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Characterization of Some Representative Calcareous Soils of Bangladesh with Respect to Soil Phosphorus Requirements

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ABSTRACT

Phosphate sorption equations have been widely used to characterize soils with respect to their phosphorus requirements (P_{req}). For the sorption study, the soils were equilibrated with 0.01 M $CaCl_2$ solution containing graded concentrations of phosphate (0, 1, 10, 25, 50, 100 and 150 mg P L^{-1}). The P_{req} values of four calcareous soils were determined from the Langmuir, Freundlich and Temkin equations. The Langmuir equation was best fitted to the P sorption data. Among the four soil series, the Ghior soil series occupying the lowest position of catena sorbed the highest amount of phosphate. The amounts of sorbed P maintaining 0.2 mg P L^{-1} in soil solution ranged from 14.14 to 33.56, 27.99 to 45.80 and 16.16 to 51.72 mg kg^{-1} soil which were derived from the respective Langmuir, Freundlich and Temkin equations. P_{req} values derived from the Freundlich and the Langmuir equations were negatively correlated with Olsen-P content of the soil ($r > -0.975$, $p<0.05$). Again, P_{req} values determined from the Freundlich equation were positively correlated with percent clay content ($r>0.901$, $p<0.05$) of the soil. Phosphate was sorbed by the soils in the following order: Ghior>Ishurdi>Gopalpur>Sara soil series. However, based on their P_{req} values, the soils can be arranged in the following order: Ishurdi>Ghior>Gopalpur>Sara soil series. To maintain a desired P concentration in the soil solution, the Ishurdi soil will be required to supply more P than others.

Key words: Calcareous soil, soil phosphorus requirement, phosphate sorption, sorption maximum

INTRODUCTION

Phosphorus (P) is one of the key components of any sustainable cropping systems in Bangladesh. Effective management of phosphate fertilization is becoming increasingly important for an economically and environmentally sustainable agricultural system. However, best management practices may vary depending on the soil and environmental factors. Earlier studies suggested that very large initial addition of P was needed to maximize crop yields and that the applied P had a large long-term residual value (Kamprath, 1967). However, long-term continuous application of P in the form of inorganic fertilizer and organic manures results in build-up of soil P which ultimately increases the likelihood of elevated P in the soil solution and surface runoff. Excess surface runoff containing P from soil eventually gives rise to freshwater eutrophication. Therefore, frequent small applications of P have been proposed as more economical in the long term (Linquist *et al.*, 1996). Soils vary greatly in the amount of P required to provide an adequate supply of available phosphorous to plants. Plants also vary in their P requirements for optimal growth (Vander Zaag *et al.*, 1979).

Better management of phosphate fertilization can be achieved by studying the P sorption-desorption behavior of the soil that reflects the partitioning of P between soil solid phase and soil solution. The sorption isotherms can be used to approximate the quantity of P that must be added in soil to raise the P concentration in the soil solution at equilibrium to a desired, or maximum value (Pierzynski *et al.*, 2005). Quantitative description of P sorption by soils has often been made with the Langmuir, Freundlich and Temkin equations (Villapando and Graetz, 2001). Barrow (1978) pointed out two main reasons for using these equations. These are (1) to understand the processes involved and (2) to summarize many results by a few parameters.

Beckwith (1964) suggested that standard solution concentration of 0.2 mg P L^{-1} provides P adequately for many crops if it is continuously maintained in the medium. This has been successfully used to determine P requirement (the amount of P that soil contains when a particular P level exists in solution) of several soils (upland) for optimum crop yield (Fox and Kamprath, 1970; Fox, 1981). Fox (1981) estimated the requirements from P sorption curves and correlated with P requirements established by field experiments. The relationships were found to be highly correlated. Use of P sorption isotherms for determining P requirements can increase the efficacy of P fertilization in crop production.

Among the soil properties affecting the P adsorption capacity are soil texture (Leclerc *et al.,* 2001), organic matter content (Daly *et al.*, 2001), soil pH (Barrow, 1984) and $CaCO_3$ (Bertrand *et al.*, 2003) content of the soil.

In view of the above facts, a study was undertaken to describe some calcareous soils of Bangladesh in terms of their phosphorus requirements and to determine the relationships between easily measurable soil characteristics and soil phosphorus requirements. Findings of this research work may be helpful to resource managers for identifying P status of soils, quantifying soil P requirements and estimating P amendment levels to satisfy crop needs and to protect water quality.

