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Quantity -intensity relationship and fixation of phosphorus in soils from shrimp farming areas of coastal India

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ABSTRACT

In the coastal environment, phosphorus release from bottom sediment plays a great role in its cycle. The availability of phosphorus in soil is controlled by the fixation mechanism. Laboratory incubation experiments were conducted with shrimp pond soils collected from Digha and Canning (West Bengal), Nellore (Andhra Pradesh), Muttukadu and Mahabalipuram (Tamil Nadu) and Mangalore (Karnataka) to determine the phosphorus fixation and quantity/ intensity relationship. The clay content was the major factor responsible for phosphorus fixation and it was high (62.1 %) in soil from Canning with 45 % clay and 8.05 pH followed by the soils from Mangalore (47.2%) having 39 % clay and 4.9 pH and silt loam soil from Nellore (39.9 %). Phosphorus fixation was positively correlated with clay ($r = 0.96$), calcium carbonate ($r = 0.68$) and silt ($r = 0.24$) and negatively correlated with phosphate potential ($r = -0.399$) and available phosphorus content ($r = -0.313$) in the soil. The average phosphate potential and equilibrium phosphate potential did not differ in soils except for acid soil, reflecting more or less similar availability of phosphorus, given the quantity of phosphorus in soils is nearly equal.

Introduction

Phosphorus often is the limiting nutrient for phytoplankton productivity in aquaculture ponds (Boyd, 1982). Rooted aquatic vegetation absorbs phosphorus (P) from mud and their growth increases in relation to the P content of mud (Golterman *et al.*, 1969; Briston and White Combe, 1971; Chiou and Boyd, 1974). The concentration of P released by pond soils is not sufficient to maintain adequate levels of phytoplankton needed for high levels of fish production (Hepher, 1966). The experience with pond fertilization suggests that addition of P fertilizer will increase fish production in most ponds (Hickling, 1962). Pond bottom soils strongly adsorb phosphorus, and because of its insolubility, soil bound phosphorus has low availability to phytoplankton (Masuda and Boyd, 1994).

The availability of phosphorus is controlled by the fixation mechanism. Prediction of response to P application is generally based on available P status as well as on the rate and magnitude at which the added P is converted into insoluble forms in soil (Tekchand and Tomar, 1993). The rate of P fixation in soil is dependent upon the properties of soil in different agro-climatic conditions and source of phosphorus (Mandal, 1975). Phosphate adsorption by soils is important because adsorbed P equilibrates with soil solution P, which in turn is immediate source of P (Kumar and Singh, 1998). While P fixation continues to receive much attention it is more important to know the effect of shrimp pond soil characteristics on P fixation.

Quantity/Intensity (Q/I) is a fundamental relationship that determines ion uptake in relation to status of ion present in the soil solution. Schofield (1955) proposed that nutrient concentration in the soil solution is characterised by an intensity factor (I) and the fraction adsorbed to the solid phase or bound to labile organic compounds by a quantity factor (Q). The Q level needed to provide a given intensity or soil solution P level will vary from soil to soil. Not only the concentration of nutrients in the soil solution but also the buffer power of soil is extremely important. The Q/I relationship of P and potential buffering capacity in shrimp pond soils are important in the determination of fertiliser P requirement.

In the shrimp pond soils, little information is available on the dynamics of phosphorus such as P fixation and Q/I relationship. Therefore, the present paper deals with studies on P fixation and Q/I relationship as affected by the physico-chemical characteristics of soils from shrimp ponds of coastal areas.

Materials and methods

Bulk surface soil samples (0-15 cm depth layer) were collected in triplicate from shrimp ponds at Digha (West Bengal) - soil 1, Nellore (Andhra Pradesh) - soil 2, Canning (West Bengal) - soil 3, Mangalore (Karnataka) - soil 4, Mahabalipuram (Tamil Nadu) - soil 5 and Muttukadu (Chengulpet District, Tamil Nadu) - soil 6 in zig - zag manner. The soil samples were air-dried, powdered and ground to pass through 2 mm sieve and analysed for physico - chemical properties such as pH, electrical conductivity, organic carbon, available phosphorus, soil texture and calcium carbonate (Piper, 1966; Jackson, 1967).

