

## Phosphorus Sorption and Release Kinetics in Soils Receiving *In-Situ* Legume-Pulse Crop Residue Conjointly with Fertilizer-P in Gram-Mungbean-Maize Cropping Sequence

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### Abstract

Phosphorus (P) sorption and its release kinetics were studied from irrigated sub-tropical soil under gram-mungbean-maize cropping sequence with *in-situ* legume-pulse residue incorporation and fertilizer-P application for three consecutive years. The equilibrium solution P concentration continues to increase with increasing amount of added P, the magnitude of which was more for soils with *in-situ* legume-pulse residue incorporation. Significant correlation coefficient with  $r^2 \geq + 0.995^*$  revealed that Freundlich equation explains the adsorption process in a better way than the Langmuir adsorption equation. Langmuir's bonding energy BE and Freundlich rate constant b were remarkably lower for plots receiving fertilizer-P for all the three crops, the extent of which further increased in soils receiving *in-situ* legume-pulse residue incorporation conjointly with fertilizer-P. On the contrary, Elovich  $\beta$  and Parabolic diffusion constant C exhibited remarkable increase with the application of P through either source (fertilizer-P / crop residue), emphasizing enhanced P availability in soil. The cumulative P release increase gradually upto 48 h of extraction, and thereafter gradually leveled off as the shaking time progressed. Highest coefficient of determination ( $R^2 \geq 0.972$ ) revealed that P release kinetics was best explained by Elovich equation.

**Key words :** Crop residue, P-adsorption, P release kinetics, Legume based cropping system.

Phosphorus (P) cycling in the soil-plant ecosystem is an essential component of sustainably productive agricultural system. Recycling of crop residue has the advantage of converting the surplus farm waste into useful product for meeting nutrient requirement of crops, besides sustaining soil organic carbon (SOC) content, improving soil physical properties and enhancing biological activities (1–3). Increased P availability in soils under laboratory and field conditions with the application of cereal crop residue (4–6) and oilseed crops (7) have been observed in several studies. But the studies on field application of residue of legume and pulse crops on P transformation are still lacking, although crop residue from these crops contains higher P content than other crops (8). Legume crops with their ability of biological  $N_2$  fixation produce high quality residue; such residue can decompose faster and enhance soil fertility through nutrient release. However, P mineralization from crop residue depends upon several factors viz. residue decomposition rate, P content, microbial immobilization and residue quality (C/P ratio)

(7, 9). In soils, further the P dynamics are controlled by combination of physical, chemical and biological processes including dissolution-precipitation, sorption-desorption, and mineralization-immobilization processes (10). These processes thus operate simultaneously to govern the dynamic equilibrium that exists between soil solid and solution P phase. Several researchers have observed the positive influence of other organics viz. FYM (11), poultry manure (12), pressmud (13), green manures (14) on P availability through reduced P-sorption, mineral solubility, conversion of non-labile to labile P. Under field conditions, Singh and Singh (15) reported spectacular increase in available-P content through reduced P-sorption in soil with the application of coca-cola bottling plant sludge in rice-wheat cropping sequence. Keeping in view the benefits of organics including crop residue from cereal crops, the information is generated on the effect of *in-situ* legume-pulse residue incorporation under field conditions in legume based (gram-mungbean-maize) cropping sequence on P transformations after three years of application.

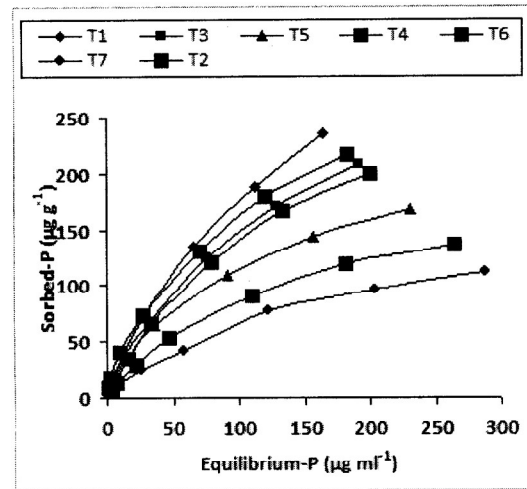
**Table 1.** Some selected properties of experimental soil (0–15 cm) at the start of the field experiment physico-chemical.