MATERIALS AND METHODS

Soil series: The experiment was carried out in the laboratory of the Department of Soil Science, University of Chittagong with four different benchmark calcareous soils of Bangladesh, namely the Sara (Calcaric Fluvisol), the Gopalpur (Calcaric Fluvisol), the Ishurdi (Calcaric Fluvisol) and the Ghior (Calcaric Fluvisol) soil series. The soils are grouped according to the World reference base for soil resources 2006 (IUSS Working Group WRB, 2006). Soils used in the investigation belong to the Ganges River Floodplain Alluvium. The soils under study were part of a catena. The Sara soil series occupied the higher and the Ghior soil series occupied the lower position of the catena.

Soil sample collection: Soil samples at a depth of 0-15 cm were collected from 20 spots from a square area of ~1 km^2 under a soil series. Approximately equal amounts (on weight basis) of these samples were mixed together to form a composite sample. The soils were then air dried at room temperature (25±2°C) for 7 days, ground and passed through a 2 mm sieve.

Chemical analysis: Soil samples were analyzed for textural classes, pH, total P, Olsen-P, organic matter and free carbonate content. Particle size analysis was done by hydrometer method (Bouyoucos, 1927). Soil organic matter, pH and total P contents were determined by following standard methods (Jackson, 1973). Available P was extracted by 0.5 M $NaHCO_3$ at pH 8.5 (Olsen *et al.*, 1954) and P in the extract was determined by ascorbic acid blue color method (Murphy and Riley, 1962). Each analysis was replicated thrice.

Phosphate sorption experiment: One gram soil sample was equilibrated in a 50 mL centrifuge tube with 20 mL 0.01 M $CaCl_2$ solution containing 0, 1, 10, 25, 50, 100 and 150 mg P L^{-1} (equivalent to 0, 20, 200, 500, 1000, 2000 and 3000 mg P kg^{-1} soil) as KH_2PO_4. The soil samples were then incubated at room temperature (25±2°C) for 3 days (Sharpley *et al.,* 1981). After centrifugation at 4500 rpm for 15 minutes, the mixtures were filtered through Whatman No. 42 filter paper and the amount of P sorbed by the soils was calculated from the difference between the concentration of soluble P added in the initial solution and the concentration of P in the solution at equilibrium. The P content of the supernatant solution was measured employing ascorbic acid blue colour method (Murphy and Riley, 1962) by a T80/T80+UV-Vis Spectrophotometer at wavelength of 882 nm. The sorption values of each soil were fitted according to the Langmuir, Freundlich and Temkin equations.

Linear form of the Langmuir (1918) equation is:

$$CX^{-1} = (K_L b_L)^{-1} + C b_L^{-1} \tag{1}$$

where, X is the amount of P sorbed (mg kg^{-1}), C is the equilibrium P concentration (mg L^{-1}) in solution, b_L is the adsorption maximum (mg P kg^{-1}), K_L is the bonding energy constant (L mg^{-1} P). A plot of CX^{-1} (y-axis variable) against C (x-axis variable) will yield a straight line with a slope of $1/b_L$ and a y-intercept of $1/K_L b_L$. The Maximum Buffer Capacity (MBC) of the soil, which is the increase in sorbed P per unit increase in final solution P concentration, was estimated from the product of Langmuir constants K_L and b_L (Holford, 1979).

Freundlich (1926) equation is:

$$X = K_f C^N$$

Logarithmic form of the Freundlich (1926) equation is:

$$\log X = \log K_f + N \log C \tag{2}$$

where, X is the amount of P sorbed (mg kg^{-1}), C is the equilibrium P concentration (mg L^{-1}) in solution, K_f is the proportionality constant (mg kg^{-1}), N is the empirical constant. A plot of log X (y-axis variable) against log C (x-axis variable) will yield a straight line with slope N and a y-intercept log K_f.

Temkin equation (Temkin and Pyzhev, 1940) is:

$$X = a + b \log C \tag{3}$$

where, X is the amount of P sorbed (mg kg^{-1}), C is the equilibrium P concentration (mg L^{-1}) in solution, a and b are constants. A plot of X (y-axis variable) against log C (x-axis variable) will yield a straight line with slope b and y-intercept a.

