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Naga Madhuri KV
Ph.D, Principal Scientist (Soil Science), Regional Agricultural Research Station, Acharya N.G Ranga Agricultural University, Tirupati, Andhra Pradesh, India

Dr. PVRM Reddy
Scientist (Soil Science), Regional Agricultural Research Station, Acharya N.G. Ranga, Agricultural University, Tirupati, Andhra Pradesh, India.

Dr. T Giridhara Krishna
Prof & Head, Dept. of Soil Science, S.V. Agricultural College, Acharya N.G. Ranga Agricultural University, Tirupati, Andhra Pradesh, India.

Correspondence
Naga Madhuri KV
Ph.D, Principal Scientist (Soil Science), Regional Agricultural Research Station, Acharya N.G Ranga Agricultural University, Tirupati, Andhra Pradesh, India

A review on long-term application of fertilizers and manures on soil phosphorus

Naga Madhuri KV, Reddy PVRM and Giridhara Krishna T

Abstract
The global availability of phosphorus (P) is limited and hence strategies to judiciously utilize this scarce resource is critical for sustainable agriculture development. An overview of various methods to estimate soil P have been presented systematically and the importance of indicator choices and establishment of interpretation thresholds. Thus for developing long-term P management strategies, it is important to ascertain the forms and characteristics of P remaining in the soil after repeated P fertilizer additions over a period of time in an agro ecosystem. A critical evaluation of P content accurately with reliable indicators is the starting point for P management strategy. The changes in available and different fractions of P due to long-term continuous P fertilization besides its effect on yield are discussed. This study summarizes important research understandings on the impact of long-term application of manures and fertilizers under different cropping systems both around the world and specifically in India.

Keywords: Organic, fertility, phosphorus-fractions, available-phosphorus, in-organic phosphorus

1. Introduction
One of the most essential nutrient in agricultural production systems is phosphorus (P) which is applied as both manure and commercial fertilizer to improve soil fertility. There is a world-wide concern about the impact of modern farming on the quality of soil and water due to indiscriminate use of chemical fertilizers (Douglas 2003). Phosphorus plays a pivotal role by participating in a wide range of biochemical and physiological processes both in soil and in plant life. About two thirds of soils around the globe respond to P application due to its high reactivity with soil making the management interesting and challenging when compared to other soil nutrients. Many problematic soils are not only because of lack of P but also due to the forms of P that are unavailable to plants. The use of commercial fertilizers is a specific concern as alternatives like organic farming are promoted for their environmentally benign nature that seem to maintain soil and water quality.

Excess application of P can lead to adverse effects on surface water quality and accumulation in soils around the globe (Liu *et al*. 2008) [22]. When P is applied in the form of fertilizer or manure exceeds the quantity which is accumulated in the harvested crops, the excess P will accrue in the soil unless there is a high runoff or leaching potential in those soils. The sink at which the excess P is associated depends on soil type, climatic conditions, duration of P application and cropping systems (Kuo *et al*. 2005) [20]. Crops recover P ranging from 10-40% of added P and the rest leading to accumulation in soil or in creating potential for leaching and run off (Garg and Aulakh 2010) [11]. Accumulation of P in soils globally has increased from 1965 due to increased application of commercial fertilizers for yield enhancement. Research on P budget studies include Bennett *et al*. (2001) [3], Slaton *et al*. (2004) [42] and Russell *et al*. (2008) [37] that confirm varying levels P surpluses across the globe. Evidence from historical P application and its impact on soil concentrations of P will be useful to assess the risk on agricultural landscapes and aid in formulating preventive strategies. Managing application of manures and fertilizers has been recognized as a strategy to combat eutrophication (Sharpley and Withers 1994) [39]. There are other strategies that help in developing P efficient cultivars which might be useful in managing P nutrition (Naga Madhuri *et al*. 2017a) [27].

This review attempts to present the past research on the long-term effects of application of fertilizers and manures on availability of soil phosphorus and suggests future areas of work drawing lessons from previous studies.

2. Soil Phosphorus
Over a third of inorganic fertilizer P is utilized by crops but before that, P fertilizer when added to soils leads to a series of reactions between P and soil constituents including adsorption, diffusion and precipitation reactions (McLaughlin *et al*. 2011) [24]. Soil Phosphorus

status and management of phosphatic fertilizers to optimize crop production was exhaustively outlined by International Atomic Energy Agency (IAEA, 2002) [13].

