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PHOSPHATE SORPTION INDICES AS AFFECTED BY THE CALCAREOUSNESS OF SOILS

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Key words: Phosphate sorption indices, Calcareousness, Phosphorus buffering capacity, Standard phosphorus requirement

Abstract

An experiment was carried out to study the effects of calcareousness on phosphate sorption indices of soils using three representative calcareous soils, namely Sara (Aquic Eutrochrept), Gopalpur (Aquic Eutrochrept), and Ishurdi (Aeric Haplaquept) series of Bangladesh. Three non-calcareous soils, namely Belabo (Typic dystrudepts), Sonatala (Aeric Endoaquepts) and Ghatail (Aeric Haplaquept) series were also selected for comparison purposes. Phosphate sorption indices of soils were calculated using Langmuir and Freundlich isotherms. Isotherms were constructed taking one gram of air-dried sieved (< 2 mm) soil into a 50 ml centrifuge tube, and subsequently adding seven initial P concentrations, namely 0, 1, 10, 25, 50, 100 and 150 µg/ml to each centrifuge tube employing a soil/solution ratio of 1 : 20 (w/v). According to the Langmuir equation, the amount of phosphate sorbed followed the order: Sonatala > Ghatail > Sara = Gopalpur > Ishurdi > Belabo. The abundance of amorphous iron rather than the calcareousness was putatively responsible for the high phosphate sorption capacity of soils. Maximum phosphorus buffering capacity (MPBC) of the calcareous soils ranged from 33.4 - 62.8 l/kg. Langmuir and Freundlich equations produced different values for soil P requirements (SPR) at 0.2 and 1.0 mg P/l. Calcareous soils would require 27 - 44 mg P/kg soil to attain 0.2 mg P/l soil solution, which is deemed sufficient for crop growth. The soils would require 32 - 58 mg P/kg soil to reach 1.0 mg P/l soil solution, which is regarded to be safe for soils in terms of susceptibility to P losses. The calculated Langmuir constant b values were higher than the threshold value of 0.07 l/mg for two of the calcareous soils. Therefore, even though the non-calcareous soils sorbed more phosphate, higher bonding energy of P sorption for calcareous soils makes them less vulnerable to loss via surface runoff.

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Introduction

Soil phosphorus (P) concentrations in an optimum range for plant growth is absolutely vital to sustain soil fertility and ensure the production of food crops. Phosphorus is therefore applied to agricultural fields as inorganic and/or organic fertilizers. However, P is a nonrenewable resource and a recent assessment indicated that natural phosphate (PO_4^{3-}) deposits will last for approximately 60 - 240 years(1). Therefore, judicious use of existing phosphate resource is absolutely necessary to ensure the long-term availability and accessibility of phosphorus sources for the present and future generations of humankind(2).

On the other hand, the amount of fertilizer applied often exceeds the uptake by plants, and this results in a build-up of P in the soil. A fraction of applied P is lost through surface runoff and leaching processes and the lost P constitute the major nonpoint source of phosphorus in water bodies(3). Elevated levels of P in freshwater systems leads to eutrophication, which results in the depletion of oxygen leading to fish death as well as affecting other aquatic life forms in an adverse manner. Therefore, the amount of P in waters should be curtailed to prevent eutrophication in lakes and other surface waters(4).

Since the concentration of P in the soil solution is critical for losses of dissolved P, processes such as P sorption and desorption are crucial. Sorption isotherm is an important tool for investigating the sorption behavior of soils. Phosphorus sorption isotherm has an edge over conventional soil P test because conventional soil tests do not take into account the physicochemical properties of soils(5). Models such as Langmuir, Freundlich, and Temkin are commonly used for describing phosphate sorption in quantitative terms, and different sorption parameters derived from these models are subsequently correlated with different soil parameters for validation. For example, the amount of P required, soil phosphorus requirements (P_{req}), to bring its desired concentration in soil solution could easily be determined by P sorption isotherm(6,7).

Soil P requirements are determined by plugging in the desired P concentrations into the fitted sorption equations. Intended land use dictates the value of choice for the P concentration. For example, 0.2 mg P/l is considered to be the standard solution concentration for most field crops(8), whereas 1 mg P/l is the maximum level of P concentration in surface runoff when water quality is the concern(9). These predetermined concentrations are called standard phosphorus requirements (SPR). Another quantity calculated from the model is maximum phosphate buffering capacity (MPBC), which gives an idea as to how much fertilization will be required to maintain a predetermined concentration of P.

In Bangladesh, calcareous soil occupies ~19% area of the country(10). Very few researches have been done on the phosphate sorption characteristics of the soils which are calcareous in nature. Therefore, a study was undertaken to investigate the effects of calcareousness on the phosphate sorption properties of three calcareous soils. More specifically, phosphate sorption indices, namely standard phosphorus requirements (SPR) and maximum phosphate buffer capacities (MPBC) were looked at along with other sorption parameters. Some selected soil properties were studied to see how they influence the sorption properties of soils along with calcareousness. Some non-calcareous soils were also studied for comparison purposes.