Statistical analysis: The incubation experiment was arranged in the laboratory according to completely randomized design. Regression curve fitting equations were drawn by the Microsoft Office Excel program. Suitability of different adsorption equations were studied by calculating the R^2 values of the respective equations. Correlation coefficients were calculated among soil P_{req} values and soil properties, namely percent clay, organic matter and Olsen-P content of the soil. Microsoft Office Excel and SPSS-16 computer programs were used to estimate relationships between phosphate sorption and different soil properties.

RESULTS

Physical and chemical properties of soils: The soils are representative of the major calcareous soils of Bangladesh and covered a wide range of soil properties (Table 1). The pH of the soils ranged from 7.05 to 7.28 with an average value of 7.16. Among the four soil series, the texture of the Sara soil series was clay loam with 17.03% clay. The clay contents of the Gopalpur, Ishurdi and Ghior soil series were 47.87, 54.50 and 62.13%, respectively. A sharp gradual increase in percent clay content was found along the catena. The organic matter content of the soils ranged from 1.62 to 2.30% with an average value of 1.97%. Total P content of the soils were 0.090 (Sara), 0.062 (Gopalpur), 0.056 (Ishurdi) and 0.054% (Ghior). Olsen-P content of the soils ranged from 11.68 to 31.30 mg kg^{-1}, with a mean value of 20.87 mg kg^{-1}. Free carbonate content of the soils varied from 0.23 to 0.81%.

Phosphate sorption behavior: Soils were equilibrated with 0.01 M $CaCl_2$ solution containing graded concentrations of phosphorus (up to 150 mg L^{-1}). The resulting change in the sorbed phosphate was then calculated from analysis of the equilibrium solution. Except 0 mg P L^{-1} application, phosphate was sorbed at all other rates in different amounts and proportions by the soils (Fig. 1). At 0 mg P L^{-1}, there was some desorption in all the soil series. Desorption of P at control was also reported by several other scientists (Vaananen *et al.*, 2008; Hossain *et al.*, 2011; Afsar *et al.*, 2012). In the present study, phosphate sorption increased gradually with increasing phosphate application in all the soil series. Increase in P sorption with increasing phosphate in

Table 1: Selected physical and chemical properties of soils

Soil series	Clay (%)	Soil texture	pH	Total P (%)	Olsen-P (mg kg^{-1})	Organic matter (%)	Free carbonate (%)
Sara	17.03^{d}	Clay loam	7.05	0.090^{a}	31.30^{a}	1.62^{d}	0.81^{a}
Gopalpur	47.87^{c}	Clay	7.28	0.062^{b}	24.90^{b}	2.05^{b}	0.23^{c}
Ishurdi	54.50^{b}	Clay	7.06	0.056^{c}	11.68^{c}	1.91^{c}	0.40^{b}
Ghior	62.13^{a}	Clay	7.25	0.054^{c}	15.61^{c}	2.30^{a}	0.46^{b}

Data followed by same letter(s) in a column do not differ significantly at $p<0.05$ level by DMRT

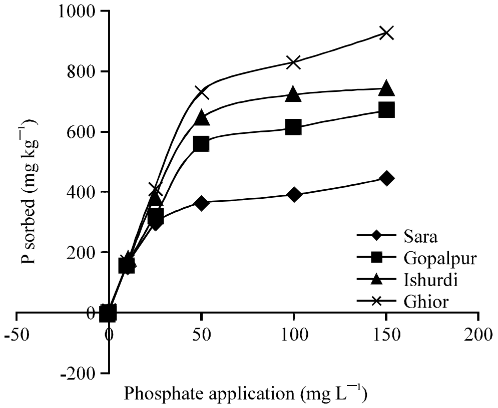

Fig. 1: Phosphate sorption capacity of soils with different rates of phosphate application

equilibrium solution was also reported by other scientists (Naseri *et al*., 2010; Hossain *et al*., 2011; Afsar *et al*., 2012). At all phosphate application rates, the Ghior soil series, occupying the lowest position of catena, sorbed the highest amount of phosphate. On the other hand, the Sara soil series located at the highest position of catena sorbed the lowest amount of phosphate. Depending on their P sorption capacity, the soils can be arranged in the following order: Ghior>Ishurdi>Gopalpur>Sara soil series (925, 745, 671 and 444 mg P kg^{-1}, when P was applied at the rate of 150 mg L^{-1}).

