Effect of Equilibrum pH on Phosphate Potential and Equlibrium Phosphate Potential in Acid Soils of Karnataka

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ARTICLE INFO

ABSTRACT

A laboratory experiment was conducted to study the effect of pH on available phosphorus (P) (Bray and Kurtz No.1 extractable), phosphate potential (PP) and equilibrium phosphate potential (EPP) in four acid soils collected from different districts of Karnataka representing various agro-climatic zones. Significant changes in soil available P was observed with a unit increment in soil pH in all the soils. At pH 4.0, available P decreased in all the soils except soils from Bangalore compared to the initial P. On the other hand, increase in pH up to 7.0 increased the available P by 83, 38, 14 and 120% in soils from Bangalore, Shimoga, Mudigere and Uttar Kannada, respectively compared to initial soil P. The PP and EPP which measure negative logarithm of inorganic phosphate ($H_2PO_4^-$) ions concentration in soil solution, decreased with increase in pH from 4.0 to 6.0 irrespective of the soils. Further increase in pH up to 7.0 decreased the PP and EPP values in all the soils except in Mudigere soil. The changes in both PP and EPP values due to the changes in pH values were found to be significant. A negative and highly significant correlation was found to exist between available P and EPP.

1. Introduction

The available P in soil is influenced by several characteristics of the soil such as amount and types of clay, amounts of iron and aluminium oxides, organic matter, calcium carbonate, soluble silica, concentration of solution cations and anions, temperature and pH (Bolan et al. 1985; Kuo 1990). Among these characteristics, soil pH primarily influences the available P concentration in soil. However, soil pH does not affect the P availability directly. Instead, soil pH levels indicate how certain minerals (iron, aluminium and calcium minerals) interact with P in the soils, and it is the interaction that affects the P availability. In acid soils iron and aluminium concentrations are high because the minerals are soluble, while calcium concentration is low because the mineral has been dissolved and leached out of the soil (Curtin et al. 1993). When P reacts with these minerals, the products formed are not very soluble and the P in the insoluble compounds has a direct impact on the availability of P for crop growth. In Karnataka about 40 per cent of the soils are acidic and therefore

In Karnataka about 40 per cent of the soils are acidic and therefore appropriate management of phosphate fertilizer is a major concern for these soils (Ramesh and Ananthanarayana 2012). Soil testing for soil pH and the P level determines the amount of P needed for the crop to be grown. Several soil test methods have been developed, and Bray's and Olsen's soil test methods are commonly used in India to determine the available P content in the acid and neutral and alkaline soils, respectively. The soil solution is the key to plant nutrition because all P that is taken by plants comes from P dissolved in soil solution. Not like common soil P testing methods (Bray, Olsen, *etc*.), Schofield's (1955) phosphate potential estimates the available P in soil solution. With some modification of Schofield's phosphate potential, White and Beckett (1964) introduced the concept of EPP to measure the available P concentration in soil solution. The information on the use of these methods to predict the P availability with different pH in acid soils is very little India, particularly in Karnataka. Hence in this study, an attempt was made to investigate the influence of pH on soil phosphorus availability with these soil-testing methods.

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2. Materials and methods

Four soils were collected from different agro-climatic zones belonging to different soil groups. The initial properties of the soils used for this experiment are given in table 1. The collected soil samples were air-dried and passed through 2 mm sieve for further analysis. In a laboratory experiment, 500 g of each soil was incubated with different pH of 4.0, 5.0, 6.0 and 7.0 by using 0.01 N HCl and 0.01 N NaOH and, the treatments were replicated thrice. The soils were incubated for one month under aerated condition. Moisture was maintained at field capacity throughout the incubation period by adding water at the rate of 35% field capacity. After one month, the soils were air-dried and used for the estimation of Bray and Kurtz No.1 solution extractable P, PP and EPP.

The PP of soil was determined by the procedure suggested by Aslyng (1954). Twenty grams of soil was taken in a 100 mL polyethylene test tube. Fifty-milli litre of 0.01 M $CaCl_2$ solution was added and shaken for one minute. The pH of the suspension was measured immediately with a glass electrode assembly. After taking reading for pH, the suspension was filtered and P concentration in the filtrate was determined by sulfomolybdenum blue colour method at 660 nm as described by Jackson (1967). Calcium concentration in the filtrate was determined by complexometric titration method (Schwartzenbach et al. 1946).