Materials and Methods

Soil selection and sample collection: Six representative soil series, including three calcareous, namely Sara, Gopalpur, Ishurdi, and three non-calcareous, namely Belabo, Sonatala and Ghatail of Bangladesh, were selected for this study (Table 1). Sara, Gopalpur and Ishurdi series were collected from Ishurdi Upazila of Pabna district, Bangladesh. Soil samples of Belabo, Sonatala and Ghatail series were collected from Ghatail of Tangail district, Bangladesh. The general type and taxonomic classification of the soils are given in Table 1. Composite sampling technique was adopted for collecting the soil samples. Six composite samples representing six soil series were made up of 20 spots from an area of 1 km^2. Only surface soil (0-15 cm) was collected for the study. The collected soil samples were taken to the lab, and the crop residues and other non-soil materials were then carefully removed. Thereafter, the soil samples were air dried, ground and sieved through a 2 mm (10-mesh) sieve.

Analysis of soil physical and chemical properties: Particle size distribution was determined by a hydrometer method(11). Soil pH was measured by Jenway Glass Electrode pH meter using a 1 : 2.5 soil to water ratio. The chemical parameters were determined following different widely used and some specific methods. Free carbonate of the calcareous soil samples was determined using rapid titration method(12). Soil organic carbon was determined by Walkley-Black wet oxidation method(13). Soil organic matter was calculated by multiplying the per cent value of organic carbon by the van Bemmelen conversion factor of 1.724. Cation exchange capacity (CEC) was determined using a neutral 1 M NH_4OAc solution as described by Jackson(14). Total Fe and Mn were determined by digesting the soil samples with HNO_3-$HClO_4$ acid and then measuring by flame atomic absorption spectroscopy (AAS) with an Agilent Technologies 200 series AA. Total phosphorus in HNO_3-$HClO_4$ acid digest was determined by using a UV-Vis spectrophotometer (Optima SP-3000 nano, Tokyo, Japan) employing the vanadomolybdate yellow color method as described by Jackson(14). Extraction of available P was made by 0.5 M $NaHCO_3$ at pH 8.5(15) and Bray and Kurtz P-1 extracting solution (0.025 M HCl in 0.03 M NH_4F)(16). Phosphorus in the extract was determined by a UV-Vis spectrophotometer (Optima SP-3000 nano, Tokyo, Japan) following the ascorbic acid blue color method(17). Some fractions of soil Fe have been extracted and determined following selective dissolution procedures. Total or free iron oxide was extracted using citrate-dithionite reagent(18). Poorly crystalline or active iron oxide was extracted using NH_4-

oxalate-oxalic acid (pH 3)(19). Pyrophosphate was used for the extraction of organically bound Fe. The extracts obtained from different Fe fractions were preserved and finally determined by flame atomic absorption spectroscopy (AAS) with an Agilent Technologies 200 series AA. All determinations were done in triplicate.

Table 1. Present land type, topography and drainage conditions of the soil series and correlation with different soil classification systems(10).

Series name	Land type and parent material	Topography	Drainage	General soil type	USDA soil family
Sara	High land, Ganges river alluvium	Nearly level to very gently undulating	Poorly drained	Calcareous brown floodplain soil	Aquic Eutrochrept
Gopalpur	Medium high land, Ganges river alluvium	Nearly level to gently undulating upper and middle slopes	Poorly drained	Calcareous brown floodplain soil	Aquic Eutrochrept
Ishurdi	Medium high land, Ganges river alluvium	Nearly level to gently undulating old, low abandoned levees	Poorly drained	Calcareous dark grey floodplain soil	Aeric Haplaquept
Belabo	High land, Madhupur clay	Nearly level	Well drained	Deep red-brown terrace soil	Typic Dystrudepts
Sonatala	High land, Old Brahmaputra alluvium	Developed on the upper slopes of ridges	Imperfectly to poorly drained	Non-calcareous dark grey floodplain soil	Aeric Endoaquepts
Ghatail	Medium high land, Old Brahmaputra alluvium	Nearly level basin	Poorly drained	Non-calcareous dark grey floodplain soil	Aeric Haplaquept

Sorption experiment: Phosphorus sorption isotherms were obtained according to the procedure outlined by Nair(20). One gram of air-dried sieved (< 2 mm) soil was taken into a 50 ml centrifuge tube. Seven initial P concentrations, namely 0, 1, 10, 25, 50, 100 and 150 µg/ml were first prepared in 0.01 M $CaCl_2$ solution using KH_2PO_4 salt and then the prepared solutions were added separately to each centrifuge tube using a soil/solution ratio of 1 : 20 (w/v). The resultant P contents were 0, 20, 200, 500, 1000, 2000 and 3000 µg/g soil. The centrifuge tubes were then shaken for 16 hrs to achieve equilibrium. After the equilibration period, the soils were centrifuged, and the phosphate contents were analyzed in the supernatants following the ascorbic acid blue color method(17). Phosphorus content was measured by a UV-Vis spectrophotometer (Optima SP-3000 nano, Tokyo, Japan) at 882 nm wavelength. The amount of sorbed P 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. All isotherms were performed in triplicate.