Multi-point adsorption equations: The P sorption data of the four soil series were plotted according to the conventional Langmuir, Freundlich and Temkin equations (Fig. 2). Among the three adsorption equations, Langmuir equation was best fitted to the equilibrium P sorption data ($R^2 = 1.0$). Different phosphate sorption parameters were calculated from the three sorption equations (Table 2). The Langmuir equation is used to derive the maximum P sorption capacity (b_L) of the soils. The b_L values of the soils varied from 454 to 1000 mg P kg^{-1}, where the Sara and Ghior soil series had the lowest and the highest values, respectively. The b_L values of other series were 715 (Gopalpur Soil Series) and 770 mg kg^{-1} (Ishurdi Soil Series). An increasing trend in the b_L values was observed along the catena of the studied soil samples. It should be noted that the b_L values are more empirical curve-fitting parameters than true sorption maxima, since input concentration were not sufficient to saturate the soil (D'Angelo *et al*., 2003). The P binding energy (K_L) of the soils ranged from 0.07 (Gopalpur Soil Series) to 0.23 (Ishurdi Soil Series). The Maximum Buffer Capacity (MBC) of the soils ranged from 50.05 to 177.10 with the Gopalpur and Ishurdi soil series had the lowest and the highest MBC values, respectively. Unlike P buffering capacity, MBC does not vary with solution phosphate concentration (Pote *et al*., 1999). Majumdar *et al*. (2004) suggested that management practices such as soil conservation measure, application of manure, etc., influence MBC of P.

The phosphate sorption data were also adequately described by the Freundlich ($R^2 \geq 0.89$) and the Temkin equations ($R^2 \geq 0.93$). Among the four soil series, Ishurdi soil series had the highest K_f values (104.62) followed by the Gopalpur (44.68), Sara (60.71) and Ghior (103.20) soil series determined from the Freundlich equation.

Soil P requirement: Sorption equations were also used to determine the soil phosphorus requirement (P_{req}), that is, the P necessary to maintain a predetermined P concentration in solution (Fox and Kamprath, 1970; Juo and Fox, 1977; Dodor and Oya, 2000; D'Angelo *et al*., 2003). Soil P requirements were determined by substituting the desired P concentration into the fitted sorption equations. The value of choice for the P concentration will depend on intended land use. The

Table 2: Fitted Freundlich, Langmuir and Temkin equations for different soil series

	Langmuir equation				Freundlich equation			Temkin equation
Soil series	$CX^{-1} = (K_L b_L)^{-1} + C\ b_L^{-1}$	b_L (mg kg^{-1})	k_L	MBC	log X = log K_f + N log C	N (L kg^{-1})	K_f (L kg^{-1})	S = a log C + b
Sara	y = 0.0022x+0.0137	454	0.16	72.64	y = 0.4811x+1.7833	0.48	60.71	y = 150.99x+121.7
Gopalpur	y = 0.0014x+0.0099	715	0.07	50.05	y = 0.5113x+1.9214	0.68	44.68	y = 223.35x+186.28
Ishurdi	y = 0.0013x+0.0057	770	0.23	177.10	y = 0.5132x+2.0196	0.51	104.62	y = 270.71x+240.94
Ghior	y = 0.001x+0.0065	1000	0.15	150.00	y = 0.5688x+2.0137	0.57	103.20	y = 290.85x+235.02

X: Total sorbed P; C: Equilibrium P concentration in solution; K_f and N are empirical constants; b_L: Phosphate sorption maximum; k_L: P binding strength; MBC: The maximum buffer capacity of the soil; a and b of Temkin equations are constants