The absorption and desorption of applied P are inversely related. Phosphate retention and reactions in soil are paramount for plant nutrition and in enabling fertilizer use efficiency. Kinetics of phosphorus desorption was described by parabolic diffusion law of first order and power function equations indicating release rates of P playing a significant role in available P accumulation and the released Pin run off (Hosseinpur and Biabanaki 2009) [14]. A simple equation to calculate the residual effect of applied P fertilizer was modeled by Janssen and Wolf (1998) [15] However, this model was applicable only for the first five years after fertilizer or manure application to calculate the residual effects. Moreover, precipitation of these reaction products on a long-term application of chemical fertilizers can have differential availability of soil residual P to the growing crops.

2.1 Phosphorus cycle

The P cycle is similar to other mineral nutrient cycles in that P exists in soils, minerals, living organisms, and in water. P is widely distributed in nature but is not found by itself in elemental form. Elemental P is extremely reactive and will combine with oxygen when exposed to air. Global phosphorus cycle has four components. Namely, 1. weathering and tectonic uplift of phosphorus rocks, 2. Chemical weathering and physical erosion of rocks producing soils and dissolved particulate phosphorus to rivers, 3. Transport of phosphorus through ravines to lakes and ocean, 4. sedimentation of phosphorus with organic and mineral matter (Ruttenberg 2003) [38].

In natural systems like water and soil, P exists as phosphate, a chemical form in which each P atom is associated by 4 oxygen atoms. Orthophosphate is the simplest phosphate having the chemical formula PO_4^{-3}. In water, orthophosphate generally exists as $H_2PO_4^-$ in acidic conditions or as HPO_4^{-2} in alkaline conditions. Phosphate is taken up by plants from soils, utilized by animals that consume plants and returned back to soils as organic residues that decay in soil (Busman *et al*. 2009). After plant materials are incorporated into the soil, then the organic phosphate will be converted into inorganic phosphate or as stable organic materials and become part of soil organic matter (Weil *et al*. 2016) [46]. The release of inorganic-phosphates from organic-phosphates is called mineralization caused by soil microorganisms that break down organic compounds. Phosphates can be lost either through soil erosion or through water running through the soil. Most phosphate compounds are not soluble in water, hence most of the phosphates in natural systems occur in solid forms. However, soil water, surface water normally contain relatively low concentrations of phosphorus. Some water bodies contain 10 ppb of dissolved orthophosphate P containing both organic P and phosphate attached to small particles of sediment (Busman *et al*. 2009) [7].

2.2 Indicators of Phosphorus status in soil

Many tools to diagnose and evaluate soil P are available in literature. Renneson *et al*. (2016) [35] described several methods exists with varying degree of complexity around the world and hence defining specific thresholds becomes critical. Existing indicators evaluate the levels of available (or exchangeable) P. This is based on the sum of P immediately available to plants and P that can be converted into available form through physical (desorption), chemical (dissolution) and biological (degradation by enzymes) in nature during the cultivation of crops. However, there are some advantages and disadvantages of various methods of phosphorus characterization and a plethora of P indicators can be found in Renneson *et al*. (2016) [35]. This review also highlighted the importance of careful observation and importance of indicators choice for assessing P status in soils.

2.3 Factors determining phosphorus availability

The availability of P depends on the nature of products formed during reactions after application of fertilizers to soil. The reaction products formed in an alkaline soil can be different with super phosphate when compared with diammonium phosphate. It is well established that single super phosphate creates acidic condition and induces dissolution of Iron (Fe), Aluminum (Al), Calcium (Ca) and Potassium (K) while diammonium phosphate creates weak acidic condition due to ammonium ions. Calcium phosphates are the major products in most soils while P precipitates as variscite ($AlPO_4$+$2H_2O$) and strengite ($FePO_4$ +$2H_2O$) in acidic soils (Taylor & Gurney, 1962) [45]. Hence it becomes pertinent to understand the processes involved in breaking down of P fertilizers in different soil scenarios for critical decision making which will impact any site specific recommendations. Godlinski *et al*. (2004) [12] found that P movement with percolating water increased with higher fertilizer inputs with higher available P in top soil. In the long-term it was also found that P forms moved up from subsoil to the top layers in P deficient soils (Oehl *et al*. 2002) [30]. Contrastingly, Opala *et al*. (2013) [31] suggested that source of P influenced the available P in maize cropping system in western Kenya where in triple superphosphate > Minjingu phosphate rock > busumbu phosphate rock. Mitran *et al*. (2016) [25] conducted a long-term 22 year study with application of fertilizer and manuring of soil in west Bengal's rice-wheat cropping system to evaluate impact on inorganic P fractions. Their study reported relative abundance of all fractions of organic P in the following order, Fe-P > reductant soluble P fraction > occluded P > Al-P > Ca-P > saloid-P. Saloid-P and Fe-P were the dominating fractions responsible for 92% variation of available P and the total P levels respectively.