Sorption parameters were calculated using the most common isotherms, namely Langmuir and Freundlich. The Langmuir adsorption model (Eq. 1)(21) is based on the assumption that all the adsorption sites have equal adsorbate affinity and adsorption at one site is independent of the adsorption at an adjacent site. Maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The bonding to the adsorption sites can be either chemical or physical but strong enough to prevent displacement of the adsorbed molecules.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \qquad (1)$$

where $C_e\left(\frac{\mathbf{mg}}{\mathbf{L}}\right)$ is the equilibrium concentration of the remaining ions in the solution; $q_e\left(\frac{\mathbf{mg}}{\mathbf{kg}}\right)$ is the amount of ions adsorbed per mass unit of adsorbent at equilibrium; $Q_0\left(\frac{\mathbf{mg}}{\mathbf{kg}}\right)$ is the amount of ions at complete monolayer, and $b\left(\frac{\mathbf{L}}{\mathbf{mg}}\right)$ is the Langmuir constant related to the affinity of binding sites which is a measure of the energy of adsorption. The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b} \qquad (2)$$

The Langmuir constants Q_0 and b were calculated from the slope and intercept of the plots of $\frac{C_e}{q_e}$ (Y-axis) and C_e (X-axis).The maximum phosphorus buffering capacity (MPBC) of the soil (the increase in sorbed P per unit increase in final solution P concentration), was estimated from the product of Langmuir constants Q_0 and b .

The Freundlich isotherm (Eq. 3)(22) can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. It also assumes that the adsorbent has a different affinity for adsorption. The Freundlich equation is expressed as:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

where K_F and n are Freundlich constants indicating adsorption capacity (mg/kg) and intensity or the favorability of the sorption process, respectively. To determine the constants K_F and n, the Freundlich equation can be described by the linearized form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

Values of K_F and n are calculated from the intercept and slope of the linear plots of $\log q_e$ vs. $log C_e$.

Statistical analysis: All statistical analyses were performed using MS. Excel and Minitab17 computer programs.

Results and Discussion

Physical and chemical properties of the soils: Results of analyses are given in Table 2. Soil textures of the studied soils were silt loam, silty clay loam, silty clay, silty clay, silt loam and silt loam for Sara, Gopalpur, Ishurdi, Ghatail, Sonatala and Belabo, respectively. Sara, Gopalpur and Ishurdi soil series were developed from calcareous parent materials and pH values of these soil series were 7.69, 7.59 and 7.1, respectively. Ghatail, Sonatala and Belabo soil series are non-calcareous in nature and pH values were between 5.2 and 6.4 in these soils. Organic matter content was very low in Sara, Ishurdi, Sonatala and Belabo series, ranging from 0.68 to 1.01%. Gopalpur and Ghatail soil series possessed 2.16 and 1.73% organic matter, respectively, which are moderate in amounts. Cation exchange capacities of the investigated soils ranged from 4.48 to 12.19 cmol (+)/kg. Free $CaCO_3$ contents of Ghatail, Sonatala, and Belabo soil series were not determined; in other soils, it varied from 3.85 to 7.06%. Available phosphorus in the studied soils ranged from 4.16 to 48.75 µg/g. Total P and total K varied from 342 to 1157 and 5801 to 9994 µg/g, respectively. Total Mn content was the highest in Belabo soil series (618 µg/g) and the lowest in Gopalpur soil series (377 µg/g). Total Fe content ranged from 15866 to 38717 µg/g in the calcareous soils. Total Fe content in the noncalcareous soils differed from 4691 to 6708 µg/g. Free iron oxide, amorphous iron, and organically bound iron were in the ranges of 3779 to 7247, 781 to 3613 and 292 to 2006 µg/g, respectively.

Phosphate sorption: Data from isotherm experiments were plotted for calcareous and non-calcareous soils by plotting the amount of phosphate sorbed (P_{sorb}) against the equilibrium concentration of phosphate (P_{eq}). The data were further used for fitting into Langmuir and Freundlich isotherm models.

Phosphate sorption efficiency: The added phosphate was sorbed by the calcareous and non-calcareous soils and the amount and percentage of phosphate sorption varied at all the rates. However, when no phosphate was added to the soils, i.e. at 0 µg P/ml, some desorption was noticed in all the soils. This phenomenon was reported by other scientists working with calcareous and non-calcareous soils(23,24,25). In the calcareous soils, phosphate sorption increased gradually up to 100 μg PO_4^{3-}-P/ml and beyond that concentration, the amount of sorption decreased substantially. This finding is in contrast to the findings of Leytem and Westermann(26). In their study, there was a sharp increase in the slope of the curve at equilibrium concentrations greater than 150 μg PO_4^{3-}-P/ml. They attributed this increase to the precipitation process associating Ca and P. In the non-calcareous soils, in the present study, the amount of P sorption progressively increased with increasing P application; this trend is in line with the findings of Naseri and his coworkers(27). The percentage of sorption ranged from 18.0 to 60.8% in Sara soil series, the lowest being at the highest loading and the highest at 25 μg/ml PO_4^{3-}-P. In Gopalpur soil series, the percentage of sorption varied from 17.1 to 74.6. In Ishurdi soil series, the

Table 2. Physical and chemical properties of soils. Differences were determined by one-way ANOVA followed by Tukey's pairwise comparison. Different letters in the same row indicate significant differences between different soils ($p < 0.05$).