Phosphorus fixation study

The capacity of bottom soil to adsorb and fix P is the major factor affecting the availability of applied P in aquaculture ponds. Hence the methods that measure the capacity of bottom soil to adsorb P may be more applicable in aquaculture than techniques that evaluate the solubility of pond P. An incubation experiment was conducted in triplicate in the laboratory to determine the P fixation in soils. Phosphorus fixation at different levels of added P was determined by the method of Ghosh *et al.* (1983). Two grams soil was weighed in separate 100 ml conical flasks. Soil was brought to one corner of the flask and 2 ml each of 17.5, 35, 70, 140, 280, 420, 560 and 700 ppm P solutions were added separately to each flask in the form of KH_2PO_4. The flasks were plugged with cotton wool and incubated for 96 hours at room temperature. A control was also taken simultaneously. After 96 hours, 1 g charcoal and 40 ml of 0.5 *M* $NaHCO_3$ solution were added and shaken for 1 hour. In acid soil Bray and Kurtz reagent (0.03 *N* NH_4 F in 0.025 *N* HCl) was added for the extraction of P. After filtration through Whatman No. 40 filter paper, 5 ml of filtrate was taken in 25 ml volumetric flask and phosphorus content was measured. The P concentration in 0 ppm P addition treatment was subtracted from those of samples of other P addition rate treatments to correct for P originally present. The amounts of added P recovered from the soil samples were then calculated. Phosphorus fixing capacity, denoted by percent phosphorus fixation was calculated by statistical analysis as given below.

$$\text{P value of available fraction} = \frac{\Sigma XY - N\bar{X}\bar{Y}}{\Sigma X^2 - N(\bar{X})^2}$$

Where, X = P added (μg/g); Y = P extracted ((μg/g); N = No. of observations.

Phosphorus Quantity -Intensity relationship study

Schofield (1955) suggested the use of phosphate potential as intensity factor in solution, which can be present in soil as mono calcium phosphate (MCP). The negative logarithm of activity product of MCP was referred as phosphate potential (PP = ½ pCa + pH_2PO_4). Beckett and White (1964) proposed the method for the determination of Q/I relationship. Five grams of each soil was taken in a series of conical flasks of 100 ml capacity. Fifty ml of solution containing varying amount of P concentration (2.5, 5, 10, 20, 40, 60, 80 and 100 ppm in 0.01 *M* $CaCl_2$ medium) were added separately to these flasks. A blank was run without soil. The flasks were then shaken for an hour on a horizontal platform shaker. Half of the content was filtered and the P in filtrate was measured by ascorbic acid blue colour method. The pH of soil suspension was measured in the remaining half of the content. The calculations for phosphate potential are shown below.

Phosphate Potential = 1/2 pCa + pH_2PO_4

$$1/2\ pCa = -1/2\ (\log C_{Ca} + \log f_{Ca})$$

Where, $C_{Ca} = 0.01$ M

$$\log f_{Ca} = \frac{0.5\, z^2 \sqrt{\mu}}{1 + 1.5\sqrt{\mu}}$$

Where,

z = Valency of ion

μ = ionic strength

$\mu = 1/2\ \Sigma\ Ci\ zi^2$

Where,

C= Concentration of ion

$$pH_2PO_4 = pC_{H_2PO_4} + pf_{H_2PO_4}$$

$$pH_2PO_4 = -(\log C_{H_2PO_4} + \log f_{H_2PO_4})$$

$$\log f_{H_2PO_4} = \frac{0.5\, z^2 \sqrt{\mu}}{1 + 1.5\sqrt{\mu}}$$

$$pC_{H_2PO_4} = pP + p\ \frac{H^+}{K^{11} + H^+}$$

Where,

P = total concentration of phosphorus in the solution.

$p\ \frac{H^+}{K^{11} + H^+}$ is a correction factor derived by Asyling which is ratio of H_2PO_4 / P to pH

K^{11} = Second ionisation constant of H_2PO_4 i.e., $10^{-7.2}$

pP = - log (P concentration)

A graph was drawn by plotting phosphate potential along abscissa and P adsorbed (+ΔP) or desorbed (-ΔP) along ordinate. This gives the Q/I curve. The equilibrium phosphate potential was calculated from the graph, where the curve meets the x-axis. Statistical correlation and regression analysis of the data was carried out as per the methods suggested by Gomez and Gomez (1984).

