Abstract: Three representative soils belonging to Amjhupi, Ishurdi and Sara series from the Ganges meander floodplain soils in Jessore district were collected to observe phosphate sorption characteristics and to evaluate the best fitted adsorption equation for the soils. The highest phosphate sorption was observed in Amjhupi series and the lowest was in Sara soil series. Differences in P sorption were significantly \((p<0.05)\) influenced by clay content, CEC and pH of the soils. Free CaCO\(_3\), EC, OM and available P were found insignificant in affecting P adsorption. The Langmuir equation was best fitted to the equilibrium P sorption data and maximum R-square. Amjhupi soil series would require more P to be supplied to maintain a desired P level in soil solution than others.

Keywords: Phosphate sorption, adsorption equation, calcareous and non-calcareous soil, Langmuir equation

Introduction

Phosphorus deficiency in soils is a widespread problem and is believed to be the second most important soil fertility problem throughout the world next to nitrogen (Warren, 1994). When phosphate fertilizer is applied to soil and dissolved by the soil water, various reactions occur between phosphate and soil constituents which remove P from the solution phase and render it less available. This phenomenon is called P sorption (Matar et al., 1992). The plant utilization efficiency of applied P fertilizers to soils is low (He et al., 1994), because of the fast adsorption and/or precipitation reactions (Reddy et al., 1980).

The sorption and desorption mechanisms of phosphorus are inextricably linked with a number of factors, including the amount and type of clay, the amount and type of hydrous oxides of Al and Fe, inorganic and organic ions, the pH of the system and reaction kinetics (Hedley et al., 1995). There is a linear relationship between P requirement by plants, over a wide range of cultural practices, and P sorption by the soil (Ozane and Shaw, 1967). 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). Fox and Kamprath (1970) estimated the requirements from

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P sorption curves and correlated with P requirements established by field experiments. The relationships were found to be highly correlated.

The Ganges floodplain comprises the vast stretches of the fabulously fertile active floodplain of the Ganges river and the adjoining meander floodplain and its soils are the major agricultural soils of Bangladesh that work as their lifeline. This physiographic unit is bounded by the Ganges tidal floodplain on the south. On its southern end it traps the Gopalganj-Khulna Beels. Ganges meander floodplain were formed by earlier river courses, comprising ridges (old levees), basins and old channels (Khan, 1991). Soils of Jessore belong to High Ganges River Floodplain.

In Bangladesh, farmers generally apply P fertilizers to the crop field without judging the phosphorus need and usually in quantities exceeding crop requirements. They apply fertilizers chiefly by the broadcast method, which enhances fertilizer and soil contact. This method of fertilizer application increases the chance of more phosphorus being sorbed in soils high in clay minerals (especially 1:1 clays) and Fe and Al oxides. In Bangladesh, research on P has given great emphasis to agronomic experiments measuring the response of crops to P. However, there is now an urgent need to use methodological approaches for assessing soil P status that are more relevant to soil-plant studies. Therefore, the research was done to characterize the P sorption characteristics in relation to soil properties of some selected soils of Bangladesh, and to evaluate the best fitted adsorption equation for the soils.
Materials and methods
The study was conducted on agricultural soils of the Jessore Sadar and Bagherpara Upazila under Jessore District (Fig. 1). The physiography was Ganges meander floodplain. The parent materials of studied areas were Ganges alluvium. General informations of sampling sites are given in Table 1.

Three soil series namely Sara (calcareous), Amjhupi (non-calcereous) and Ishurdi (calcereous) were collected from two Upazillas e.g. Bagherpara and Sadar Upazilla of Jessore District, Bangladesh. Soil samples at a depth of 0-15 cm were collected. The composite samples were taken in plastic bags and transported to the laboratory. The collected soil samples were dried, ground and passed through a 2 mm sieve. The sieved soils were then preserved in plastic bag and labeled properly. These were later used for various physical and chemical analyses.