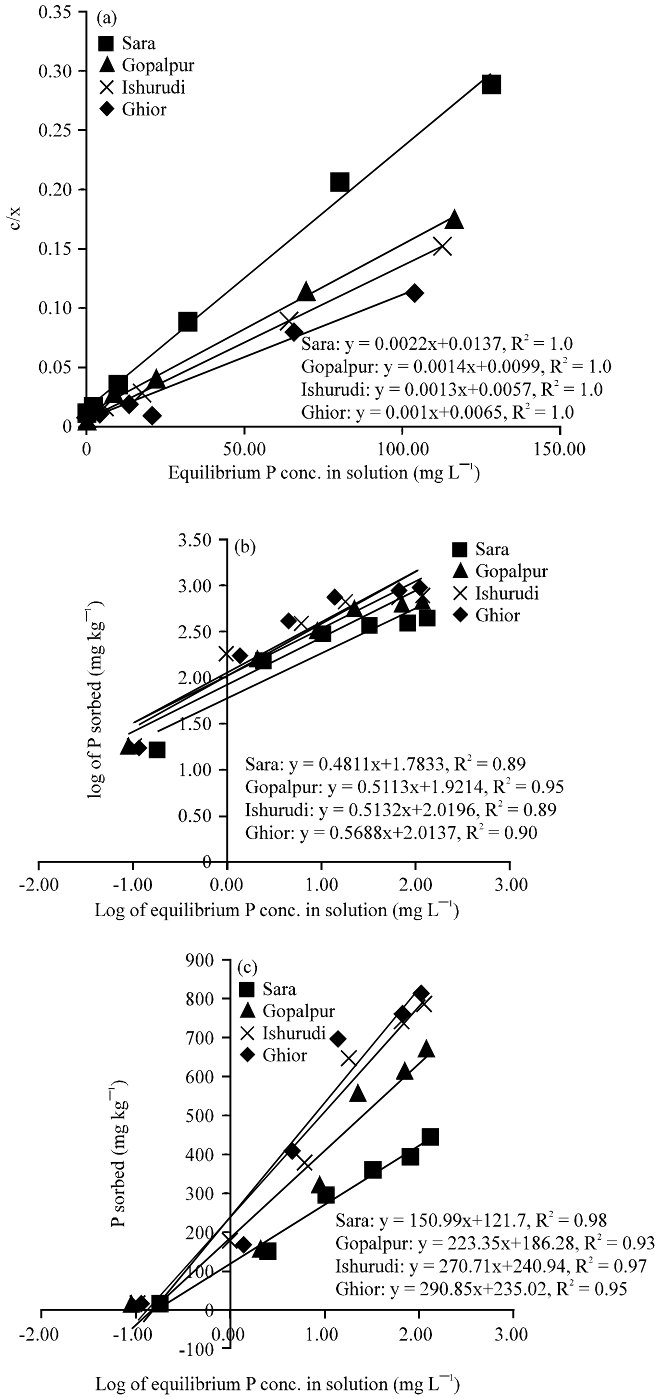

Fig. 2(a-c): Phosphate sorption equations of the soils fitted by the (a) Langmuir, (b) Freundlich and (c) Temkin equations

amount of P sorbed at 0.2 mg L^{-1} equilibrium concentration is considered to be adequate for most field crops and is widely accepted as the Standard Phosphorus Requirement (SPR) of soils (Fox, 1981; Barber, 1995). However, for the purposes of P disposal and water quality protection, USEPA has recommended a maximum level of 1 mg P L^{-1} in surface runoff (USEPA, 1996).

Table 3: Soil P requirements, P_{req} to reach 0.2 and 1.0 mg L^{-1} in equilibrium solution, as determined by isotherm equations

	Soil P requirement (mg kg^{-1}) to reach desired solution concentration (mg L^{-1})							
	Langmuir equation		Freundlich equation		Temkin equation		Average	
Soil series	0.2	1.0	0.2	1.0	0.2	1.0	0.2	1.0
Sara	14.14	62.89	27.99	60.72	16.16	121.7	19.43	81.77
Gopalpur	19.65	88.49	36.65	83.44	30.16	186.28	28.82	119.40
Ishurdi	33.56	142.86	45.80	104.62	51.72	240.94	43.69	162.81
Ghior	29.85	133.33	41.32	103.20	31.72	235.02	34.30	157.18

Table 4: Correlation coefficient between selected soil properties and the soil P requirements to reach 0.2 and 1.0 mg L^{-1} in equilibrium determined from different adsorption equations

	Langmuir equation		Freundlich equation		Temkin equation		Average	
Soil properties	0.2	1.0	0.2	1.0	0.2	1.0	0.2	1.0
Clay (%)	0.853	0.881	0.901*	0.956*	0.468	0.973*	0.723	0.948*
OM (%)	0.584	0.639	0.621	0.753	0.038	0.823	0.344	0.757
Olsen-P	-0.999**	-0.997**	-0.98*	-0.975*	-0.711	-0.947*	-0.916*	-0.976*