Results and discussion

Soil characteristics

The average values of physico - chemical characteristics of experimental soils are presented in Table 1. Mechanical analysis revealed a wide range in the soil texture. The sand, silt and clay content in experimental soils ranged from 35.75 to 92.5 %, 0.5 to 40 % and 6.75 to 45 % respectively. The textural class of soils from 1 to 6 was sandy, silt loam, clay, silty clay loam, sandy loam and loamy sand respectively. Soil pH values ranged from 4.9 to 8.35 i.e., from acidic to alkaline. The Electrical Conductivity (EC) in different soils ranged from 0.31 dS/m (soil 4 from Mangalore) to 4.96 dS/m (soil 3 from Canning). Organic carbon content in the soils ranged from 0.14 to 0.34 %. Soil 2 (Nellore) and soil 1 (Digha) registered maximum organic carbon content of 0.33 and 0.34 per cent, respectively. A maximum calcium carbonate content of 1.88 % was registered in silt loam soil from Nellore and a minimum of 0.13 % in sandy soil from Digha.

The available phosphorus content in soils ranged from 0.32 to 2.29 C mol (p^+) kg^{-1}. The lowest amount of available phosphorus was observed in soil 4 (Mangalore soil with pH value of 4.9). Similar results of low phosphorus content in acid soil were also reported by Patiram *et al.* (1990) and Mongda *et al.* (1998). The low availability of phosphorus in acid soils may be mainly due to sorption of phosphorus on the active surfaces of aluminium and iron oxides and on clay minerals.

Correlation matrix of soil properties

The correlation matrix of soil properties given in Table 2 shows that several physical and chemical variables were correlated with each other. However, many of these correlations were not significant. Available phosphorus content of soil was negatively correlated with clay and positively correlated with pH. Similar type of correlations was observed by Das *et al.* (1993) and Tekchand and Tomar (1993). Available phosphorus was

TABLE 1: *Physico-chemical characteristics of experimental soils*

Soil property		Soil 1	2	3	4	5	6
Soil Texture	Sand (%)	92.5	40	42	35.75	78	74.25
	Silt (%)	0.5	40	13	25.25	7	19
	Clay (%)	7	20	45	39	15	6.75
Textural class		Sandy	Silt loam	Clay	Silty clay loam	Sandy loam	Loamy sand
pH (1:2.5)		7.92	8.10	8.05	4.9	7.37	8.35
Electrical conductivity (dS/m)		0.69	3.60	4.96	0.31	0.65	1.25
Organic carbon (%)		0.34	0.33	0.14	0.28	0.14	0.18
$CaCO_3$ (%)		0.13	1.88	1.78	0.63	0.87	0.63
Available Phosphorus (C mol (p^+) kg^{-1})		2.29	1.58	1.34	0.32	0.98	1.09

TABLE 2: *Correlation matrix of soil characteristics*

	Sand	Silt	Clay	pH	OC	EC	$CaCO_3$	AP
Sand	1.000							
Silt	- 0.755* (0.045)	1.000						
Clay	- 0.825* (0.043)	0.252 (0.630)	1.000					
PH	0.417 (0.411)	- 0.150 (0.776)	- 0.486 (0.329)	1.000				
OC	- 0.039 (0.951)	0.318 (0.517)	- 0.215 (0.672)	- 0.169 (0.746)	1.000			
EC	- 0.529* (0.049)	0.334 (0.517)	0.493 (0.320)	0.482 (0.333)	- 0.186 (0.711)	1.000		
$CaCO_3$	- 0.697* (0.048)	0.563* (0.046)	0.541* (0.049)	0.282 (0.593)	-0.222 (0.699)	0.905* (0.017)	1.000	
AP	0.518* (0.05)	-0 .331 (0.522)	- 0.479 (0.336)	0.709* (0.05)	0.408 (0.422)	0.239 (0.649)	-0.042 (0.936)	1.000

Note : OC - Organic carbon EC - Electrical conductivity AP - Available phosphorus
* - Significant ($P \leq 0.05$). Values in parentheses indicate level of significance

positively correlated with organic carbon content in the soils. Organic matter might have increased the solubility of phosphate in soils. The organic anions compete with phosphate ions for the binding sites on the soil particles or these anions may chelate with aluminium, iron and calcium and thus decrease phosphate-precipitating power of these cations. The positive correlation of available phosphorus content with organic carbon was also confirmed by Gupta *et al.* (1999). A negative correlation between available P and $CaCO_3$ was registered. Calcium carbonate in considerable amounts will decrease the phosphorus availability by forming apatites of low solubility.

