

RESEARCH ARTICLE

Fractions, uptake and fixation capacity of phosphorus and potassium in three contrasting soil orders

D. Chatterjee^{1,2,*}, S.C. Datta¹ and K.M. Manjaiah¹

¹*Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi- 110 012, India.* ²*ICAR Research Complex for NEH Region, Nagaland Centre, Jharnapani, Medziphema, Nagaland- 797 106, India.* *Corresponding author: dibyenducha@gmail.com

Abstract

A controlled greenhouse experiment was conducted to study the fraction, uptake and fixation of phosphorus (P) and potassium (K) in three soils with contrasting characteristics. The experiment was carried out in two phases, *viz.*, sorghum-Sudangrass depletion and test crop experiment with maize with three levels of fertility status (depleted, original and fertilized with 40 mg kg⁻¹ P and K) and two levels of rhizospheric status (rhizosphere and non rhizosphere). Clay was separated by ultrasonic vibration followed by fractionation into colloidal and non colloidal clay and short-range order (SRO) minerals, P and K fixation were measured in these clays. Phosphorus and potassium fractions and uptake were measured in soil samples. The results showed that, available and non-exchangeable potassium was highest in Vertisol and Inceptisol, respectively. Calcium-P was the dominant fraction in soil and highest in Inceptisol. Maximum K-fixation capacity for both the clay fractions was found in Vertisol (32.57% for colloidal clay and 37.94% for non colloidal clay), depleted soils (30.58% for colloidal clay and 31.04% for non colloidal clay) and rhizosphere (28.34% for colloidal clay and 29.59% for non colloidal clay). Phosphorus fixation was highest in Alfisol (58.72% for colloidal clay and 67.26% for non colloidal clay), depleted fertility status (53.41% for colloidal clay 55.45% for non colloidal clay) and non-rhizosphere (52.53% for colloidal clay and 54.26% for non colloidal clay) for both the clays. Phosphorus fixation was positively correlated with different pools of iron and aluminum compounds whereas, potassium fixation showed positive significant correlation with amorphous ferri-alumino silicate content.

Keywords: Clay, fixation, phosphorus, potassium, Alfisol, Vertisol, Inceptisol, maize, short-range order mineral

Abbreviations: LMOWAs low-molecular weight organic acids, P phosphorus, K potassium, AFAS amorphous ferri-alumino silicate, SRO short-range order, NEK non-exchangeable potassium, Ca-P- calcium P fraction

1. Introduction

Fixation of plant nutrients is the major concern for economical use of fertilizer. Huge amount of applied phosphorus (P) and potassium (K) are fixed into the soil in such a form, which is not readily available to the plants. This is a soil problem and to meet the plants' need, a higher dose of nutrient is required. Phosphorus fixation in soils depends upon many factors, *viz.*, the pH of the soil, organic matter content, type of clay and sesquioxides *etc.* Potassium is second only to nitrogen (N) in the quantities required by plants; hence its fixation is also a matter of apprehension. Potassium fixation capacity of the chemically synthesized amorphous minerals was reported in the range of 2-6 meq 100 g⁻¹ (Van Reeuwijk and De Villiers, 1968).

The effect of low-molecular weight organic acids (LMWOAs) on the sorption and desorption of phosphorus by clay minerals was established since fifties. Hydrous oxides of aluminum and iron were mostly responsible for the fixation of phosphate in soils. Research work revealed that tri and di-carboxylic acids were effective in reducing phosphate sorption, whereas monocarboxylic acids had little effect on phosphate fixation (Violante *et al.*, 1996).

The clay size inorganic colloidal fraction of soils contains appreciable quantities of 'free' and 'combined' oxides of Si, Al and Fe, known as short-range order (SRO) minerals. For example, allophane, proto-imogolite allophane, imogolite, allophane like constituents, imogolite like constituents, ferrihydrite, *etc.* Since the size of these minerals fall under 1-100 nm range, these can be considered as soil inherited nano-minerals. Volcanic ash soils, by virtue of the short-range order variable charged nano-materials (allophane, imogolite, aluminum (Al) and iron (Fe) oxides) and organo-mineral complexes, may adsorb high amounts of phosphate characterized by high surface area and reactivity (Vacca *et al.*, 2003). The chelation of P-fixing elements by LMWOAs could be another mechanism governing the role of plant materials in P solubilization in the rhizosphere or decomposition system.