Table 1: General Information of sampling sites

<table>
<thead>
<tr>
<th>Spot No</th>
<th>Address</th>
<th>GPS Reading</th>
<th>Cropping Pattern</th>
<th>Soil Series</th>
</tr>
</thead>
</table>

Analysis of physical and chemical parameters of soil: The particle size analysis of the soils was done by the combination of sieving and hydrometer method as described by Gee and Bauder (1986). Textural classes were determined using Marshall's Triangular Coordinate systems. Soil pH was determined electrochemically with the help of glass electrode pH meter using soil to water ratio of 1:2.5 as suggested by Jackson (1973). The EC of the soil was measured at a soil: water ratio of 1:5 with the help of EC meter and then converted into 1:1 ratio as USDA (2004). The CEC of the soils were determined by extracting the soil with 1N KCl (pH 7.0) followed by the replacing the potassium in the exchange complex by 1 N NH₄OAc. The displaced potassium was determined by a flame analyzer at 589 nm (Jackson, 1967). Soil organic carbon was determined by Walkley and Black’s wet oxidation method as outlined by Jackson (1973). Soil organic matter was calculated by multiplying the percent value of organic carbon by the conversion factor 1.724. Available Phosphorus was extracted from the soil with 0.5 M NaHCO₃ (Olsen et al., 1954) at pH 8.5 and ascorbic acid blue color
Phosphate sorption experiment: Phosphorus sorption was estimated according to the procedure outlined by Nair et al. (1984). Seven 50 mL centrifuge tubes were taken. One gram of air-dried sieved soil was taken into each of them. Solution of seven initial P concentrations, such as 0, 1, 2, 5, 10, 25 and 50 µg P mL⁻¹ (prepared by dissolving KH₂PO₄ in 0.01 M CaCl₂ solution) were added separately to each centrifuge tube using a soil/solution ratio of 1:20 (w/v). The resultant P contents were 0, 20, 40, 100, 200, 500 and 1000 µg P g⁻¹ soil. The centrifuge tubes were then shaken and equilibrated for 16 h. The mixtures were centrifuged and the supernatants were analyzed for phosphate following the ascorbic acid blue color method (Murphy and Riley, 1962) by a T60 Visible Spectrophotometer at wavelength of 882 nm. Sorbed P was inferred from the difference between the concentration of soluble P added in the initial solution and the concentration of P in the solution at equilibrium. Each treatment was replicated thrice. The sorption values of each soil were fitted according to the Freundlich, Langmuir and Temkin equations.

Freundlich (1926) equation: \( X = K_f C^{1/N} \). Logarithmic form of the Freundlich (1926) equation is \( \log X = \log K_f + N \log C \). 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 \( \log K_f \).

Linear form of the Langmuir (1918) equation: \( CX^{-1} = (K_L b_L)^{-1} + C b_L^{-1} \). 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).

Temkin equation: \( X = a \log C + b \). 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 intercept and regression coefficient, respectively. A plot of \( X \) (y-axis variable) against \( \log C \) (x-axis variable) gives a straight line. The \( b \) is considered as the P buffering capacity.

Statistical analysis: Regression curve fitting equations were drawn by the Microsoft Office Excel program. Analysis of variance followed by pair wise comparison of means was performed by Minitab Release 13.20 (Minitab 2000). Microsoft Office Excel 2007 was used to estimate simple correlation coefficients between amount of P sorption and soil properties.

Results and discussion
The soils are representative of the major calcareous and non-calcareous soils of Bangladesh and having a wide range of soil properties.
**Phosphate sorption behavior.** Soils were equilibrated with 0.01 M calcium chloride solution containing graded concentrations (0 to 50 µg mL⁻¹) of phosphorus. The resulting change in the sorbed phosphate was then calculated from analysis of the equilibrium solution. Except 0 µg P mL⁻¹ application, phosphate was sorbed at all other rates in different amounts and proportions by the soils included for the present study (Fig. 2).

![Figure 2: Phosphate sorption capacity of different soils series as affected by varying rates of phosphate application](image)

At 0 µg P mL⁻¹, there was some desorption in all the soil series. Similar result was reported by Vaananen *et al.* (2008), Hossain *et al.* (2012) and Afsar *et al.* (2012). In the study, phosphate sorption increased gradually with increasing phosphate application in all the soil series. Naseri *et al.* (2010), Hossain *et al.* (2012) and Afsar *et al.* (2012) also reported increase in P sorption with increasing phosphate in equilibrium solution. At all phosphate application rates, the Amjhupi and Ishurdi soil series sorbed the highest and the Sara soil series sorbed the lowest amount of phosphate.