OM: Organic matter, *Correlation is significant at 0.05 level, **Correlation is significant at 0.01 level

Soil P requirements at 0.2 and 1.0 mg P L^{-1} were determined from the Langmuir, Freundlich and Temkin equations (Table 3). The models generated slightly different P_{req} values. To reach 0.2 mg P L^{-1} in soil solution, P_{req} values ranged from 14.14 to 33.56, 27.99 to 45.80 and 16.16 to 51.72 mg kg^{-1} soil that were derived from the respective Langmuir, Freundlich and Temkin equations. The mean P_{req} values (considering all the three equations) were between 19.43 and 43.69 mg kg^{-1}. Samadi (2006) also reported that the amount of P sorbed by different soils at 0.2 mg L^{-1} ranged from 5 to 114 mg kg^{-1} soil. On the other hand, For 1 mg P L^{-1} in soil solution, soil P requirement values varied from 60.72 to 104.62, 62.89 to 142.86 and 121.7 to 240.94 mg kg^{-1}. The average P_{req} values were between 81.77 and 162.81 mg kg^{-1}. For both desired solution P concentrations, P_{req} values were the highest for Ishurdi soil series and the lowest for Sara soil series.

Soil P requirements are thought to be related to the amounts of P-retaining agents in soils. Soil P requirement values determined from the Langmuir, Freundlich and Temkin equations were negatively correlated with Olsen-P content of the soil ($r>-0.947$, $p<0.05$). However, P_{req} values determined from the Freundlich equation were positively correlated with % clay content ($r>0.901$, $p<0.05$) of the soil (Table 4).

DISCUSSION

The phosphate sorption capacity increased along the catena of the soil. The highest P sorption capacity of the Ghior soil series can be attributed to its high organic matter and clay content. Significant relationships between P sorption capacity and several soil properties like organic matter and clay contents have been reported by several authors (Johnston *et al.*, 1991; Toor *et al.*, 1997; Daly *et al.*, 2001).

Among the sorption equations, Langmuir equation was best fitted to the sorption data. Similar results have been reported for Langmuir equation over Freundlich and Temkin equations by other scientists as well (Gichangi *et al.*, 2008; Moazed *et al.*, 2010). However, Dubus and Becquer (2001) and Zhou and Li (2001) reported that based on R^2 values, the Freundlich equation was better in predicting the P sorption capacity of calcareous soils than the other two equations. According to Mead (1981), the good fit of the Langmuir adsorption equation indicates that the P sorption affinity of soils remained constant with increasing surface saturation.

The Ishurdi soil series had the highest K_L values. Mehadi and Taylor (1988) suggested that high K_L value indicates strong bonding of phosphate by soil particles. As a result, due to the highest K_L values, the Ishurdi soil series will retain P better than other studied soils and possibly be the better sink at similar P adding rates.

Significant negative relationships between P_{req} values determined from the sorption equations and Olsen-P content of the soil imply that the fractions of soil P that can be readily extracted by Olsen solution are important in P sorption study. Kamprath and Watson (1980) proposed that the Olsen solution (0.5 M sodium bicarbonate, pH 8.5) removes P from several forms including Al-P, Ca-P and to a lesser extent P adsorbed on iron-hydrated oxides. Kamprath and Watson (1980) and Hue and Fox (2010) observed a significant linear relationship between solution P as established by the phosphate sorption equations and P extracted by Olsen method.

Significant positive relationships between percent clay content and P_{req} values of the soils suggest that clay content affects the ability of soils to adsorb freshly added P in soil. The positive role of clay content on P sorption has also been reported by some other researchers (Solis and Torrent, 1989; Afif *et al.*, 1993; Samadi, 2006).

CONCLUSION

Results from this sorption study showed that the calcareous soils varied considerably in their phosphate retention capacities. Considerable variations were also observed in P requirements (P_{req}) values, i.e., the amount of P that a soil contains when a particular P level exists in solution. P_{req} values determined from the Langmuir and the Freundlich equations were highly correlated with percent clay and Olsen-P content of the soil. Among the four soil series, the Ishurdi soil requires more P fertilization than others to maintain a desired solution P concentration. However, relationships determined in this study are needed to be verified across a wide range of soils. These relationships could be readily integrated into existing management practices for improving soil fertility and safeguarding water quality.

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