). The standard phosphate requirement (SPR) was reported to decrease by 48.9 (45.0%) and 99.4 kg P_2O_5 ha^{-1} (90.9%), as quantity-intensity relationship because of PM application @ 0.5 and 1.0% under aerobic moisture regime, respectively in calcareous soil. A complete supplementation was, however, observed in non-calcareous soil in saturated soils where all the soil pores are water-filled and conducting it. Increased solubility of phosphatic compounds due to manure application has been related to decrease in phosphate potential (pH_2PO_4 + 1/2 pCa) of soils inculcated under soils at 60% water-filled pore space) and nearly saturated (90% water-filled pore space) moisture regimes (Table 12.4).

12.8 Artificial Intelligence for Predicting Soil P Availability

Modeling of nutrients availability in soils with contrasting physical and chemical properties and moisture regimes is important, which is normally used to develop relationships for variables. It has been effectively applied at different scales to

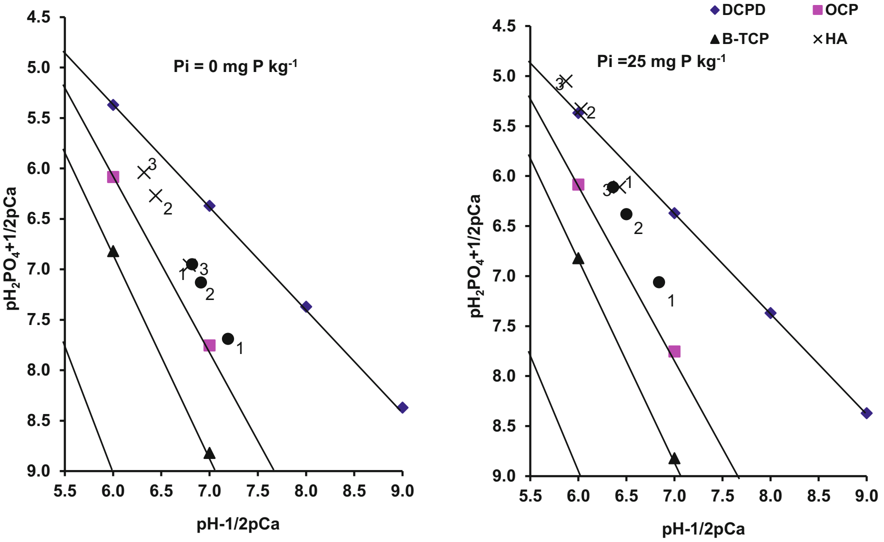

Fig. 12.4 Reaction products of P in sub-tropical non-calcareous soils (0—15 cm) without and with press mud (PM) and inorganic-P addition after 12 weeks of aerobic and nearly- saturated incubation (Source: Singh et al., 2010)

Table 12.4 Phosphate potential (pH_2PO_4 + 1/2pCa) of floodplain calcareous and non-calcareous soils amended with inorganic P and press mud incubated at aerobic (60% water-filled pore space) and nearly saturated (90% water-filled pore space) moisture regime (Source: Singh et al. 2010)

Inorganic P (mg kg^{-1})	No-Pressmud	Pressmud @ 0.5%	Pressmud @1.0%	Mean
	Calcareous soil, Aerobic (60% water-filled pore space) moisture regime			
0	7.83	7.42	7.31	7.52
25	7.30	6.74	6.52	6.85
	Non-calcareous soil, aerobic (60% water-filled pore space) moisture regime			
0	7.69	7.13	6.95	7.26
25	7.06	6.38	6.11	6.52
	Calcareous soil, nearly saturated (90% water-filled pore space) moisture regime			
0	7.22	6.69	6.50	6.80
25	6.53	5.58	5.64	6.02
	Non-calcareous soil, nearly saturated (90% water-filled pore space) moisture regime			
0	6.96	6.27	6.04	6.42
25	6.11	5.33	5.05	5.50

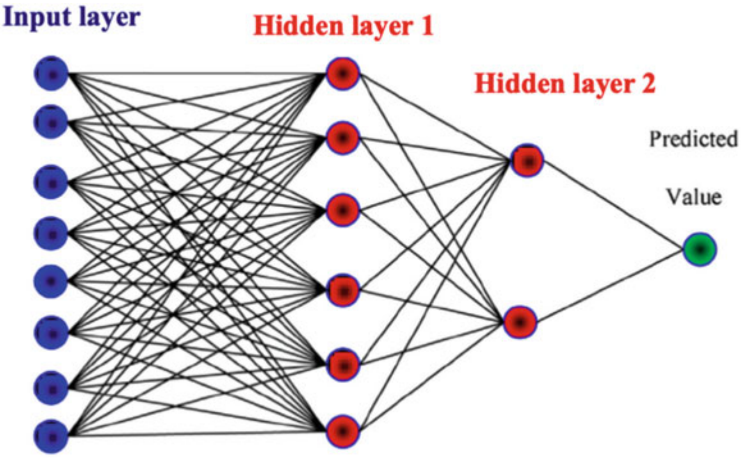

Fig. 12.5 The configuration of multi-layer artificial neural networks (ANN) for predicting variables