The organic P is made available after hydrolysis to inorganic P. The effect of long-term farming systems (conventional, biodynamic and bio-organic) on organic P fraction is critical for managing P nutrition. Importance of soil properties like texture and organic matter along with P adsorption capacity are important when assessing the efficacy of P nutrient management (Emadi *et al*. 2009). It is well known that organic amendments have a direct impact on the availability of different chemical fractions of P in soil. Kumar *et al*. (2015) conducted a lab research by applying 20 t ha^{-1} of FYM, vermicompost, poultry manure or paddy straw revealed that organic amendments increased Olsen-P and the order of increase was paddy straw > FYM > vermicompost > pig manure. The total P and available P ranged from 351.38-423.21 and 14.42-25.52 kg ha^{-1}in soils after an incubation period of up to 60 days. The range of saloid-P, Al-P, Fe-P and Ca-P was at 4.22-22.4, 8.45-32.43, 12.67-35.38 and 164.85-215.29 mg kg^{-1}respectively. The Absorption maxima, desorption maxima and maximum buffering capacity are the major parameters governing P availability in soils (Singh *et al*. 2006) [41].

3. Long-term effects

3.1 Long-term Fertilizer application

The effect of annual application of super phosphate on available soil P was evaluated after 16 years (1982-1998) in wheat cropping system in South Africa showed soil P content increased rapidly with application of fertilizers at levels above 20 kg P ha^{-1} with minimal increases occurring at lower levels of application (Otto and Kilian 2001). Long-term effects of fertilizers on soil fertility and productivity of rice-wheat cropping system in North India showed buildup of 3 fold available P with regular application of P fertilizer (single super phosphate) over a 20 year period (Kumar and Yadav 2001) [18]. However, there are reports of soil P accumulation even at a depth of 75 cm as investigated in Danish soil (Rubaek *et al*. 2013) [36]. Interestingly 43-58 % of Olsen-P migrated beyond the active root zone from 60-150 cm depth from top soil, increasing the potential for leaching to ground water and laterally into streams (Aulakh *et al*. 2007) [1]. A long-term 34 year trial that accumulation of P in the form of inorganic P (74-89%), followed by organic P (11-26 %) and Olsen-P (9-19%) suggesting that inorganic P is the major sink for fertilizer P. Higher accumulation was recorded in the plow layer (0-30 cm) and only 6-29% of P moved beyond 30 cm depth in rice, wheat cropping systems (Garg and Aulakh 2010) [11]. A long-term fertilization research for 26 years on paddy in south eastern china showed that most inorganic P fractions decreased with time due to depletion by rice plant in no-fertilized treatment plots. Yields of rice were limited by the soil P availability in red soils. Generally soil P fractions increased with time when treated with NPK fertilizers due to continuous supply of P to the soils.

3.2 Long-term manuring

It is well documented that application of organic matter increases P solubility in soil and decreases fixation leading to improvement of available P to plants (Bhattacharyya *et al*. 2015) [5]. A long-term experiment on maize for 32 years by incorporation of farm yard manure showed prevention of residual P into metastable P forms and increased availability of P to the crops (Singh *et al*. 2006) [41]. The long-term application of manures effect the activity of enzymes involved in nutrient turnover. The availability of organic substrates promotes the growth of microbial populations and enhanced the activity of alkaline P while having no effect on the acid P (Krey *et al*. 2013). Combining Plant growth promoting Rhizobacteria containing Rhizobium, Azotobacter, Pseudomonas and Trichoderma along with FYM was found to accumulation of available P in Mungbean (Da S and Singh 2014).