Property	Value	Property	Value
pH (1:2, soil : water)	8.10	DTPA-Fe (mg/kg)	6.42
EC (1:2, soil : water), dS/m	0.25	DTPA-Mn (mg/kg)	4.56
SOC (g/kg)	3.95	<b>Particle size distribution</b>	
NaHCO <sub>3</sub> -P (kg/ha)	18.4	Sand (%)	78
KMnO <sub>4</sub> -N (kg/ha)	98.6	Silt (%)	12
CH <sub>3</sub> COONH <sub>4</sub> -K (kg/ha)	165.8	Clay (%)	10
DTPA-Zn (mg/kg)	0.63	Texture	Sandy Loam
DTPA-Cu (mg/kg)	0.34	Classification	Typic Ustochrept

## Methods

### Cropping Sequence and Treatments

The field experiment was conducted at Punjab Agricultural University, Ludhiana research farm for three consecutive years (2003-04 to 2006-07) in a semi-arid, sub-tropical irrigated loamy sand (Typic Ustochrepts) soil. The important physical properties of the soil before the start of experiment were however, favorable for crop production (Table 1). Gram-summer mungbean-maize were grown for three years in a sequence with *in-situ* incorporation of gram residue (GR) and summer mungbean residue (MR) at 2.5 t/ha per year. Fertilizer-P treatments for gram consisted of four rates (0, 8.7, 17.5 and 26.2 kg P/ha), for summer mungbean, two treatments (0 and 17.5 kg P/ha plus GR) and for maize three treatments (0, 13.1, and 26.2 kg P/ha plus MR) applied through single super phosphate each year in three replications to create direct,

**Figure 1.** Effect of *in-situ* legume-pulse residue incorporation on P-sorption characteristics of soil.

residual and cumulative P plots for succeeding crop. However, the P-sorption and release kinetics study was conducted for some selected treatments (Table 2).

### Phosphorus Sorption

Phosphorus sorption isotherms were obtained by equilibrating 3.0 g of soil sample with 15.0 ml of 0.01 M CaCl<sub>2</sub> (1:5) containing varying amounts of P through KH<sub>2</sub>PO<sub>4</sub> in 50 ml centrifuge tubes to make final concentrations of the solution as 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 µg P/ml. Two drops of toluene were added to each centrifuge tube to minimize microbial activity. The centrifuge tubes were shaken for

**Table 2.** Effect of differential rate of P-fertilization and *in-situ* legume-pulse residues incorporation on adsorption constants. (1) GR and MR = Gram and mungbean residues, respectively applied at 2.5 t/ha, (2) AM and BE = Adsorption maxima and bonding energy, respectively, (3) a and b represent extent and rate of adsorption, respectively.

Treatment details	Langmuir's constants <sup>2</sup>			Freundlich's constants <sup>3</sup>		
	AM × 10 <sup>3</sup> (µg/g)	BE (ml/g)	R <sup>2</sup>	a (µg/g)	b (ml/g)	R <sup>2</sup>
T <sub>1</sub> (P <sub>0</sub> P <sub>0</sub> P <sub>0</sub> )	2.89	3.83	0.965	5.64	5.55	0.997
T <sub>2</sub> (P <sub>17.5</sub> P <sub>17.5</sub> P <sub>26.2</sub> )	5.48	1.81	0.976	4.23	3.38	0.995
T <sub>3</sub> (P <sub>17.5</sub> P <sub>17.5</sub> +GR <sup>26.2</sup> +MR)	6.83	1.35	0.952	4.05	2.78	0.996
T <sub>4</sub> (P <sub>17.5</sub> P <sub>17.5</sub> P <sub>0</sub> )	3.52	2.96	0.966	4.38	4.66	0.995
T <sub>5</sub> (P <sub>17.5</sub> P <sub>17.5</sub> +GR <sup>0</sup> +MR)	4.92	2.20	0.957	4.28	3.53	0.997
T <sub>6</sub> (P <sub>17.5</sub> P <sub>0</sub> P <sub>26.2</sub> )	3.74	3.73	0.955	4.76	5.28	0.998
T <sub>7</sub> (P <sub>17.5</sub> P <sub>0</sub> +GR <sup>26.2</sup> +MR)	4.90	3.21	0.974	4.38	5.09	0.995

**Table 3.** Effect of conjoint and separate crop residues and differential rate fertilizers application on kinetic of P release. (1) GR and MR = Gram and mungbean residues, respectively applied @ 2.5 t/ha.