Properties	Series					
	Sara	Gopalpur	Ishurdi	Ghatail	Sonatala	Belabo
Sand (%)	30	12	1	5	15	15
Silt (%)	53	56	51	51	66	70
Clay (%)	17	32	48	44	19	15
Textural class	Silty loam	Silty clay loam	Silty clay	Silty clay	Silty loam	Silty loam
pH	7.7	7.6	7.1	6.4	5.7	5.2
Organic carbon (%)	0.68 ± 0.12e	2.16 ± 0.07a	1.01 ± 0.07c	1.73 ± 0.07b	0.84 ± 0.07d	0.80 ± 0.01d
Free carbonate (%)	7.06	3.85	5.78	—	—	—
CEC (cmol(+)/kg	6.53 ± 0.36bc	8.83 ± 1.05b	12.19 ± 4.02a	7.47 ± 0.54bc	4.48 ± 0.24c	4.64 ± 1.30c
Total P (%)	0.116 ± 0.007a	0.070 ± 0.013b	0.059± 0.005bc	0.038 ± 0.002cd	0.077 ± 0.006b	0.034 ±0.012c
Available P ($\mu g\ g^{-1}$)	35.83 ± 3.82ab	34.17 ± 7.64a	25.83 ± 2.89b	4.17 ± 0.83c	10.00 ± 0.00c	48.33 ± 1.91a
Total Mn (%)	0.038 ± 0.003b	0.039 ± 0.007b	0.042 ± 0.002b	0.051 ± 0.002ab	0.038 ± 0.007b	0.062± 0.014a
Total Fe (%)	1.59 ± 0.15d	2.84 ± 0.25bc	3.87 ± 0.33a	3.47 ± 0.05ab	2.54 ± 0.36c	1.12 ± 0.37d
Free iron oxide (μg/g)	3779 ± 132e	6937 ± 119c	10128 ± 140a	7793 ± 222b	4691 ± 187d	6832 ± 14c
Amorphous Fe (μg/g)	781 ± 70e	2397 ± 141d	2248 ± 112d	4723 ± 102a	2904 ± 130c	3296 ± 131b
Organically bound Fe (μg/g)	292 ± 14d	433 ± 23cd	909 ± 39bc	1066 ± 48b	2006± 176a	835 ± 83bc

percentage of sorption decreased gradually with an increase in phosphate loading concentration (63.3 to 18.6). A similar kind of phenomenon was reported by other scientists in Ishurdi soil series(23). On the other hand, the non-calcareous soils exhibited varying sorption capacities. The development of soils on different parent materials can be accounted for the observed phenomena. The percentage of sorption ranged from 26.0 to 79.6 in Ghatail soil series, the lowest being at the highest loading and the highest at 10 µg/ml PO_4^{3-}-P. In Sonatala soil series, the percentage of sorption varied from 25.6 to 92.5. The percentage of sorption decreased gradually with an increase in phosphate loading concentration (63.3 to 27.8) in Belabo soil series.

The isotherms constructed (Figs 1 and 2) using the experimental data exhibit that they conformed to the L-curve isotherm type. It is an indication of the strong affinity between soil constituents and the phosphate ions, particularly at lower concentrations of phosphate(28). All the calcareous soil series behaved similarly exhibiting an increased P sorption with an increase in P application up to 100 µg/ml. At the highest loading (150 µg/ml), P sorption decreased in all the soils. This phenomenon can be explained by looking into two mechanisms whereby phosphate anions get adsorbed onto soil micelles. Phosphate adsorption takes place through specific and non-specific adsorption processes. Specific adsorption is related to high-affinity adsorption sites and micropore diffusion adsorption(29,30,31), whereas non-specific adsorption is associated with low-affinity sites. While specific adsorption is preponderant during the fast adsorption stage, non-specific adsorption predominates during the slow adsorption stage. The percentage of adsorption via non-specific adsorption process increases when phosphate loading increases(32). In the present study, at 150 µg/ml PO_4^{3-}-P application, phosphate sorption decreased in all the soils than what was sorbed at 100 µg/ml PO_4^{3-}-P application. Non-specific adsorption process might have played apredominant role for the additional P when P application was increased from 100 to 150 µg/ml. Therefore, even though the amount of P sorption was higher during the fast-adsorption stage at higher loading (150 µg/ml), in the slow adsorption process the phosphate was initially adsorbed and then desorbed (the adsorption experiment was run for 72 hrs). As a result, more phosphate was sorbed at 100 µg/ml than 150 µg/ml PO_4^{3-}-P application. Comparing the experimental highest amount of P sorbed in these soil series, it is evident that each soil series has a different capacity to sorb P. Gopalpur soil series (743.33 µg/g) had the highest value of maximum adsorption, followed by Sara soil series (700 µg/g) and Ishurdi soil series (637.04 µg/g). On the other hand, in the non-calcareous soil series, Sonatala soil series had the highest value of maximum adsorption (869.89 µg/g), followed by Ghatail soil series (781.43 µg/g) and Belabo soil series (464.53 µg/g).

Phosphate sorption isotherms: The sorption isotherm data of P was modeled into the Langmuirand Freundlich equations. The goodness of the fit of the models was checked by the coefficient of variation (R^2) values. When the Langmuir equation applied to the experimental data, all the soils showed a good fit except Sonatala soil series (Fig. 3, Table 3). R^2 value was the highest in the Ishurdi soil, followed by Gopalpur and Ghatail, Belabo, Sara and Sonatala. Sorption parameters were calculated from the Langmuir and Freundlich equations (Table 4). The maximum amount of sorbate sorbed by the soil (Q_0) was calculated for all the soils and Sonatala was found to sorb the highest amount of P from the solution according to the Langmuir equation. However, since the model did not fit well into the experimental data from Sonatala soil, that quantity was not considered for comparing calcareous and non-calcareous soils in terms of their Langmuir model-derived maximum sorption capacities. It is worth mentioning that the Q_0 value is an