Phosphorus fixation

The amounts of P that were extracted in different soils which had been treated with different concentrations of P after 96 hours of incubation were plotted against respective P addition (Fig. 1). Even at the highest P addition rate (700 ppm), little of the added P was extracted from the soils reflecting the high P fixation values. The available phosphorus fraction value and percent phosphorus fixation for different soils are given in Table 3. A maximum of 0.715 available phosphorus fraction was recovered in sandy soil (soil 1) and a minimum of 0.378 was registered in clay soil (soil 3). A maximum phosphorus fixation of 62.14

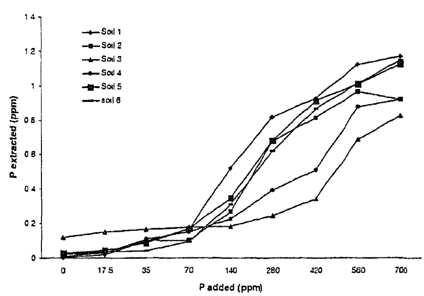

Fig. 1. Amount of phosphorus recovered after 96 hours in different soils

TABLE 3: *Phosphorus fixation capacity in different soils*

Soil	P available fraction	% P available	% P fixed
Soil 1	0.715	71.5	28.5
Soil 2	0.6002	60.02	39.98
Soil 3	0.3786	37.86	62.14
Soil 4	0.5276	52.76	47.24
Soil 5	0.6743	67.43	32.57
Soil 6	0.6967	69.67	30.33

% and a minimum of 28.5% were observed in clay and sandy soils respectively, whereas the acidic soil from Mangalore (soil 4) registered 47.24% phosphorus fixation capacity. In acid soil, phosphate fixation was more. It may be due to the presence of iron and aluminum at low pH values, which resulted in the precipitation of insoluble iron and aluminum phosphates.

In the present study, the major factor responsible for phosphorus fixation is clay content in the soil. Kadstha *et al.* (1997) reported that soil components such as clay, extractable amorphous and crystalline Al, amorphous and crystalline Fe have had a significant positive relationship with the P fixing capacity. The removal of clay attributed to maximum decrease in the phosphorus fixation capacity followed by the removal of organic matter. The Fe and Al hydrous oxide clays react rapidly forming a series of difficultly soluble hydroxy phosphates.

$$\begin{array}{ccc} OH & & OH \\ | & & | \\ Al\text{-}OH + H_2PO_4 & \rightarrow & Al\text{-}H_2PO_4 \\ | & & | \\ OH & & OH \end{array} \quad \text{(Insoluble)}$$

The amount of P fixed by this reaction usually exceeds that fixed by phosphate retention (reaction between phosphate and Fe and Al hydrous oxides or between phosphates and silicate minerals). Such a reaction is not limited to Al and Fe hydrous oxide clays, but non-hydrous oxide clays and amorphous clays are also known to have considerable phosphate fixing capacities. In contrast to phosphate retention that occurs mainly in acid soil conditions phosphate fixation by hydrous oxide clays occurs over a relatively wider pH range. Clays with low $SiO_2:R_2O_3$ (sesqui oxide) ratios have a higher phosphate fixing capacity than clays with high $SiO_2:R_2O_3$ ratios.

Fixation of phosphate is not limited to acid conditions only, but also occurs readily in alkaline soil reactions. Many alkaline soils contain high amounts of soluble and exchangeable Ca^{2+} and frequently $CaCO_3$. Phosphate is reported to react with both the ionic and the carbonate form of Ca.

$$3\,Ca^{2+} + 2\,PO_4^{3-} \rightarrow \underset{\text{Insoluble}}{Ca_3(PO_4)_2} \downarrow$$

$$3\,CaCO_3 + 2\,PO_4^{3-} \rightarrow \underset{\text{Insoluble.}}{Ca_3(PO_4)_2} + 3\,CO_2 \uparrow$$

Such type of fixation is a serious problem in soils of the arid region. However, it can also become significant in the humid region when the shrimp pond soils receive high application of lime.

