



Effect of Submergence and Phosphatic Fertilizers on Phosphate Potentials - A Measure of Phosphorus Availability in Acid Soils of Karnataka

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ARTICLE INFO

Article history:

Received 12 June 2018

Revision Received 26 December 2018

Accepted 14 February 2019

Key words:

phosphate potential, equilibrium phosphate potential, single super phosphate, diammonium phosphate, Missouri rock phosphate, phosphorus supplying power

ABSTRACT

The use of phosphate potential (PP) and equilibrium phosphate potential (EPP), a measure of readily available phosphorus in soil, to predict the phosphorus supplying power of submerged soil is reliable but the information so far available is insufficient to draw a valid conclusion. An experiment was conducted with single super phosphate (SSP), diammonium phosphate (DAP) and Missouri rock phosphate (MRP) (applied @ 200 ppm P) and two period of submergence (up to 30 and 60 days) to study the effect of submergence and different sources of phosphatic fertilizers on PP and EPP. Due to submergence up to 30 days, decrease in PP and EPP was noticed in all four soils irrespective of different phosphatic fertilizer sources. This decrease in PP and EPP indicates the increased availability of inorganic phosphate ($H_2PO_4^-$) ions due to the submergence. On prolonged submergence up to 60 days, decrease in PP and EPP was noticed in soils having low pH. Among the four soils, Shimoga soil recorded increased PP and EPP with all phosphatic fertilizer sources including control. Among the phosphatic fertilizers, the highly soluble fertilizers like DAP and SSP application significantly increased $H_2PO_4^-$ ion concentration in soil solution when compared to MRP, which is acid soluble one. The correlation studies revealed that changes in PP and EPP due to submergence and different phosphatic fertilizers application were found to be significant. However, available phosphorus was more negatively and significantly correlated with EPP.

1. Introduction

Phosphorus (P), one of the major essential nutrient elements, plays a major role in chemical and biological processes in the plant. It is involved in energy transfer for cellular metabolism and also is an important structural constituent of cell membrane, nucleic acids and several other critical materials (Wiedenhoeft 2006). Several factors affect the P availability such as amount and type of clay, soil pH, other nutrients, crop type, moisture, soil

compaction and aeration, soil organic matter, soil temperature and soil texture. Submergence of soil greatly influence the P availability by making various changes in soil physical, chemical, biological and pedological characteristics as compared to aerable soils. Submergence causes decrease in red-ox potential (Eh), changes in pH, increase in specific conductance, cation exchange capacity involving Fe^{2+} ion and sorption and desorption of ions (Ponnamperuma 1972). Among these electrochemical changes, changes in pH and red-ox potential mainly influence the available phosphorus in soil. Since soluble iron and aluminium phosphate constituted about 50 to 66 per cent of total soil phosphorus in acid soil

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(Bhangoo and Smith 1959) and these and their isomorphous crystalline compounds of variscite and strengite series formed a major fraction of ultimate reaction products of applied phosphates in soil by way of fixation (Wright and Peech 1960), any reductive chemical transformation was likely to shift solubilization of these phosphates to raise the available phosphorus concentration in soil. Turner and Haygarth (2001) and Vadas and Sims (1998) reported inconsistent responses or no response to phosphorus fertilization under submerged conditions, even where upland crops responded to applied phosphorus. Ruiz *et al.* (1997) and Abolfozli *et al.* (2012) concluded that, in flooded soils, the solubility of phosphorus increases with the development of reducing conditions and this increase was attributed to reduction processes and dissolution of Fe-P minerals or Fe-hydroxide dissolution and release of the adsorbed P. Patrick *et al.* (1985) and Yu (1985) reported the major physiochemical changes, which increase the available P concentration in acid neutral soils. These changes are (i) microbially mediated reduction of soil Fe-PO₄ resulting in accumulation exchangeable Fe²⁺ and consumption of exchangeable acidity with a concomitant rise in soil pH reduction of other oxidants in the soil also consumes acidity (ii) accumulation of CO₂ formed by organic matter decomposition, increasing soil acidity and there by curbing the increase in soil pH brought by the above changes, and causing an increase in the concentration of HCO₃⁻ in soil solution; and (iii) an increase in the ionic strength of soil solution as a result of a) the increase in exchangeable Fe²⁺ and b) the increase in concentration of HCO₃⁻ ions in solution, which causes a further desorption of exchangeable cations (principally Fe²⁺, Ca²⁺, Mg²⁺ and NH₄⁺) to maintain electro-neutrality in the solution. To measure the available phosphorus in soil different chemical extractants are used in the laboratory and these measure only the quantity factor. The quantity factor is not a good index because of much interaction of soil factors (Rajukannu and Ravikumar 1979). Schofield (1955) introduced the concept of phosphate potential (PP) to measure the available phosphorus in soils and suggested that the availability of soil phosphate is mainly determined by the appropriate chemical potential and by its rate of decrease with phosphate withdrawal. According to him, it is not the amount of available phosphorus in the soil that controls its uptake by plants, but the work needed to withdraw it from the pool. He proposed the negative chemical potential of monocalcium phosphate ($\frac{1}{2} pCa + pH_2PO_4$) determined in a 0.01M CaCl₂ solution. Later, Ramamoorthy and Subramaiam (1960) pointed out the difficulties in equilibrating a soil with a solution containing no phosphate initially, and they introduced the concept of