Treatments <sup>1</sup>	Elovich constants			Parabolic Diffusion constants		
	$\alpha$ ( $\mu\text{g/g/h}$ )	$\beta$ ( $\mu\text{g/g}$ )	$R^2$	R ( $\mu\text{g/h/h}^{-1/2}$ )	C ( $\mu\text{g/g}$ )	$R^2$
T <sub>1</sub>	0.81	8.6	0.992	0.47	8.5	0.884
T <sub>2</sub>	0.79	17.4	0.984	0.46	12.9	0.833
T <sub>3</sub>	0.80	18.4	0.994	0.46	17.3	0.854
T <sub>4</sub>	0.78	15.1	0.993	0.47	15.9	0.923
T <sub>5</sub>	0.90	15.9	0.994	0.53	13.9	0.874
T <sub>6</sub>	0.79	13.0	0.983	0.47	14.7	0.852
T <sub>7</sub>	0.81	14.9	0.992	0.47	13.3	0.864

24 h on an end-to-end mechanical shaker at 150 oscillations per minute. The tubes were then centrifuged at 3000 rpm for 10 minutes and supernatant was decanted. The concentration of P in the equilibrium solution was determined colorimetrically using ascorbic acid method (16). Phosphorus sorption parameters were calculated using the Langmuir and Freundlich equations.

Langmuir equation :

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$$

Where,  $x/m$  is the amount of P adsorbed ( $\mu\text{g/g}$  soil),  $c$  is concentration of P in the equilibrium solution ( $\mu\text{g/ml}$ ) after centrifugation;  $b$  ( $\mu\text{g/g}$  soil) is the Langmuir adsorption maxima,  $k$  Langmuir bonding energy ( $\text{ml/g}$ ), and are denoted as AM and BE, respectively. The constants  $k$  and  $b$  were obtained from intercept and slope, respectively.

Freundlich equation :  $x/m = ac^{1/n}$

Where,  $x/m$  is the amount of P adsorbed ( $\mu\text{g/g}$  soil);  $c$  is the concentration of P in the equilibrium solution ( $\mu\text{g/ml}$ ). Constants  $a$  and  $n$  were worked out from the intercept and slope, respectively.

#### Kinetics of P Release

Kinetics of P release from the surface (0–15 cm) soil samples was studied by using 0.5 M  $\text{NaHCO}_3$  ( $\text{pH}=8.5$ ; 1:5 soil : solution ratio). The soil suspension was equilibrated for eight different periods of time,

viz. 0.5, 1.0, 3.0, 6.0, 12.0, 24.0, 48.0 and 72.0 h. The supernatant solution was analyzed for P concentration by using ascorbic acid method (16). The amount of P release was calculated for different equilibration periods and P release data was interpreted using zero order kinetics :  $C_A = C_{A0} + k_A t$ . Elovich equation :  $C_A = (1/\beta) \ln(\alpha \beta) + (1/\beta) \ln t$  (17) and Parabolic diffusion equation :  $P = Rt^{1/2} + C$  (18).

## Results and Discussion

### Phosphate Sorption

The changes in phosphate sorption pattern of an irrigated sub-tropical soil amended with *in-situ* legume-pulse crop residue incorporation and fertilizer-P were evaluated after completion of three consecutive legume based (gram-mungbean-maize) cropping sequences. Equilibrium solution P concentration continues to increase with increasing amount of added P (Fig. 1). As the amount of P applied through  $\text{CaCl}_2$  solution increased, the per cent of added P adsorbed in the soil decreased accordingly. However, the magnitude of decrease was more in plots receiving *in-situ* legume-pulse residue conjointly with fertilizer-P, for three consecutive years (Fig. 1). The reduced P-sorption capacity as a consequence of residue incorporation can be attributed to the production of organic acids after decomposition (14, 19). In a study on flood-plain soils, Singh et al (13) reported that organics application to soil has not only solubilized the native soil-P pool, by converting non-labile P to labile-P pool, but also has prevented the formation of meta-stable compounds like  $\beta$ -tri-calcium phosphate and hydroxyl apatite in the soil. Our results corroborates the findings of Ohno and Erich (20), who also substantiated decrease in P-sorption due to application dissolved organic carbon (DOC) isolated from field maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.) residue. Crop residue DOC (20, 21) and synthetic organic acids (22) have been shown to affect P soil chemistry in short reaction periods (<24 h) under laboratory studies.