Under K-stress environment, K from non-exchangeable pool replenishes the available pool which contributes in plant K uptake (Srinivasarao *et al.*, 2007). Studies have shown that a significant portion of K (70–90%) required by plants comes from the nonexchangeable pool in the absence of easily supplied K, thus indicating the beneficial role of the fixed K. The quantity of interlayer K in vermiculite and illite containing soils high compared with the amount of K taken by crops. This interlayer K is also the major source controlling the long-term K supplying potential of soils. Soils derived from volcanic materials have a strong K⁺ or NH₄⁺ retention (Escudéy *et al.*, 1997). But, no common mechanism has been identified account for this high K selectivity. Niebes *et al.* (1993) reported that the contribution of non-exchangeable K to K uptake ranged from 50% in the fine clay to 80-100% in the coarser fractions and due to high supplying power and their relative abundance, the silt fractions provided a major part of the supply of K. Potassium fixation capacities of some Inceptisols of India were decreased with increasing size of the clay-humus complex (Kumar *et al.*, 2004) and the removal of allophane, peroxidation and CBD treatment resulted in an increase in K-fixation capacity.

There is a very scanty of work on the role of the short-range order minerals in P and K fixation capacity. Moreover, most of the studies are made under artificial environment with synthetic materials. So far, under the complexity of natural soil environment a few attempts might be made. Keeping all the above facts under consideration, a study was conducted on phosphorus and potassium fractions, uptake and fixation capacity in relation to plant roots mediated changes of SRO minerals.

2. Materials and Methods

2.1. Collection and properties of initial soil samples

Three soils representing soil orders *viz.* Alfisol (Typic Haplustalfs), Inceptisol (Typic Haplustept)

and Vertisol (Typic Haplustert) from Parvathipuram (Andhra Pradesh), IARI research farm (New Delhi) and Rajahmundry (Andhra Pradesh), respectively was used for the present study. The surface (0-15 cm) soil samples were collected, ground and passed through 2-mm sieve and characterized for physico-chemical properties and mineralogical compositions. The pH in soil water suspension (1:2.5) was measured using combined electrode (glass and calomel) in a digital pH meter. The electrical conductivity was measured in the supernatant liquid of the soil water suspension (1:2.5) with the help of Conductivity Bridge, expressed in dS m^{-1} at 25 °C. Normal sodium acetate (pH 8.2) was used to determine cation exchange capacity of soils. Organic carbon was determined by wet digestion method and mineralizable nitrogen by alkaline- KMnO_4 method (Subbiah and Asija, 1956). Available phosphorus in soil was determined by 0.5 M NaHCO_3 (pH 8.5) extraction method (Olsen *et al.*, 1954) for Inceptisol and Vertisol and Bray-Kurtz no 1 method (Bray and Kurtz, 1945) for Alfisol, followed by colour development by ascorbic acid method (Murphy and Riley, 1962). Estimation of Ca-P and non occluded Al and Fe-P were done by modified Chang and Jackson method of P-fractionation (Olsen and Sommers, 1982). Available potassium was extracted by *IN* neutral NH_4OAc and determined by flame photometer (Hanway and Heidal, 1952). Non exchangeable K was determined by boiling *IN* HNO_3 method (Wood and De Turk, 1941). The sand, silt and clay contents % were determined by hydrometer method (Bouyoucos, 1951). The clays ($<2 \mu\text{m}$) were isolated by removing organic matter, sesquioxides and allophane. Basally oriented clay samples (Mg-air, Mg-glycerol, K-air dried, K-300 °C and 550 °C heated) were X-rayed. The X-ray diffractograms were recorded in Philips diffractometer (Model PW 1710) using Ni-filtered $\text{Cu-K}\alpha$ radiation at a scanning speed of $1.5^\circ 2\theta$ per minute. Identification and semi-quantitative estimation of clay minerals was also carried out (Jackson, 1975). Selective dissolution of SRO minerals was performed by boiling NaOH , acid ammonium oxalate in dark, citrate-bicarbonate-dithionite (CBD)

and Na-pyrophosphosphate. Different parameters *viz.*, amorphous ferri-alumino silicate (AFAS), allophane plus imogolite, ferrihydrite, crystalline iron, poorly ordered iron, poorly ordered aluminum, organically bound aluminum, organically bound iron were calculated from Al, Si and Fe concentrations measured in the aliquot of selective dissolutions.