equilibrium phosphate potential (EPP) to avoid such difficulties. The outstanding merit of these phosphate potentials is that its evaluation is not tied to any arbitrary methods or procedures. In a multiphase system of soil, a chemical equilibrium exists between phosphate present in the solid phase and solution phase. Transformation of iron and aluminium phosphates in submerged acid soil (Ponnamperuma 1964) and equilibria of H₂PO₄⁻ ions in soil solution with solid phase iron and aluminium phosphates are the determinants in the phosphate supplying capacity of the soil. Since little information to date is available on the use of these thermodynamic methods to predict the phosphorus supplying power in submerged soils, a study was under taken on PP and EPP with the following objectives: (i) to understand the influence of submergence and phosphatic fertilizers (ii) to identify the reliable phosphorus testing method with the help of correlation study.

2. Materials and Methods

For understanding the influence of submergence and different sources of phosphatic fertilizers on phosphate potentials, which is a measure of phosphorus availability, incubation studies were undertaken with four major acid soils of Karnataka. Four surface soil samples (0-20 cm), belonging to different orders namely Alfisols, Inceptisols, Ultisols and Entisols were collected from four districts of Karnataka *viz.* Bangalore, Shimoga, Chikmagalur and Uttara Kannada, respectively. The soils (less than 2mm) were analyzed for some important soil characters using standard methods (Jackson 1958) and are presented in Table 1. About 500 g soil samples were taken in number of test tubes and requisite quantities of DAP, SSP and MRP were added to it at the rate of 200 ppm P. Submerged conditions were simulated by maintaining 5 cm of water over the soil surface, and the treatments were replicated thrice. The submerged soil samples were then allowed to incubate for 30 and 60 days at room temperature of 26 ± 2 °C. After the requisite period of incubation, the samples were analyzed for PP (Aslyng 1954) and EPP (White and Beckett 1964). For the determination of PP, 20 g of soil sample was taken in 100 mL polyethylene test tube and 50 mL of 0.01M CaCl₂ was added to the test tube. The contents were shaken for one minute and the pH of the suspension was measured immediately with a glass electrode assembly. After taking reading for pH, the suspension was filtered through Whatman No. 40 filter paper. The phosphorus concentration in the filtrate was determined by sulfomolybdenum blue color method at 660 nm as described by Jackson (1967). The concentration of Ca in the filtrate was determined by complexometric titration method (Schwartzbach *et al.*, 1946).