Phosphate potential (PP) = ½ p Ca + pH$_2$PO$_4$
Where, ½ pCa = -1/2 (log$_{10}$ Conc. Ca + log$_{10}$ fi)
Where, Conc. Ca = Molar concentration of Ca ions in filtrate

Activity co-efficient (fi) was calculated by Debye and Huckel's (1923) equation, where fi = Activity coefficient
$$-\log fi = Z^2 A \sqrt{\mu}$$
where, Ionic strength, μ = 0.5 Ci Zi^2
A = 0.5 (constant)
Zi = Valency of the particular ion
Ci = Molar concentration of particular ion in solution
pH$_2$PO$_4$ was calculated by pP + p $\dfrac{H^+}{K'' + H^+}$

pP = log$_{10}$ (P), where (P) = Total concentration of inorganic phosphorus in solution, p = Correlation factor worked out by Aslyng (1954) and it is the K'' + H$^+$ proportion of H$_2$PO$_4$/P at different pH, where, H$^+$ is the Hydrogen ion concentration; K'' is the second dissociation constant of phosphoric acid and was calculated to be 7.0 when 0.01M $CaCl_2$ was used.

Equilibrium phosphate potential was estimated by the procedure given by White and Beckett (1964) with some modification of various higher equilibrium P concentrations and longer shaking period of two hours. When relatively large amount of P was added, longer period of shaking was suggested by Jension (1971).

3. Results and Discussion

The soil available P content extracted by Bray and Kurtz No.1 solution, PP and EPP values observed after the incubation period are presented in table 2. It is clearly evident from the table 2 that initially available P content in all the soils increased with increase in pH up to 6.0 and, further increase up to pH 7.0 also increased the available P in all soils except in Mudigere soil. Bangalore soil recorded the maximum available P content of 15.8 mg kg^{-1} followed by Uttar Kannada (11.9) and Mudigere (7.2) soils. Shimoga soil recorded the lowest available P content of 6.6 mg kg^{-1} at pH 7.0. Compared to initial soil P, at pH 7.0 the maximum increase in available P content was recorded in soils from Uttar Kannada soil (120%) followed by Bangalore (83%) and Shimoga (38%) while Mudigere soil recorded the lowest increase of 14%. The changes in available P concentration with a unit increase or decrease of pH may simply be related to (i) the possibility that phosphate minerals are equilibrating with iron and aluminium phosphates controlling the low pH and calcium phosphates controlling the high pH end of the range (Sato and Camerford 2005) or (ii) P sorption reactions which are affected by pH may have contributed to these changes in available P concentration (Rodenburg et al. 2003). Since these changes have been found to be similar in native soils and with P addition, it seems that at high pH calcium phosphate is dominant, but at the lower pH range may be that predominantly sorption is increased by the oxides of iron and aluminium in the soil (Sato and Camerford 2005). It is known that fixation of P is less at higher pH (White 1980). Perassi and Borgnino (2014) reported that P adsorption was consistently higher at high pH and negative values of P adsorption were found at low pH. This has been attributed to the perception of calcium with phosphate ion.

Table 1. Physico-chemical characteristics of the soils

Soil property	Bangalore	Shimoga	Mudigere	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) dS m^{-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_2O_3 (%)	12.76	6.93	14.50	10.50
Total Al_2O_3 (%)	4.91	8.58	16.91	11.01
CEC (meq 100g^{-1})	12.8	18.3	12.3	12.9
PP*	7.40	7.60	7.46	7.31
EPP**	8.01	8.19	8.09	7.98

*PP: Phosphate potential; **EPP: Equilibrium phosphate potential

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

Location	pH	Bray's P (mg kg^{-1})	PP*	EPP**
Bangalore	4.0	10.8	7.70	7.98
	5.0	12.2	7.50	7.69
	6.0	14.0	7.31	7.52
	7.0	15.8	7.18	7.31
Shimoga	4.0	4.0	7.74	8.25
	5.0	5.0	7.31	8.07
	6.0	6.2	7.21	7.78
	7.0	6.6	7.09	7.63
Mudigere	4.0	5.2	7.40	8.23
	5.0	6.4	7.20	7.99
	6.0	7.4	7.08	7.85
	7.0	7.2	7.10	7.87
Uttar Kannada	4.0	5.0	7.45	8.08
	5.0	7.2	7.30	7.83
	6.0	11.0	7.18	7.73
	7.0	11.9	6.98	7.48
	SEm	0.15	0.09	0.12
	CD	0.43	0.26	0.33
	F Test	**	**	**

*PP – Phosphate potential   **EPP – Equilibrium phosphate potential

Table 3. Relationships between pH and Brays P, phosphate potential and equilibrium phosphate potential

Location	Brays' P	PP	EPP
Bangalore	0.998**	-0.996**	-0.994**
Shimoga	0.983**	-0.935**	-0.993**
Mudigere	0.905**	-0.899**	-0.902**
Uttar Kannada	0.977**	-0.995**	-0.988**

** Significance at 1% level

Table 4. Correlation between soil properties and, phosphate and equilibrium phosphate potential

Soil properties	PP	EPP
pH	-0.251	-0.787**
pOH	0.251	0.787**
Available P	-0.664	-0.789**
Organic carbon	-0.831**	-0.556
Clay	0.041	0.380