estimate soil physicochemical properties using attribute analysis (Omran 2012; Merdun et al. 2006). Soil P at field and landscape scales has been predicted from different related secondary variables using primary variables that can easily be obtained and be deduced from correlation and regression analysis with primary factors (McBratney et al. 2003). However, the efficiency of any model in predicting nutrient availability depends on several factors viz. complexity of land under consideration, digital elevation model (DEM) resolution, and input data quality (Wilson and Gallant 2000). These methodologies had the advantage of being cost-effective and time-saving in tedious soil analytical techniques, and often require a small sample size (McBratney et al. 2003; Sidhu and Kaur 2015; Sidhu and Kaur 2016; Kaur 2020). Over years, several statistical and multivariate techniques are developed for studying the relationships between spatially variable soil attributes across landscapes including geostatistical techniques, fuzzy logic, neural networks, linear and multiple regression techniques, etc. (Keshavarzi et al. 2015; Landeras et al. 2008; Kaur 2020). Artificial neural networks (ANN) are extensively used artificial intelligence tool used for predicting systems' performance particularly in the situations where the accuracy in prediction of highly complex systems are required, but limited field or laboratory experimental dataset is available (Najafi et al. 2009; Kaur 2020). A typical ANN consists of large numbers of highly interconnected processing units usually known as neurons (Thurston 2002; Singh and Kaur 2015; Sidhu and Kaur 2016; Kaur 2020). The ANN functions help to understand the non-linearity in datasets into neural networks that are more powerful compared with the linear transformation. Each ANN model is constituted by an input layer, sandwiched hidden layers, and lastly by outer layer (Fig. 12.5). The two elements of neural networks are the types of neural interconnection arrangement and algorithm type used to set the strength of relations. For modeling the complex

Table 12.5 Statistical measures for evaluating the performance of artificial neural network (ANN) used for predicting soil P (Source: Keshavarzi et al. 2015)

Topology	Training algorithm	Activation function	Epoch	Root mean square error (RMSE) (%)	Coefficient of determination (R^2)
3-6-1	Levenberg–Marquardt	Sigmoid	752	1.65	0.68

linkages between systems attributes, algorithms are mostly used which are capable of performing the assignment, without computing the explicit formulation of the relationships. The ANNs for delineating the input-output variables are not dependent on specific functions (Schaap and Bouten 1996; Singh and Kaur 2015; Sidhu and Kaur 2015; Sidhu and Kaur 2016).

Keshavarzi et al. (2015) used a neural network model for estimating soil P using terrain analysis by using the randomization technique and splitting of data sets into training and testing data. The finest structure of network was projected from coefficient of determination (R^2) and root mean square analysis (RMSE) values (Table 12.5). Their findings suggested that neural network model is highly affected by the slope and elevation, respectively that strongly influence soil P availability. The scatter plot for measured and simulated values for soil P showed that ANN model used for predicting P availability explained ~68% of the variation in the dataset.

For the estimation of soil P availability from easily measurable soil properties viz. soil organic C, clay content, $CaCO_{3,}$ and pH, Keshavarzi et al. (2016) used a new model, which could explain ~50% of the total variations in the datasets. By using support vector machine (SVM), multiple linear regressions (MLR), and ANNs, Li et al. (2014) revealed that through some important soil properties as independent variables, while soil nutrient content was taken as dependent variable for estimating the soil P status. They reported that SVM and general regression neural network (GRNN) models accuracy in judging soil nutrients were ~ 77.9 to 92.9%, respectively. Therefore, both the models viz. SVM and GRNN could be used for predicting the inherent nutrients levels in the fields which further helps for sustainable nutrient management. This helps in improving the resource as well as nutrient use efficiency for feeding the burgeoning population from declining land and water resources.

12.9 Conclusions

Phosphorus is one among the most yields limiting plant nutrients in the worlds' soil under crop production. It undergoes series of transformations immediately after its soil application, causing only a small fraction of it in available forms that tend to form an equilibrium with soil solution P concentration. Phosphorus chemistry in soils is highly dynamic and is often governed by soils' physicochemical properties. For better crop response of applied P, a pH range of 6.0 to 7.0 is considered important. The predominance of HPO_4^{2-} ions in a soil solution occurred between soil pH = 7.5–8.2 and preferential uptake of $H_2PO_4^-$ by plants, compared to HPO_4^{2-} which results in its reduced availability in alkaline soils. Among different clay types, 1:1 type clay (Kaolinite) has a higher P fixation capacity relative to 2:1 type clays (montmorillonite, illite, vermiculite, etc.). Phosphate sorption and release curves for silt and clay fractions revealed that clay fractions adsorbed 1 to 1.5 and 2 to 10-times higher P than silt fractions, respectively at the same equilibrium P concentration. About 90% variability in Po and Pi is related to soil texture with a negative correlation with the sand content of the soil. The presence of $CaCO_3$ (amorphous and crystalline forms) in the calcareous soils results in high P sorption reactions at reactive $CaCO_3$ surfaces due to increased Ca ion activity in the liquid phase. Conversely in the acidic soils, Al^{3+} and Fe^{3+} get attached to SOM and leads to the formation of metal-OM complexes causing P fixation. The integrated nutrient management (organic+ inorganic P) resulted in super-saturation with DCPD, delineating higher P availability in calcareous and non-calcareous soils. The non-calcareous soil pre-treated with manure and inorganic P under nearly saturated moisture regime exhibited a shift in the solubility points above DCPD, as a consequence of lowering of phosphate potential, indicating super-saturation with respect to DCPD. The SPR estimated from the Q/I relationships showed a significant decrease for calcareous as well as non-calcareous soils with integrated P management. Therefore, judicious and efficient P management is prerequisite for increased P availability and PUE, and food security of projected ~9 billion human populations by 2050. Estimates revealed that up to ~70% of the global P demand could be met through enhanced PUE, while the remaining demand could be met through a higher resurgence and P use from its sources.

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