When P adsorptional data was plotted according to Langmuir isotherm, a linear relationship was obtained indicating that P adsorption in the soil could be defined by Langmuir adsorption equation. The results revealed that P-fertilization through either source (crop residue/fertilizer-P) has decreased the

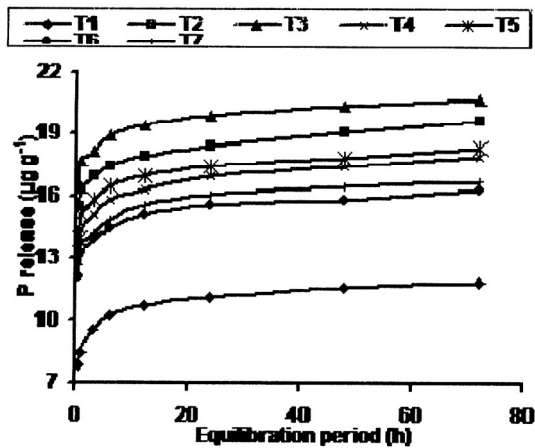


Figure 2. Kinetics of P release (zero order kinetics) in soil as influenced by *in-situ* legume-pulse residue incorporation.

bonding energy (BE) over control (Table 2). Results revealed that, BE has decreased by 52.7% with the application of fertilizer-P to all the three crops at recommended rate ( $T_2$ ) during three consecutive years over control ( $T_1$ ). However, *in-situ* legume-pulse residue incorporation conjointly with fertilizer-P application at recommended rate to all the three crops ( $T_3$ ) has decreased the BE by 64.8% over control ( $T_1$ ). Interestingly, the decrease in phosphate BE in soils receiving fertilizer-P to gram and summer mungbean ( $T_4$ ), was more as compared to soils receiving fertilizer-P to gram and maize only ( $T_6$ ) in a cropping sequence (Table 2). However, the decrease in phosphate BE was more in soils receiving *in-situ* legume-pulse residue conjointly with fertilizer-P ( $T_5$  and/or  $T_7$ ).

A straight-line correlation was also obtained with Freundlich equation when log of equilibrium P concentration was plotted against the log of adsorbed P. Significant correlation coefficient with  $r^2 \geq 0.995^*$  revealed that Freundlich equation explains the adsorption process in a better way than the Langmuir adsorption equation. Freundlich constant 'a' that represents the extent of adsorption, decreased by 14.4% in soils receiving fertilizer-P to all the three crops during three consecutive years ( $T_2$ ) over control ( $T_1$ ). However, Freundlich's constant a decreased by 28.2% in soils with conjoint fertilizer-P and *in-situ* residue incorporation ( $T_3$ ) over control ( $T_1$ ) (Table 2). The decrease in Freundlich constant a value was 15.6 and 22.3%, respectively in soils receiving fertilizer-P to gram and maize ( $T_6$ ) and gram and summer mungbean

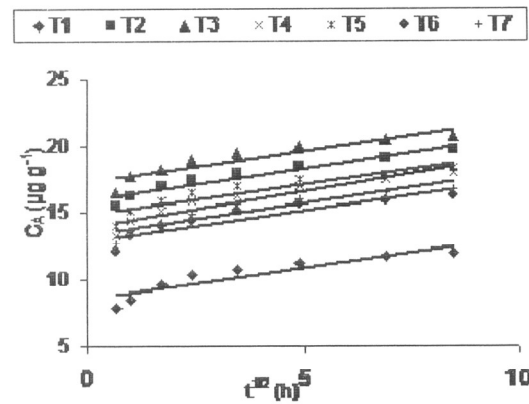


Figure 3. Kinetics of P release (Parabolic diffusion equation) in soil as influenced by *in-situ* legume-pulse residue incorporation.