Table 1. Physicochemical characteristics of the soils

Soil property	Bangalore	Shimoga	Chikmagalur	Uttar Kannada
Soil group	Kandic Haplustalfs	Fluvent Ustropepts	Ustic Haplumults	Aquic Ustorthents
pH (1:2.5)	5.9	4.8	5.1	5.4
EC (1:2.5) dSm ⁻¹	0.11	0.12	0.04	0.12
Organic Carbon (g kg ⁻¹)	8.2	6.8	5.8	13.7
Available P (mg kg ⁻¹)	8.6	4.8	6.3	5.4
Texture	SCL	SL	SL	SCL
Total Fe ₂ O ₃ (g 100g ⁻¹)	12.76	6.93	14.50	10.50
Total Al ₂ O ₃ (g 100g ⁻¹)	4.91	8.58	16.91	11.01
CEC (meq 100g ⁻¹)	12.80	18.30	12.31	12.90
Phosphate potential	7.40	7.60	7.46	7.31
Equilibrium phosphate potential	8.01	8.19	8.09	7.98

Phosphate potential (PP) = $\frac{1}{2} p \text{Ca} + p\text{H}_2\text{PO}_4$

Where, $\frac{1}{2} p \text{Ca} = -1/2 (\log_{10} \text{Conc. Ca} + \log_{10} f_i)$

Where,

Conc. Ca = Molar concentration of Ca ions in filtrate

f_i = Activity co-efficient

Activity co-efficient (f_i) was calculated by Debye and Huckel's (1923) equation.

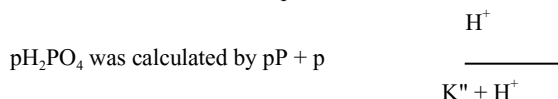
$$-\log f_i = Z^2 A \sqrt{\mu}$$

Where, Ionic strength, $\mu = 0.5 \sum C_i Z_i^2$

A = 0.5 (constant)

Z_i = Valency of the particular ion

C_i = Molar concentration of particular ion in solution



Where, $p\text{P} = \log_{10} (P)$

(P) = Total concentration of inorganic phosphorus in solution

p = Correlation factor worked out by Aslyng (1954) and it is the proportion of $\text{H}_2\text{PO}_4^- / \text{P}$ at different pH.

Where, H^+ = Hydrogen ion concentration

K'' = Second dissociation constant of phosphoric acid and was calculated to be 7.0 when 0.01M CaCl_2 was used (Jensen 1970).

For EPP, 3 g of soil was taken with 30 mL of 0.01 M CaCl_2 solution of known phosphorus concentration (0, 0.2, 0.5, 1.0, 1.5 and 2.5 ppm) in a number of test tubes and were shaken for 2 hours on a horizontal shaker. The samples were centrifuged at 3000 rpm for 3 minutes and the supernatant solution was analyzed for total inorganic phosphorus (Jackson 1967), Ca concentration (complexometric titration) and pH. The activity of H_2PO_4^-

for each phosphorus solution *i.e.* a H_2PO_4^- in the filtrate was thermodynamic available soil phosphorus testing methods, *viz.* PP and EPP to identify the reliable available phosphorus testing method in acid soils (Sundar Raj *et al.*, 1972).

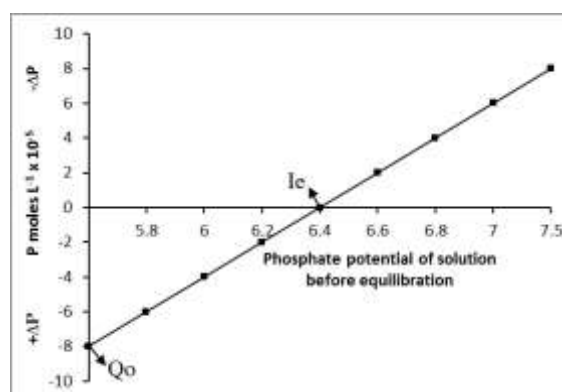


Figure 1. Relationship between change in P concentration due to the equilibration with soil and phosphate potential of solution.

3. Results

Data on the PP and EPP due to submergence and different phosphatic fertilizers application in respect of four soil groups at two sampling stages (30 and 60 days) are given in table 2. The PP and EPP were calculated from the activities of Ca^{2+} and H_2PO_4^- ions. In general both PP and EPP decreased due to submergence up to 30 days of incubation irrespective of phosphatic fertilizers in all the soils including control. Among different phosphatic fertilizers, the soils treated with DAP recorded lowest PP and EPP followed by SSP and MRP over the control. Shimoga soil recorded the highest value of PP and EPP (7.32 and 8.19) at 30 days of submergence while Uttara Kannada soil recorded very values (7.15 and 7.90) followed by Bangalore (7.19 and 8.01) and Chikmagalur (7.23 and 8.09) at 30 days of submergence.