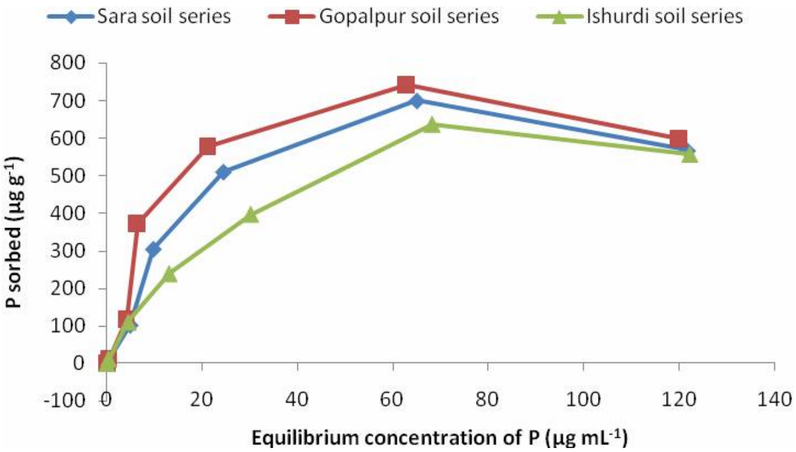

Fig. 1. Phosphate sorption isotherm of calcareous soils.

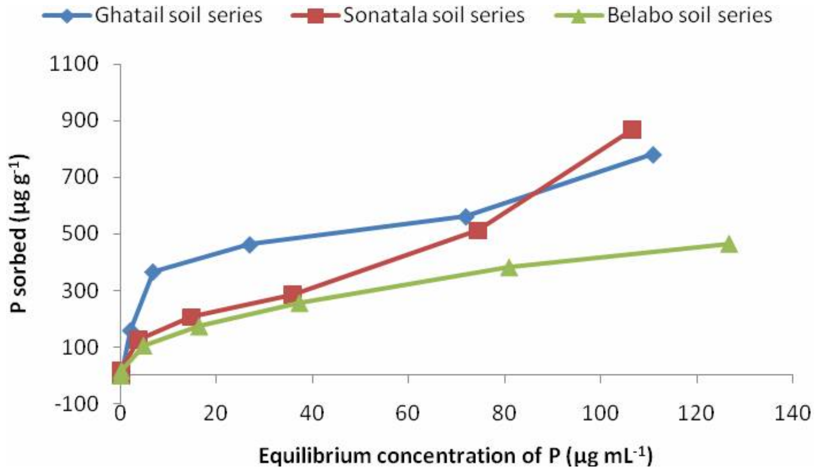

Fig. 2. Phosphate sorption isotherm of non-calcareous soils.

empirical curve-fitting parameter and is not necessarily the true sorption maxima(3). In this study, the input concentrations were not sufficient for some soils. Reduced P levels were chosen to simulate most soil environments and are also useful for determining the soil P requirement in the lower concentration range(3). Values of Langmuir sorption maximum (Q_0) for these soils ranged from 526 to 769 µg/g (Sonatala soil's data was not used). However, the Langumir equation-derived maximum sorption capacities overestimated the experimental data. According to the Langmuir equation, the amount of phosphate sorbed followed the order: Ghatail > Sara = Gopalpur > Ishurdi > Belabo. On the other hand, in the actual study maximum phosphate sorption followed the following order: Sonatala > Ghatail > Gopalpur > Sara > Ishurdi > Belabo.

The highest sorption capacity of Sonatala soil series could be attributed to its organically bound iron, amorphous iron content, and pH. Sonatala soil had a pH value of 5.7 which was lower than the soils having comparable organically bound and amorphous iron content. The lower pH value and iron fractions in the soil might have worked in concert in removing the applied phosphate from the solution. Belabo soil series possessed the lowest amount of total iron content and accordingly the sorption capacity was the lowest in that soil series. Among the calcareous soils, Gopalpur was found to sorb more phosphate from the other two soil series. Despite having the lowest amount of total iron content among the calcareous soils, Gopalpur had more amorphous iron oxide than the other two soils. This feature can be accounted for the highest sorption potential of Gopalpur soil series among the calcareous soil series.

The Langmuir constant *b* is related to the affinity of the binding sites, i.e. the bonding energy of P sorption and ranges from 0.027 to 0.088 L/mg. Varied values of *b* indicate that the bonding energy of P sorption is different for the studied soil series. The binding energy was the highest for Sara soil series (0.105 L/mg), followed by Gopalpur (0.0880 L/mg), Ghatail (0.078 L/mg P), Ishurdi (0.050 L/mg), Belabo (0.043 L/mg) and Sonatala (0.027 L/mg). The binding energy values for the noncalcareous soils and one of the calcareous soils (Ishurdi series) are below the threshold value of 0.07 L/mg proposed by Mcdowell(33). Soils having less than this value of binding strength are subject to enhanced loss of P through surface and subsurface flows. Thus, the studied calcareous soils are less susceptible to phosphate loss via surface runoff and other avenues. Even though the non-calcareous soils have sorbed more phosphate, they do not bind phosphate strongly, thereby predisposing the soils to lose more phosphate compared to calcareous soils. Therefore, fertilizer should be applied to these soils judiciously so that applied phosphate does not find its way into the nearby water bodies posing environmental concerns.