( $T_4$ ) in a cropping sequence, over control ( $T_1$ ) (Table 2). However, the extent of this decrease was more in soils amended conjointly with fertilizer-P and *in-situ* legume-pulse residue incorporation ( $T_2$ ,  $T_4$  and  $T_6$ ), over their respective controls ( $T_3$ ,  $T_5$  and  $T_7$ ). In consonance, Freundlich constant b that represents rate of P adsorption in soil exhibited a remarkable decrease with P-fertilization through either crop residue or from fertilizer-P. The rate of P adsorption has been observed to be decreased from 5.55 to 3.38 ml/h (39.1%) with the application of fertilizer-P to the crops at recommended rate ( $T_2$ ) over control ( $T_1$ ) (Table 2). The results thus, revealed the positive influence of *in-situ* legume-pulse residue incorporation in conjunction with fertilizers-P. However, the effect of added crop residue was more in soils receiving fertilizer-P to gram and summer mungbean ( $T_5$ ) as compared to soils receiving fertilizer-P to gram and maize ( $T_7$ ). Our results corroborates the earlier findings (14, 23–25) who reported decreased sorption capacity of soils receiving P from fertilizers and organics. Increased equilibrium solution P concentration in plots receiving legume-pulse residue for three years, might be due to the release of organic acids, which competes with the orthophosphate anions for active sorption sites in the soil system, and thereby results in enhanced P availability in the soil. The organic acids chelate metal cations particularly  $Ca^{2+}$  ions in an alkaline and calcareous soils (14, 26), and thus results in reduced P sorption. Our results found support from the work of Toor and Bahl (12) who reported that the beneficial

effect of fertilizer-P applied conjointly with organics on P availability was more than sum of the increase from either applied singly. There are reports that manure-P might be equally or even more available than fertilizer-P (27, 28). Globally, the conservative estimates revealed that about one-fourth (26%) of total-P fertilizer consumption was found in crop residue generated during the year (29). The gram and summer mungbean residue used in the present investigation contains 0.14 and 0.16% total P, respectively that had a supplemental effect on soil available P. Our results corroborate the findings of Mishra et al. (30), who reported 0.10 to 0.20% increased P concentration in soil due to the decomposition of rice straw. They reported that about 23 and 59% of the total-P present in rice straw was released within 5 and 23 weeks, respectively, after its incorporation into the soil. Berton and Pratt (31) reported decreased P-sorption in a Typic Xerofluvent soil receiving barley straw.

#### *Kinetics of P Release*

A time dependent change in soil P availability was studied on the surface soil samples collected after completion of three consecutive cropping sequences. The cumulative P concentration (zero order equation) in the equilibrium soil solution increased with the increase in the reaction period indicating mobilization and release of P (Fig. 2). The amount of cumulative P release was highest at the longer period of equilibration (72 h). It was more during the initial period and then gradually leveled off as the shaking time progressed (Zero order kinetics) which revealed the mobilization and desorption of pre-sorbed P. A linear relationship obtained between cumulative P release and time ( $t^{1/2}$ ) suggested P release as diffusion controlled mechanism. A linear relationship was observed between 3 to 6 h of reaction, and thereafter P release from soil gradually leveled off as the extraction period progressed (Fig. 3). The initial faster reaction corresponded to the rapid dissolution of poorly crystalline or amorphous phosphates in the soil, which are meta-stable and ultimately converted to the crystalline forms (32). The Elovich's rate constant  $\beta$  increased from 8.6  $\mu\text{g/g}$  in control ( $T_1$ ) to 17.4  $\mu\text{g/g}$  in soils receiving fertilizer-P to all the three crops during three consecutive cropping sequences ( $T_2$ ), that reflects an increase of 2.0-times. However, the conjoint

*in-situ* legume-pulse residue incorporation and fertilizer-P application to all the three crops has resulted in 2.1-times increase in Elovich's rate constant  $\beta$ , over control ( $T_1$ ) (Table 3). In soils receiving fertilizer-P to gram and summer mungbean ( $T_4$ ), Elovich's rate constant  $\beta$  decreased by 1.80-times in comparison to soils receiving fertilizer-P to gram and maize ( $T_6$ ), where constant  $\beta$  decreased by 1.85-times, over control ( $T_1$ ) (Table 3).

Overall diffusion rate constant R calculated from parabolic diffusion equation remained relatively the same in different treatments. However, equilibrium concentration C exhibited an increase with P application through either fertilizer or from *in-situ* incorporated crop residue. Highest value was however, obtained from soils dressed conjointly with fertilizer-P and *in-situ* legume-pulse residue incorporation, during the three years of experimentation. Our results found support from the work of Iyamuremye and Dick (24), who reported that decomposition of organic materials added to the soil produces organic acids which are effective in decreasing P-sorption in soil by blocking P retention sites and consequently enhancing P availability.

The results also showed that the Elovich equation was the best among the various kinetic models used to describe the rate of P release in soil under gram-summer mungbean-maize cropping sequence, as evident from overall higher values of coefficient of determination ( $R^2$ ). The superiority of Elovich equation in explaining kinetics of P release data from soils over other equation has also been reported earlier (17, 33).

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