Table 2. Effect of submergence on phosphate potential and equilibrium phosphate potential

Location	P fertilizers	Phosphate potential			Equilibrium phosphate potential		
		Air dried	Submerged		Air dried	Submerged	
			30 days	60 days		30 days	60 days
Bangalore	Control	7.40	7.19	7.05	8.01	7.80	7.48
	SSP		6.81	6.93		7.25	7.39
	DAP		6.62	5.61		7.10	6.95
	RP		7.21	7.18		7.35	7.20
Shimoga	Control	7.61	7.32	7.59	8.19	8.03	8.15
	SSP		6.62	6.94		7.37	7.50
	DAP		6.87	7.12		7.27	7.53
	RP		7.09	7.55		7.85	8.00
Chikmagalur	Control	7.46	7.23	7.09	8.09	7.87	7.60
	SSP		6.90	6.99		7.28	7.40
	DAP		6.75	6.62		7.15	7.01
	RP		7.31	7.28		7.60	7.35
Uttar Kannada	Control	7.28	7.15	7.01	7.90	7.48	7.35
	SSP		6.60	6.69		7.13	7.25
	DAP		6.49	6.53		7.05	7.12
	RP		7.35	7.18		7.30	7.18
SEm			0.19	0.15		0.26	0.18
CD			0.54	0.43		0.74	0.52
F-Test			*	**		*	**

calculated from the concentration of phosphorus in the solution. The amount of phosphorus gained or lost by soil (ΔP) was calculated by the difference in concentration of phosphorus in soil solution before and after the equilibration. From a plot of ΔP (loss or gain of phosphorus by soil) against the intensity (a $H_2PO_4^-$), Q_0 and I_e parameters were obtained (Figure 1). The $aH_2PO_4^-$, where ΔP is zero on the $aH_2PO_4^-$ (calculated in terms of PP) axis was taken as intensity factor (I_e). The slope of the curve gives phosphate potential buffering capacity (PBC) of soil. The ΔP when $aH_2PO_4^-$ is zero is taken as quantity factor (Q_0) and from this equilibrium a $H_2PO_4^-$, EPP was calculated (Muralidharadu and Omanwar 1987). A simple correlation study was also made between the soil properties and On prolonged submergence (up to 60 days), PP increased in the highly acid soil of Shimoga (4.8), where as for the soils of Bangalore (5.9), Chikmagalur (5.1) and Uttara Kannada (5.4) further decrease in PP was noticed. Similar trend was also noticed in case of EPP. However, the rate of decrease in EPP was relatively higher as compared to PP. Among the different phosphatic fertilizer sources, all soils treated with SSP recorded increased PP and EPP on prolonged submergence up to 60 days where as in Shimoga soil, all the phosphatic fertilizer sources including control showed an increase in both PP and EPP values. All the soils except Shimoga soil treated with MRP showed a decrease in PP and EPP values upon prolonged submergence up to

60 days. More specifically, during the initial period submergence, MRP showed much higher phosphate potentials than SSP and DAP but on prolonged submergence (up to 60 days), the difference narrowed down in all the soils except in Shimoga soil. Both SSP and DAP behaved more or less similarly in all the soils, as both are water-soluble fertilizers. In control, phosphatic fertilizers application decreased the phosphate potentials in all the soils. This effect was more so with soluble fertilizers like DAP and SSP. The changes in PP and EPP values due to submergence up to 30 and 60 days and with different phosphatic fertilizer sources were found to be significant. Correlation studies presented in table 3 showed that available phosphorus was negatively correlated with both PP and EPP, but only with EPP, it showed a significant correlation (-0.789**).

4. Discussion

In acid soils, fixation of phosphorus through double decomposition reactions involving solubility products is very common. These reactions are mainly due to the activity of iron and aluminium ions or hydrated oxides (Ch'ng *et al.*, 2017). Following flooding, oxygen entrapped in the soil is rapidly consumed in aerobic microbial respiration, then the other inorganic electron acceptors are used in microbial respiration in the well-known sequence of NO_3^- , Mn(IV), Fe(III), SO_4^{2-} (Fageria *et al.*, 2011).