The adsorption isotherms were also examined by the linear form of the Freundlich adsorption equation by plotting $\log q_e$ against $\log C_e$ (Fig. 4, Table 3), and all the soils showed a good fit except Gopalpur and Ghatail soil series. The R^2 values for the Freundlich model with Belabo, Sonatala and Ishurdi soil series indicated a good fit

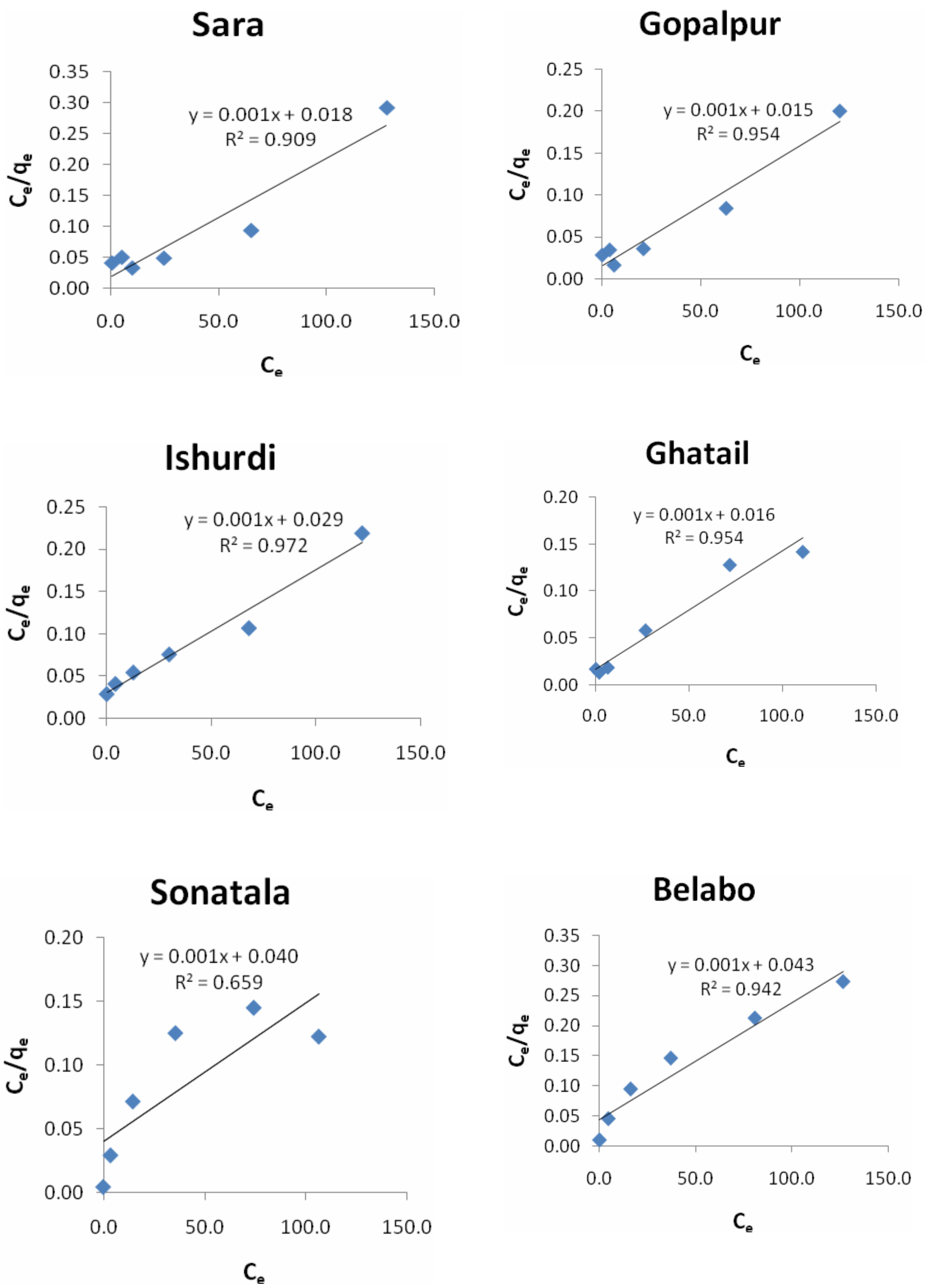

Fig. 3. Adsorption isotherms fitted to Langmuir equation.

between the experimental and isotherm data. The R^2 value was the highest in Belabo soils series (0.9976), followed by Sonatala (0.9785), Ishurdi (0.9636), Sara (0.9088), Ghatail (0.8835) and Gopalpur (0.8570). Sorption parameters were also calculated from the Freundlich equation (Table 4). Freundlich isotherm describes sorption behavior better when heterogeneity is present in the adsorbents(34,35). In the present study, data conformed to Langmuir equation more meaning the soils possessed energetically homogeneous surface which is unlikely to happen. However, as phosphate is known to be chemisorbed by a select metal sites, this phenomenon can occur. If the putative metal sites are uniformly distributed on the soil particles, a virtually homogeneous surface is possible. This could be a plausible explanation for the phosphate adsorption data following the Langmuir equation.