** Significance at 1% level

The PP and EPP showed an opposite trend to available P as they measure the negative logarithm of inorganic phosphate ($H_2PO_4^-$) ion concentration in the soil solution. Shimoga soil recorded the highest values of PP (7.74) and EPP (8.25) followed by Bangalore and Uttar Kannada at pH 4.0. At pH 7.0, Uttar Kannada soil showed lowest PP (6.98) while soils from Bangalore recorded lowest EPP (7.31). However, the per cent decrease in PP was highest in Shimoga soil, while for EPP, it was highest in Bangalore soil in relative to the initial soil PP and EPP values. The relationships between the pH and Brays P, PP and EPP are given diagrammatically (Figure 1). The lowest amount of P in Shimoga soil may be related to its higher content of iron and aluminium oxides, which are responsible for phosphate retention, results in low availability of P (Ramesh and Ananthanarayana 2012). In general, the values of PP and EPP decreased with increasing pH up to 6.0 in all the soils and, further increase up to 7.0 also decreased these values in all the soils except Mudigere soil. At the pH about 5.5 and below, the concentration of Al ions is more (Brady and Weil 2002). Below this pH values, soluble Al, Fe and Mn react with $H_2PO_4^-$ ions resulting in the formation of insoluble hydroxyl phosphates (Gosh 2015), which might have caused the increase in PP and EPP values. Iron and aluminium phosphates have a minimum solubility around pH 3.0-5.0.

At higher pH values, some of the bound P is released and the fixation capacity is somewhat reduced. As the pH approaches 6.0, P precipitation as calcium compounds occurs that is soluble and at pH 6.5, the formation of slightly soluble calcium minerals is the key factor in reducing P availability. Above pH 6.5, even more insoluble P is formed which might have increased the PP and EPP values in all the four soils. The reaction of P with Fe and Al and their hydrous oxides result in stronger P binding at the lower pH values (Kumar 2015). On the other hand, above pH 7.0, Ca and Mg ions and carbonate result in added P to precipitate and the available P decreases. It has been stated that P concentration in pH range of 5.0 to 8.5 is governed by the calcium phosphate minerals (Kumar 2014). The changes in Bray's P, PP and EPP with a unit increase in pH were found to be significant. Soil pH had positive and significant correlation with available P while showing negative and significant relation with PP and EPP irrespective of the soils (Table 3) suggesting increasing in pH in acid soils enhances the availability of phosphate ions to the plants. In the correlation study, available phosphorus had shown negative and highly significant correlation with EPP (-0.769**) suggesting that EPP may successfully be used to estimate the available P in acid soils (Table 4). In the future, field experiments will be conducted to evaluate the crop response to P based on these three available phosphorous estimation methods.
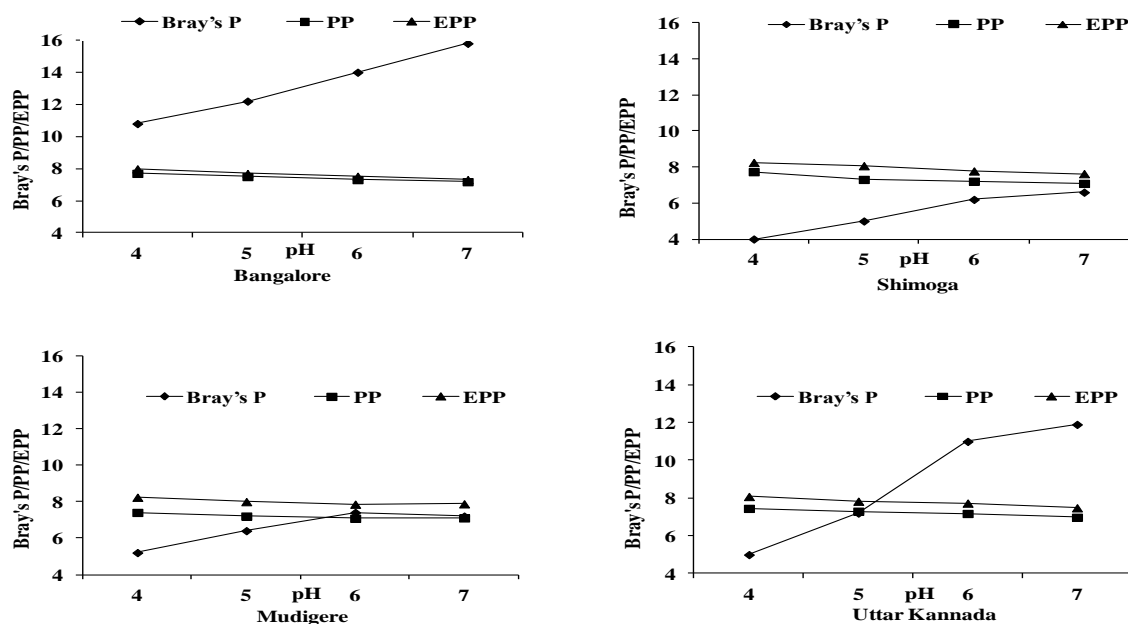

Figure 1. Relationships between the pH and Brays P, PP and EPP

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