It was reported that soil P was enriched by manures much below 30 cm when compared to fertilizer P and suggested that this might be due to leaching of organic P (Johnston and Poulton 1992) [16]. Contrastingly Shepherd and Withers (1999) [40] found no effect on soil P up to 1 m depth due to manures or by fertilizers. This leads to an unsolved issue of whether organic P is leached by a unique mechanism or is it due to saturation of soil P that needs to be considered for which further research is needed. The ratio of nutrients in manures is different from the ratio of those removed by crops leading to excessive accumulation of P unlike the use of long-term fertilizers. Soils with low P retention lead to greater losses through leaching and this can be compounded by manures which can contribute to poor quality of water by adding materials having high demand for oxygen. Hence, long-term use of manures may not always enhance soil quality when compared to applying the same amounts of nutrients as a fertilizer. Previously fertilizer recommendations were made with special attention on soil inorganic P pools (Steffens *et al*. 2010) [44]. However, organic soil amendments like manures comprise both organic (30-65%) and inorganic forms of P (Pagliari and Laboski 2012) [33].

3.3 Combined effects of long-term fertilizers and manures

It was recommended that combination of chemical fertilizers along with manures (cow dung or rice straw) was beneficial to get higher rice yields and for maintaining soil health (Lan *et al*. 2012) [21]. Effect of long-term fertilizer and manure application for 17 years in paddy in eastern china showed that accumulation of total soil P, Olsen-P and Mehlich 3P was significant when inorganic fertilizer P was combined with manure. However, straw in combination with fertilizer P did not lead to increase in soil P. Fractionation of P revealed that residual fertilizer P accumulated as moderately labile and sparingly labile forms of P irrespective of type of P applied. Application of organic manure appears to prevent conversion of applied fertilizer P into recalcitrant P forms and resulted in larger proportion of available P in soil (Mao *et al*. 2015) [23]. A long-term experiment with application of compost and fertilizer P in paddy cropping system after 34 years at National Youngnam Agricultural Experimentation Station, Korea showed that while application of compost and fertilizer P increased organic P fraction of the soil, the ratio of organic P to total P declined at the same time (Park *et al*. 2006) [34]. This research suggests that Phosphorus fixation was significantly increased due to long-term application of compost and chemical fertilizers whereas available P increased in the treatments that received only chemical fertilizers.

In a long-term experiment conducted for 25 years on rice with either fertilizer or farm yard manure, Naga Madhuri *et al*. (2013) [26] compared the soil under cultivation with those under natural vegetation; their study found that C/N ration of soil under natural vegetation was higher in comparison to soils under continuous cultivation especially in the surface layers when compared to sub-surface layers. In a long-term (42 years) experiment conducted using fertilizer and manure application on tropical flooded rice, Bhattacharyya *et al*. (2015) [5] reported that Iron-P fraction was highest when compared to Calcium-P or Aluminum-P when FYM and NPK were applied together. The P adsorption capacity of soil was highest in low-input treatment when compared to long-term FYM plus NPK treatment.

Long-term effects of fertilizers and FYM in rice-wheat rotation was studied after 39 years found maximum yields when 100% of NPK was applied in combination with 15 t ha^{-1} of FYM. The results from this study show high counts of bacteria, fungi and actinomycetes in soil when compared to other treatments (50% NPK, 150 % NPK, 100% N, 100% NPK (-S) or unfertilized controls and found that imbalanced used of fertilizers had harmful effects on soil biological health (Bhatt *et al*. 2015) [4]. An 18 year old long-term fertilizer and manure treated experiment of Pearl millet-cluster bean-castor rotation was conducted in entisols of western India. Results from this study indicate higher grain yields of pearl millet, cluster bean and castor by integrating fertilizers with manures (Srinivasarao *et al*. 2014) [43].

The results of Long term experiment on application of manure and fertilizers in groundnut for 35 years at Regional Agricultural Research Station, Tirupati on P fraction by Naga Madhuri *et al*. (2017b) [27] revealed that the Fe-P was significantly correlated with available P and total P; likewise Al-P and occluded P with total P and total P with P uptake. Available P was positively and significantly related with Al-P and Fe-P. Results of this experiment showed a dramatic accumulation of available P over 35 years (Figure 1).