Table 3. Simple correlation between phosphate potential and equilibrium phosphate potential and soil properties

Soil properties	Phosphate potential	Equilibrium phosphate potential
pH	-0.251	-0.787**
Available Phosphorus	-0.664	-0.789**
Clay	0.041	0.380
Organic carbon	-0.831**	-0.556
Total Fe ₂ O ₃	0.225	0.109
Total Al ₂ O ₃	0.499	0.275

** Significant at 1 per cent

Concomitantly, organic matter is oxidized, dissolved CO₂ accumulates and the pH of acid soils tends to increase and that of alkaline soils to decrease, stabilizing in the range 6.5 to 7.0 (Kirk *et al.*, 2003). These changes in the red-ox potential and pH values due to submergence of acid soils have an indirect bearing on iron phosphate availability (Savant and Ellis 1994). Application of soluble fertilizers like DAP and SSP also increased the available phosphate concentration in the soil solution *i.e.* decreased the PP and EPP. This may be due to their rapid release of phosphate ions in the initial period of their application (Brandon and Mikkelsen 1979; Simpson and Williams 1970; Willett 1986). The decrease in PP and EPP due to submergence up to 30 days indicated that there was an increase in the inorganic phosphate ion concentration (H₂PO₄⁻) in the soil solution. Since both the PP and EPP measure the negative logarithm of inorganic phosphate ion (H₂PO₄⁻) in the soil solution, this decrease in PP and EPP indicates the increase of inorganic phosphate ion (H₂PO₄⁻) in soil solution and vice versa. The greater activities of H₂PO₄⁻ ion in soil solution up to 30 days of submergence probably due to its release from solid phase inorganic phosphate in soil and release from the applied phosphatic fertilizers (Abolfazli *et al.*, 2012). The mechanism of phosphate release in the submerged soil may be explained by (i) reduction of insoluble ferric phosphate to more soluble ferrous phosphate (Shenker *et al.*, 2005), (ii) release of occluded phosphate by reduction of hydrated ferric oxide coatings (Shenker *et al.*, 2005) (iii) displacement of phosphate from ferric and aluminium phosphates by organic anions (Guppy *et al.*, 2005) (iv) hydrolysis of ferric and aluminium phosphates due to increase in alkalinity (Ponnamperuma 1955). On prolonged submergence, the PP and EPP of soils treated with MRP and DAP recorded further decrease and other recorded increase in the PP and EPP irrespective of the soil groups. The increase of both PP and EPP upon prolonged water logging might be due to the reprecipitation of released phosphate due to the simultaneous increase in

the activities of Fe²⁺, as a result of which took place a depletion of H₂PO₄⁻ ionic activity (Sarkar *et al.*, 1986). This reprecipitation occurs once a sufficient saturation of ions has been reached, and the reprecipitated compounds later re-order to more crystalline forms (Kirk *et al.*, 2003). Regarding control, the application of phosphatic fertilizers reduced the PP and EPP in all the soils. This reduction is more so with soluble phosphatic fertilizers like DAP and SSP, which suggests the greater capacity of phosphate treated soils for supplying phosphate to plants. However, only a slight decrease in PP and EPP for the insoluble phosphatic fertilizer source, *viz.* MRP was observed in highly acidic soils. The relationship between the phosphatic fertilizer and PP and EPP is given diagrammatically in figure 2. In majority of the acid soils, the rate of rock phosphate dissolution should decline following flooding as the pH rises, but to what extent will depend on the rate of reduction (Ponnamperuma 1972). Clark and Peech (1955) and Lindsay *et al.* (1959) showed that reactions between added phosphorus and soil were not complete even after 18 months period of incubation. In the present study the incubation period was only 60 days, assuming that part of added phosphorus may have existed in the forms, other than iron phosphates, *i.e.* in the forms of Ca or Al- phosphates. Since forms like Ca-PO₄ or Al-PO₄ are not directly affected by a decrease in red-ox potential the availability of applied phosphorus and of native phosphorus would not be affected to the same extend (Savant and Ellis 1964). The negative and significant correlation of available phosphorus with PP and EPP suggests that increase in available phosphorus concentration will decrease the PP and EPP as both measures the negative logarithm of inorganic phosphate (H₂PO₄⁻) ion concentration in soil solution (Rajgopal and Idnani 1963). Ramamoorthy and Subramanian (1971) also reported the same results.