**Relationships between soil properties and phosphate adsorption:** Physical and chemical properties of the studied soils are presented in Table 2. According to BARC (2005) the investigated soils were low to medium in fertility. The phosphate sorption capacity of different soils was influenced by the soil properties (Table 3). The highest P sorption capacity of the Amjhupi soil series might be attributed due 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 Toor *et al.* (1997), Daly *et al.* (2001) and Hossain *et al.* (2012). Soil containing high contents of clay adsorbs more P than those with small amounts (Borrero *et al.*, 1988; Pena and Torrent, 1990; Solis and Torrent, 1989; Afif *et al.*, 1993). Organic matter is known to influence phosphorus sorption greatly (Quang *et al.*, 1996). But contradictory findings, negative, positive and no effects, have been reported by Borggaard *et al.* (1990) and Brennan *et al.* (1994). Soils that are highly weathered and the presence of organic matter reduce P-sorption capacity due to direct result of competition for sorption sites between phosphate and organic ligands (Hakim, 2002). In the study, the
amount of P sorption was positively correlated to organic matter but the correlation coefficients were not significant. Ayaz et al. (2010) showed that coefficient for soil OM to predict maximum P adsorption had positive sign and the soils with high OM suggest inhibiting effect on iron oxide crystallization through complexation increasing sorption capacity for phosphate.

Table 2: Physical and chemical properties of Amjhupi, Ishurdi and Sara soil series from Jessore Sadar and Bagherpara Upazilla, Jessore

<table>
<thead>
<tr>
<th>Soil series</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Texture</th>
<th>pH</th>
<th>EC (dS/m)</th>
<th>Available P (ppm)</th>
<th>Organic matter (%)</th>
<th>Free carbonate (%)</th>
<th>CEC (cmol(+)/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amjhupi</td>
<td>11</td>
<td>41</td>
<td>48</td>
<td>Silty clay</td>
<td>7.72</td>
<td>0.35</td>
<td>67.43</td>
<td>2.05</td>
<td>Nil</td>
<td>26.38</td>
</tr>
<tr>
<td>Ishurdi</td>
<td>9</td>
<td>50</td>
<td>41</td>
<td>Silty clay</td>
<td>7.74</td>
<td>0.6</td>
<td>105.02</td>
<td>1.38</td>
<td>1.14</td>
<td>25.63</td>
</tr>
<tr>
<td>Sara</td>
<td>20</td>
<td>57</td>
<td>23</td>
<td>Silt loam</td>
<td>7.87</td>
<td>0.48</td>
<td>78.30</td>
<td>1.12</td>
<td>1.9</td>
<td>18.17</td>
</tr>
<tr>
<td>Mean</td>
<td>13.33</td>
<td>49.33</td>
<td>37.34</td>
<td></td>
<td>7.78</td>
<td>0.89</td>
<td>83.58</td>
<td>1.51</td>
<td>1.01</td>
<td>23.39</td>
</tr>
</tbody>
</table>

Table 3: Correlation coefficients (r) between adsorbed amount of P and other estimated parameters

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>EC</th>
<th>Clay</th>
<th>OM</th>
<th>Available P</th>
<th>CaCO₃</th>
<th>CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>-0.351</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>-0.989</td>
<td>0.205</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>OM</td>
<td>-0.795</td>
<td>-0.289</td>
<td>0.878</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Available P</td>
<td>-0.115</td>
<td>0.971</td>
<td>-0.036</td>
<td>-0.511</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.870</td>
<td>0.157</td>
<td>-0.935</td>
<td>-0.991</td>
<td>0.389</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC</td>
<td>-0.999</td>
<td>0.388</td>
<td>0.982*</td>
<td>0.770</td>
<td>0.156</td>
<td>-0.849</td>
<td></td>
</tr>
<tr>
<td>Adsorbed P</td>
<td>-0.998</td>
<td>0.404</td>
<td>0.978*</td>
<td>0.759</td>
<td>0.173</td>
<td>-0.840</td>
<td>1.000*</td>
</tr>
</tbody>
</table>

Significant at <0.01 (*);

Adsorption and precipitation are major mechanisms of P retention in calcareous soils depressing its availability after fertilizer application. In an experiment, Afif et al. (1993) observed that at high application rates, available P is negatively correlated to the amount of lime in soil. Other investigators showed that P retention increases with the ratio of Fe oxides to CaCO₃ (Careira and Lajtha, 1997). However, correlation between P application and free CaCO₃ was not significant in the study whereas CEC significantly correlated with the adsorbed P. A negative and significant relationship exists between P sorption maximum

32
and soil pH. The negative relationship between P sorption and pH is corroborated with the findings of Adepoju (1993), Ioannou et al. (1994) and Zhang et al. (1996).