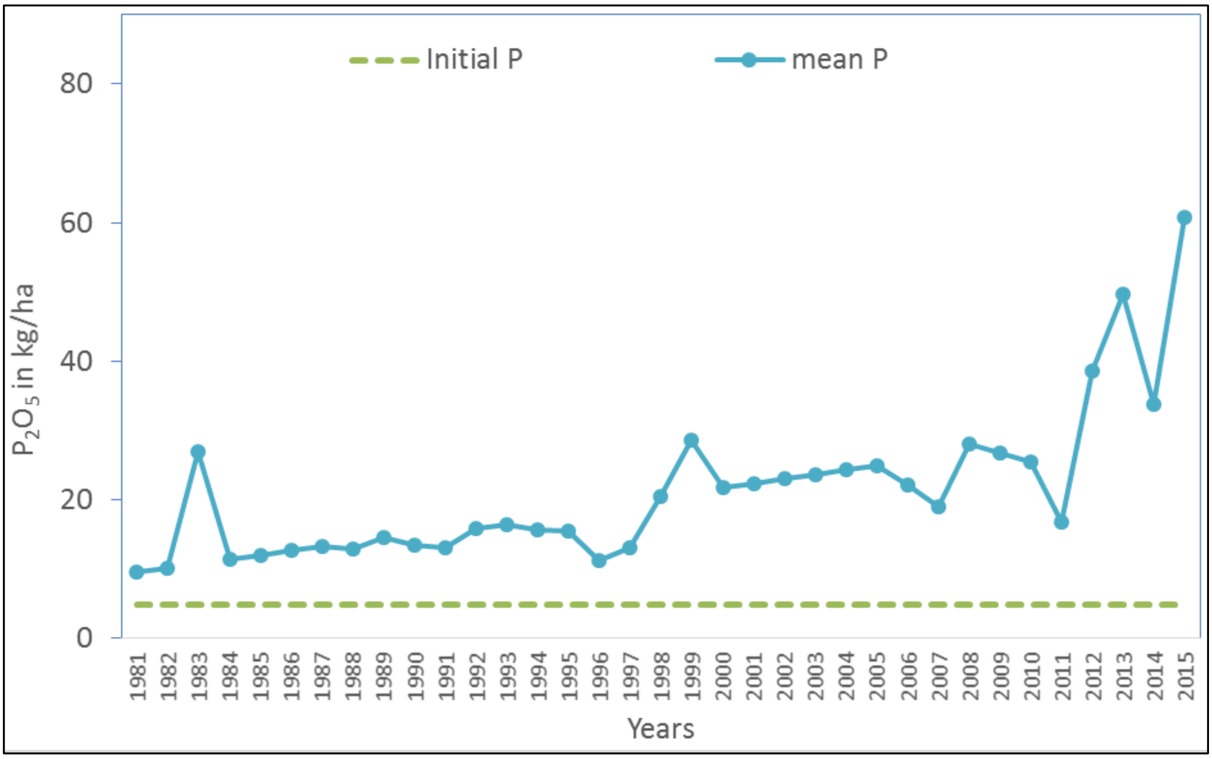

Fig 1: Long-term application of fertilizers and manures on soil available P (Naga Madhuri *et al*. 2017b) [27]

An economic evaluation of long-term research on phosphorus and manure addition to sandy sahelian soils was evaluated using stochastic efficiency framework (Baidu-Forson and Bationo 1992) [2], who recommended either annual application of 8.7 kg P ha^{-1} in the form of single super phosphate in combination with 5 Tons of manure applied every three years or annual application of 17.5 kg P ha^{-1} as SSP (as stand-alone). The choices of these amendments depend on their availability to farmers. However, after one hundred years of long-term application of rock phosphate in western Australian soils revealed that rock phosphates are ineffective source as they do not dissolve in soil (Bolland and Gilkes 1990) [6].

4. Conclusion and way forward

A. Phosphorus like any other plant nutrient is present in soil as two major components i.e. organic and inorganic forms. Organic P is mainly confined to surface layer and mineralized into inorganic forms.
B. It is essential to accurately evaluate P content in soil and this requires reliable indicators of soil P status. The importance and choice of indicators and interpretation of their thresholds is well understood.
C. For developing long-term P management strategies, it is important to ascertain the forms and characteristics of P remaining in the soil after repeated fertilizer P addition over a period of time in an agro ecosystem. There is paucity of work on relationships between P fractions on P availability and uptake. These studies can be useful in recommending effective formulations to address P requirements of Plantae.
D. There is tremendous progress in identifying P-efficient cultivars in field crops research which would contribute to limiting application of P fertilizer. There is a need to accelerate the release of varieties that yield normally in P-starved conditions. This has been demonstrated in field crops (Naga Madhuri *et al*. 2018) [26]. A holistic approach using all the avenues of science and technology should result in addressing shortage of scarce P sources globally and sustain our environmental by limiting the effects of P accumulation in soils and water bodies.

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