The Freundlich value (K_f) provides an indication of the average sorption capacity of the soil. In other words, the coefficient is a measure of the amount of P sorption sites. In the studied soils, the K_f values ranged from 30.13 to 63.02 µg/g. According to Freundlich parameter K_f, Ghatail soil has the highest sorption sites followed by Sonatala, Gopalpur, Belabo, Ishurdi, and Sara. The slope 1/n being 1 indicates that sorption carried out over the range of chemical concentrations used in the experiment is not affected by the concentration of the chemical in solution. A slope less than 1 indicates that there is proportionally more chemical sorbed when the concentration is low and less chemical is sorbed when the concentration is high. The calculated values of 1/n are indicating that the soils in question sorbed more phosphate over the range of low concentrations. The highest 1/n was found in Sara soil series (0.7487), followed by Gopalpur (0.6903), Ishurdi (0.6843), Ghatail (0.5891), Belabo (0.4993), and Sonatala (0.4940).

Table 3. Fitted Langmuir and Freundlich equations using sorption data from studied soil series.

Soil series	Langmuir equation		Freundlich equation	
	Equation	R^2 value	Equation	R^2 value
Sara	$y = 0.0019x + 0.0181$	0.9094	$y = 0.7487x + 1.4790$	0.9088
Gopalpur	$y = 0.0014x + 0.0159$	0.9541	$y = 0.6903x + 1.6478$	0.8570
Ishurdi	$y = 0.0015x + 0.0298$	0.9720	$y = 0.6843x + 1.5107$	0.9636
Ghatail	$y = 0.0013x + 0.0166$	0.9543	$y = 0.5891x + 1.7995$	0.8835
Sonatala	$y = 0.0011x + 0.0402$	0.6597	$y = 0.4940x + 1.7989$	0.9785
Belabo	$y = 0.0019x + 0.0439$	0.9423	$y = 0.4993x + 1.6315$	0.9976

Maximum phosphorus buffering capacity (MPBC): The maximum phosphorus buffering capacity (MPBC) is a product of the Langmuir model Q_0 and b (36). It is a useful estimate of the P supplying and immobilization capacities and rates by soils(36,37). The MPBC is regarded as an inherent property of soils. The MPBC values shown in Table 4 indicate that Sonatala, Belbao amd Ishurdi will need less P fertlization compared to other soils having higher values of MPBC. Therefore, farmers will be able to maintain an optimum concentration of phosphorus for crop growth in those three soils with less capital(38).

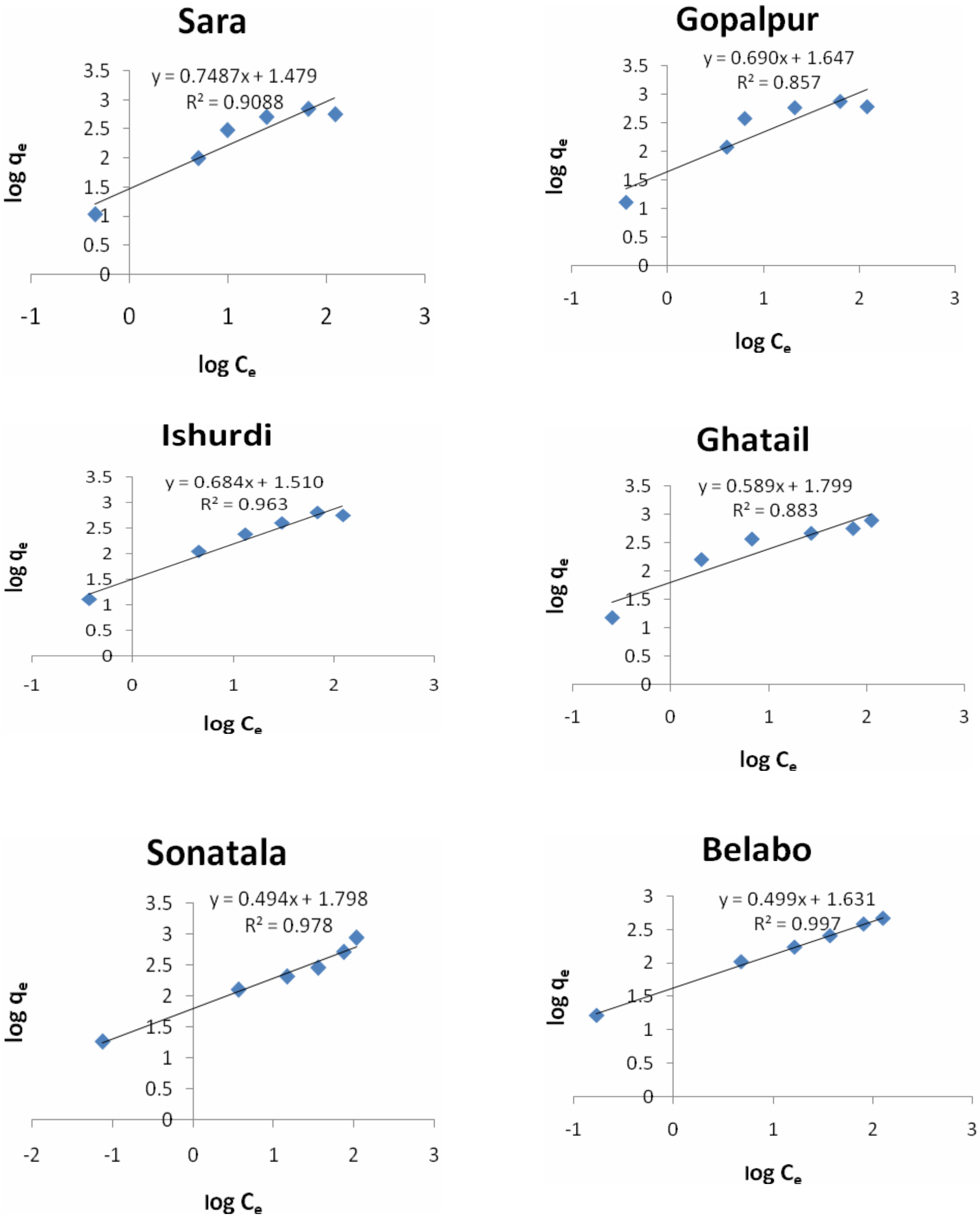

Fig. 4. Adsorption isotherms fitted to Freundlich equation.