Phosphorus fixation vs. soil characteristics

The correlation coefficient values along with level of significance and simple regression equations of phosphorus fixation as dependent variable are given in Table 4. Organic carbon, available phosphorus, sand content and soil pH were negatively correlated, whereas clay (r = 0.960), calcium carbonate (r = 0.677) and silt were positively correlated with phosphorus fixation in soil. These results are corroborated with the findings of Dongale (1993), Ghosh and Sarkar (1997), Tomar and Tekchand (1992) and Das *et al.* (1993).

Q/I relationship

In the present study whether the soils are acidic, alkaline or neutral, P concentrations in the soil solution were very low. The phosphate potential calculation as an example along with Asyling's factor is shown for sandy soil in Table 5. The quantity of P adsorbed or desorbed ($\pm \Delta P$) was plotted against phosphate potential in different soils is represented in Fig. 2 and 3. The equilibrium phosphate potential (EPP) values calculated from the graph and average phosphate potential (APP) values for different soils are given in Table 6. Except for acid soil the average phosphate potential and EPP did not differ much among the other soils. Acid soil with more clay content had lowest average phosphate potential value of 4.51 and EPP of 5.46 whereas in other experimental soils APP and EPP ranged from 5.11 to 5.39 and 5.96 to 6.26 respectively.

The ionic strength of supporting electrolyte is one of the important experimental variables that affect the phosphate sorption by soils. In the present study 10^{-2} $CaCl_2$ solution has been used on the premise that it provides a medium of constant ionic strength similar to the composition of ambient soil solution under natural conditions

TABLE 4: *Phosphorus fixing capacity as affected by different soil characteristics*

Soil property	Correlation coefficient	Regression equation
Sand	-0.7902 * (0.042)	Y = -0.422 x + 65.59
Silt	0.2391 (0.649)	Y = 0.218 x + 36.31
Clay	0.9602 ** (0.002)	Y = 0.756 x + 23.39
pH	-0.2260 (0.667)	Y = -2.249 x + 56.78
Organic carbon	-0.2845 (0.572)	Y = -38.885 x + 49.23
Electrical conductivity	0.6993* (0.048)	Y = 4.703 x + 31.14
Calcium carbonate	0.6774* (0.046)	Y = 12.073 x + 27.99
Available phosphorus	-0.3129 (0.547)	Y = - 6.114 x + 47.86
Phosphate potential 129.06	-0.3998 (0.347)	Y = -17.508 x +

Note: Values in parentheses indicate level of significance.

* - Significant ($P \leq 0.05$)

** - Significant ($P \leq 0.01$)

TABLE 5: *Model calculation of phosphate potential in sandy soil*

Concentration of P added (ppm)	Concentration of P added (moles/l)x10^{-4}	Concentration of extracted P (ppm)	Concentration of P extracted (moles/l)x10^{-4}	Added P-Extracted P (moles/l)x10^{-4}	pH	1/2 p^{Ca}	pf_{H2PO4}	Asyling's factor	pP	Phosphate potential
0.0	0.081	2.760	0.089	-0.008	7.850	1.138	0.069	0.738	4.147	7.777
2.5	0.161	4.440	0.143	0.018	7.680	1.138	0.069	0.604	4.333	6.143
5.0	0.323	7.020	0.226	0.096	7.540	1.138	0.069	0.504	4.912	6.621
10.0	0.645	13.710	0.442	0.203	7.450	1.138	0.069	0.444	3.308	4.958
20.0	1.290	21.480	0.693	0.597	7.400	1.138	0.069	0.412	3.841	5.460
40.0	1.935	27.250	0.879	1.056	7.350	1.138	0.069	0.383	3.128	4.716
60.0	2.581	28.530	0.920	1.660	7.300	1.138	0.069	0.354	2.915	4.475
80.0	3.226	30.350	0.979	2.247	7.280	1.138	0.069	0.343	2.766	4.315
100.0	3.226	30.350	0.979	2.247	7.200	1.138	0.069	0.301	2.636	4.143