Conclusions and Recommendations

The application of phosphate fertilizers under submerged conditions decreased the PP and EPP in all the soils. Highly soluble fertilizers like DAP and SSP increased the phosphorus availability only up to 30 days of submergence whereas MRP application increased the phosphorus availability up to 60 days of submergence. But the increase in phosphorus availability was not as much of the highly soluble phosphatic fertilizers. However, with the increase in days of submergence the phosphate potentials in the soils increased, particularly with SSP and DAP due to the reprecipitation of released phosphorus with increased activity of Fe²⁺ and other ions. The study confirmed that in addition to applied phosphate fertilizers, increased pH due to submergence in acid soils also contributed the increased phosphorus

availability due to the dissolution of phosphorus containing minerals. The study also suggests that the changes in phosphorus availability due to submergence was more in soils with low buffering capacity than the soils with high buffering capacity. It may be economical to apply rock phosphate as a phosphorus source under submerged conditions where the availability of rock phosphate is high and the application of high-cost P fertilizers is not feasible.

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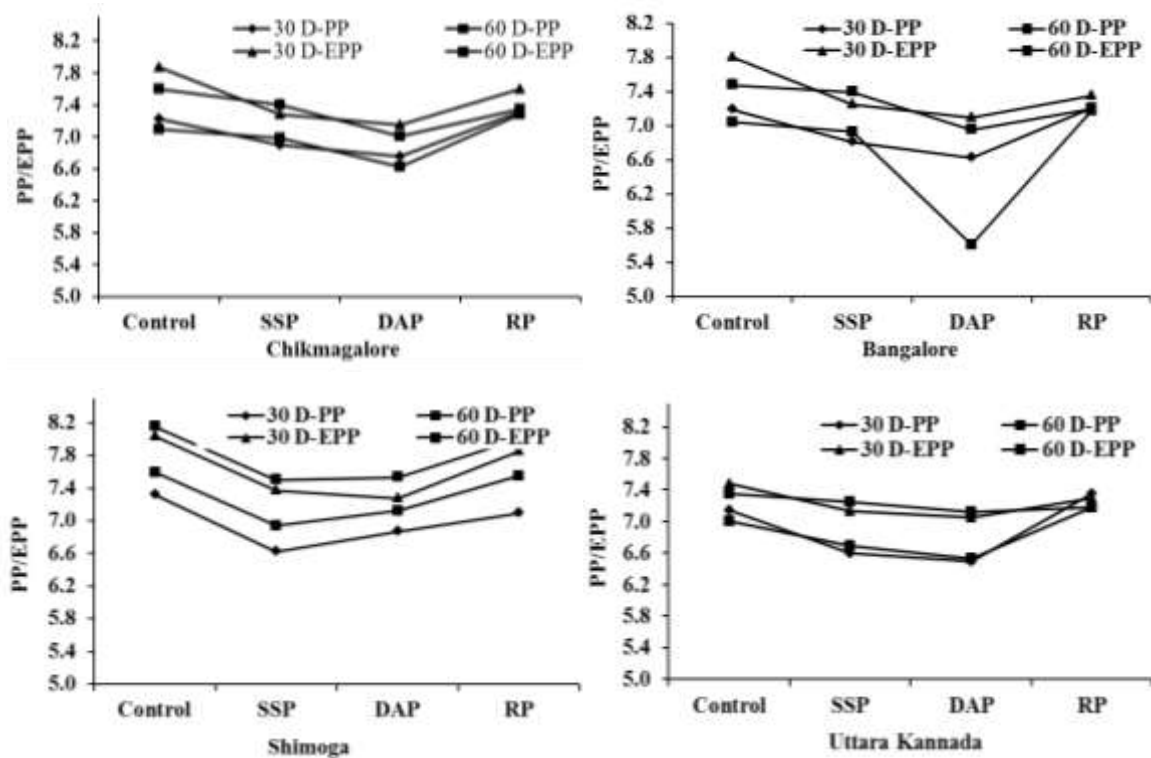


Figure 2. Relationship between different sources of phosphorus and phosphate potential and equilibrium phosphate potential