Standard phosphate requirement (SPR): Sorption equations were used to determine the soil phosphorus requirement (SPR), which is the P required to maintain a predetermined P concentration in solution(6). Soil P requirements were calculated by plugging in the desired P concentration into the fitted sorption equations. Desired P concentrations, however, depend on the intended land use. For example, if someone wants to use their land for crop production purposes, a value of 0.2 mg P/l is regarded as an appropriate value(39). Since P is a nutrient contaminant in waterbodies, other levels of P are also used for the calculation of soil P requirements. For instance, the USEPA recommended a maximum level of 1 mg P/l in surface runoff(9).

Table 4. Sorption parameters derived from Langmuir and Freundlich equations.

Soil series	Langmuir equation			Freundlich equation	
	Q_0 (mg/kg)	b (l/mg)	MPBC (l/kg)	K_F	$\frac{1}{n}$
Sara	526	0.105	55.2	30.13	0.7487
Gopalpur	714	0.088	62.8	44.44	0.6903
Ishurdi	667	0.050	33.4	32.41	0.6843
Ghatail	769	0.078	60.0	63.02	0.5891
Sonatala	909	0.027	24.5	62.94	0.4940
Belabo	526	0.043	22.6	42.81	0.4993

Soil P requirements at 0.2 and 1.0 mg P/l were determined using Langmuir and Freundlich equations (Table 5). The models generated slightly different SPR values. As Langmuir equation fitted well into sorption data for Sara, Gopalpur, Ishurdi and Ghatail soil series, Langmuir equation-derived values were used to estimate soil P requirements for these soil series. For Sonatala and Belabo soil series, Freundlich-equation derived values were used for soil P requirements. To attain 0.2 mg P/l in the soil solution, SPR values ranged from 27 - 44 mg/kg for calcareous soils. Afsar and Hossain(40) previously worked with calcareous soils in Bangladesh and reported SPR values between 19 and 44 mg/kg. Samadi(41) also worked with calcareous soils in Iran and according to his calculations, SPR values were within a range of 5 - 114 mg/kg to maintain a soil solution concentration of 0.2 mg P/l. For non-calcareous soils, soil P requirements ranged from 19 - 43 mg/kg. Soil P requirements to reach 1 mg P/l were 32, 56 and 58 mg P/kg for Ishurdi, Ghatail and Gopalpur soils, respectively. For Sara, Sonatala and Belabo soils, the soil P requirements were 30, 63 and 43 mg/kg. In the present study, calcareous and non-calcareous soils did not differ in terms of soil phosphorus requirements.

Correlation between phosphate sorption coefficient and soil properties: In order to elucidate the mechanism of phosphate sorption in the studied soils, Pearson correlation coefficients were calculated between the various parameters of the phosphate sorption isotherms and soil properties which are thought to be responsible for phosphate sorption. However, it was done with a caveat that such correlations might not always indicate causality. No significant relationship was found between the clay content and the phosphate sorption at 100 μg/ml of P application. The findings agree with the results of Ayodole and Agboola(42).

Table 5. Soil P requirements (P_{req}) in mg/kg to reach 0.2 and 1.0 mg/l in equilibrium solution as determined by isotherm equations.

Soil series	Soil P requirement to reach desired concentration (mg/l)			
	Langmuir		Freundlich	
	0.2	1.0	0.2	1.0
Sara	36	50	9	30
Gopalpur	44	58	15	44
Ishurdi	27	32	11	32
Ghatail	43	56	24	63
Sonatala	22	24	28	63
Belabo	19	22	19	43

However, many other scientists reported a positive correlation between clay contents and sorption maximum(6,24). A statistically significant relationship ($R^2 = 0.952$; $p = 0.001$) was found between pH and phosphate sorbed at 100 μg/ml PO_4^{3-}-P application. Significant relationships were also found between pH and Freundlich exponent (1/n) ($R^2 = 0.945$, $p = 0.001$). The positive relationship between pH and Freundlich exponent indicates that proportionally more phosphorus is sorbed as pH increases. No statistically significant relation was found between the organic matter content and the amount of phosphate sorption in the studied soils.

Conclusions

In the present investigation, some calcareous and non-calcareous soils were studied to determine the effects of calcareousness on phosphate sorption indices which are important quantities from agricultural and environmental perspectives. Adsorption experiments' data were modeled into Langmuir and Freundlich isotherms to derive the phosphate sorption indices. Langmuir and Freundlich equations produced different values for soil P requirements (SPR) at 0.2 and 1.0 mg P/l. In general, calcareous soils showed higher maximum phosphorus buffering capacity (MPBC) indicating that they will need less P fertilization compared to non-calcareous soils. For two of the three calcareous soils, the Langmuir equation-derived constant b values were higher than 0.07

l/mg. Therefore, higher bonding energy of P sorption for calcareous soils makes them less vulnerable to loss via surface runoff.

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