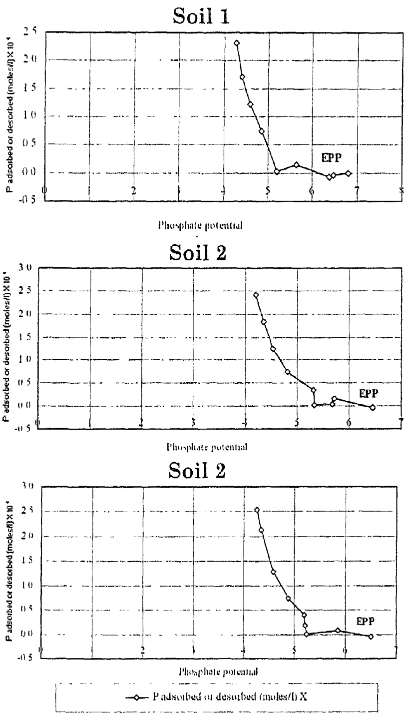

Fig. 2. Quantity- intensity curve for phosphorus in shrimp pond soils from Digha, Nellore and Canning.

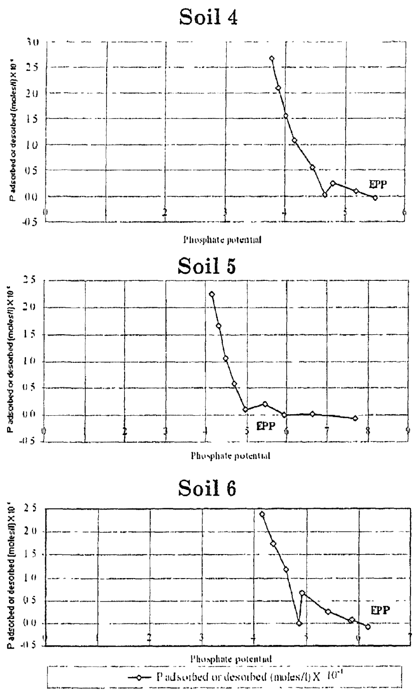

Fig.3. Quantity- intensity curve for phosphorus in shrimp pond soils from Mangalore, Mahabalipuram and Muttukadu.

TABLE 6: *Phosphate potential as affected by different soil properties*

Soil property	Correlation coefficient	Regression equation
Sand	0.6139 (0.107)	Y = -0.008 x + 4.63
Silt	-0.3798 (0.322)	Y = -0.008 x + 5.22
Clay	-0.5788 (0.172)	Y = -0.010 x + 5.31
pH	0.8496 * (0.042)	Y = 0.193 x + 3.64
Organic carbon	-0.2759 (0.819)	Y = -0.861 x + 5.28
Electrical conductivity	0.2123 (0.813)	Y = 0.033 x + 5.02
Calcium carbonate	0.1336 (0.974)	Y = 0.054 x + 5.03
Available phosphorus	0.6995* (0.047)	Y = 0.283 x + 4.72
Phosphorus fixation capacity	-0.3998 (0.347)	Y = -0.009 x + 5.45

Note: Values in parentheses indicate level of significance
* - Significant ($P \leq 0.05$)

TABLE 7: *Average phosphate potential and equilibrium phosphate potential in different soils*

Soil	Average phosphate potential	Equilibrium phosphate potential
Soil 1	5.392	6.26
Soil 2	5.157	6.24
Soil 3	5.113	6.21
Soil 4	4.509	5.46
Soil 5	5.357	5.96
Soil 6	5.132	6.00

without any inducing changes on the clay surface.

Phosphate potential vs. soil characteristics

The correlation coefficient values along with level of significance and regression equations of phosphate potential as dependent variable are given in Table 7. The clay, silt, organic carbon content and phosphorus fixation capacity of soils are negatively correlated with phosphate potential. There exists a significant positive correlation between phosphate potential and pH ($r = 0.849$) and available phosphorus content ($r = 0.699$) in the soil.

In the present study phosphorus fixation was maximum in soil from Canning with high clay content (45 %) followed by soil from Mangalore with clay content of 39 per cent. Once the maximum P adsorption capacity of pond sediment is known, the amount of P required to saturate the mud can be calculated and fertilization rate determined. More phosphorus is needed in soils with high clay content in order to get the same response, when all the other factors are equal.

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