**Freundlich adsorption isotherm.** Freundlich adsorption isotherm fitted better than other isotherms in the studied soils. The highest $r^2$ value 0.954 was observed in Amjhupi soil and the lowest value 0.836 in Sara soil (Fig. 3, 4 and 5).

![Fig. 3: Freundlich adsorption isotherm of phosphorus for Amjhupi soil series](image1)

![Fig. 4: Freundlich adsorption isotherm of phosphorus for Ishurdi soil series](image2)

![Fig. 5: Freundlich adsorption isotherm of phosphorus for Sara soil series](image3)
The slopes of the sorption curves show that the amount of P sorbed by the soils differed among various soil series. The highest slope of 0.630 was observed in Ishurdi Soil and the lowest of 0.330 in Amjhupi soil series. The lower $r^2$ value of the Freundlich equation than that of the Langmuir equation in soil series (Amjhupi, Ishurdi, Sara), explains that the sorption affinity of these soils did not decrease logarithmically with an increase in surface saturation (Mead, 1981).

**Langmuir adsorption isotherm**

The Langmuir adsorption isotherm explains the adsorption maxima and energy of adsorption. Langmuir adsorption isotherms for Amjhupi, Ishurdi and Sara soil series are presented in Fig. 6, 7 and 8. The Langmuir equation was found to be a favorable method to explain the P adsorption in most soils. The highest value (0.970) of $r^2$ was observed in Amjhupi soil and the lowest (0.824) in Sara soil series. The good fit of Langmuir adsorption isotherm explained that the sorption affinity of soils remains constant with increasing surface saturation (Mead, 1981).

![Langmuir adsorption isotherm of phosphorus for Amjhupi soil series](image)

![Langmuir adsorption isotherm of phosphorus for Ishurdi soil series](image)
Temkin adsorption isotherm: The $r^2$ value of the Temkin equation of Amjhupi, Ishurdi, and Sara soil series were 0.983, 0.966 and 0.709, respectively where the highest value of 0.983 was observed in Amjhupi soil and the lowest value of 0.709 in Sara soil (Fig. 9, 10 and 11). The soil series showed the poorest fit to the Temkin adsorption isotherm, meaning that these soils adsorption capacities did not decrease linearly with an increase in surface saturation.

Fig. 8: Langmuir adsorption isotherm of phosphorus for Sara soil series

Fig. 9: Temkin adsorption isotherm of phosphorus for Amjhupi soil series

Fig. 10: Temkin adsorption isotherm of phosphorus for Ishurdi soil series
Fig. 11: Temkin adsorption isotherm of phosphorus for Sara soil series

The P sorption data of the three soil series were plotted according to the conventional Langmuir, Freundlich and Temkin equations. Among the sorption equations, Langmuir equation was best fitted to the sorption data. Similar results are reported by Gichangi et al. (2008) and Moazed et al. (2010). Based on $r^2$ values, the Freundlich equation was better in predicting the P sorption capacity of calcareous soils than the other two equations (Dubus and Becquer, 2001; Zhou and Li, 2001). The good fit of the Langmuir adsorption equation indicates that the P sorption affinity of soils remained constant with increasing surface saturation (Mead 1981).

The Amjhupi 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 Amjhupi soil series will retain P better than other studied soils and possibly be the better sink at similar P adding rates. The Sara soil series had the lowest $K_L$ values. The soils that show lower P buffering capacities may need more frequent application of P fertilizer than the soils with relatively high buffering capacities.

Conclusion
Phosphate was sorbed by the three soil series in the following order: Amjhupi > Ishurdi > Sara soil series. So, to maintain a desired P concentration in the soil solution, the Amjhupi soil will be required to supply more P than others. There is significant correlation between maximal value of surface-adsorbed phosphorus and clay content of soil suggesting that clay content affects the ability of a soil to retain P applied to soil. The Freundlich, Langmuir and Temkin isotherms described the P adsorption data. Among the three adsorption equations, Langmuir equation was best fitted to the equilibrium P sorption data. Langmuir equation is able to explain the P behavior in the soils with respect to buffering capacity and P supplying capacity.

References


36