2.2. Pot experiment under greenhouse condition

The experiment was conducted in two phases. In first phase *i.e.* sorghum-Sudangrass depletion experiment, an exhaustive crop, sorghum-sudangrass hybrid (Multicut GSC-40 variety) was grown for 100 days in one part of the soil to deplete it from P and K. Only nitrogen was applied at the rate of 50 mg N kg^{-1} . In second phase *i.e.* test crop experiment with maize (HPQM-1 variety), in each pot, 2 kg of soil was taken and one healthy seedling was grown up to 60 days after germination. Nitrogen was given through urea at the rate of 80 mg N kg^{-1} to all the treatments in two splits. Three levels of fertility status were made *viz.*, 'original', 'depleted' (sorghum-Sudangrass pre-depleted soil) and 'fertilized' (original soil + 40 mg L^{-1} P + 40 mg L^{-1} K). Similarly treated soil without any plant was kept as 'non-rhizosphere', thereby two rhizospheric status were also created, *viz.*, 'rhizosphere' and 'non-rhizosphere'.

2.3. Fractionation and analysis of soils in pot culture experiment

Fractionation of untreated soil was done by ultrasonic vibration technique for dispersion and finally clay was separated out by following Stokes' Law. The collected soil suspension was centrifuged at 5000 rpm for 12 minutes (calculated by using Stokes' Law average specification data of the Remi centrifuge, C-24) to separate colloidal ($<0.2 \mu\text{m}$) and non colloidal ($0.2-2 \mu\text{m}$) fraction and used as sample in fixation study.

The whole soil was analyzed for P fractions like available P (Olsen *et al.*, 1954; Bray and Kurtz, 1945;

Murphy and Riley, 1962), Ca-P (Olsen and Sommers, 1982) and Al-P (Olsen and Sommers, 1982) and K fractions like available K (Hanway and Heidal, 1952) and non-exchangeable K (Wood and de Turk, 1941). Oven dried shoot and root samples were digested by using di-acid mixture (concentrated HNO_3 and HClO_4 in the ratio of 9:4 by volume) for phosphorus and potassium. Total phosphorus and potassium content was measured by vanado-molybdate phosphoric acid yellow color method and by using flame photometer, respectively. Uptake of each nutrient was calculated by multiplying per cent nutrient with dry matter weight. Phosphorus fixation capacity of both colloidal and non colloidal clay was estimated by the procedure of Waugh and Fitts (1966) and K -fixation capacity by the STCR (1968) methods with little modification by the author for clay sample. For P fixation capacity, 0.1 g clay was taken in a series of 150 mL conical flask. Then 1 mL monocalcium phosphate of varying strength (0, 100, 250 and 500 $\mu\text{g P g}^{-1}$ of clay) were added. After that, these flasks were put into the oven for 4 days at 35°C. After drying, a pinch of charcoal and 10 mL of Olsen reagent was added. Then it was shaken for 30 minutes followed by filtration through Whatman no. 42 filter paper. Phosphorus in the filtrate was estimated by ascorbic acid blue colour method at 660 nm. For K fixation capacity, 1 mL potassium chloride of varying strength (0, 50, 300 and 1000 $\mu\text{g K g}^{-1}$ of clay) were added in 0.1 g clay taken in a series of 150 mL conical flask. After that, these flasks were put into the oven for 3 days at 35 °C. After drying, potassium was extracted by shaking with 15 mL of 1N neutral NH_4OAc for 30 minutes followed by filtration through Whatman no. 1 filter paper. Potassium content of the aliquot was determined by flame photometer.

2.4. Statistical analysis

The data were processed for analysis of variance for factorial CRD to test differences among the treatment means (Snedecor and Cochran, 1967) using MSTAT-C software. Treatment means were compared at the $p < 0.05$ level using LSD for all the parameters. Correlation coefficients and regression (enter and

stepwise) equations were computed using SPSS program (SPSS version 12).

3. Results

3.1. Properties of initial soil samples and SROs in treated soils

Properties of initial soil samples as shown in Table 1, indicated that Alfisol was acidic in nature, whereas Inceptisol and Vertisol showed alkalinity. There was no problem of high salt concentration as evidenced by low electrical conductivity value. Cation Exchange capacity was lowest in Alfisol, medium in Inceptisol and highest in Vertisol. Oxidizable organic carbon content was low in Alfisol, whereas medium in Inceptisol and Vertisol. Mineralizable nitrogen content was medium for all the soils. However, lower content of mineralizable N in Vertisol signified the presence of nitrogen in organic form. Available P ranged from low to high in these soils and it was highest in Vertisol followed by Inceptisol and Alfisol. Ca-P was the dominant fractions among different pools of P and highest in Inceptisol and much lower in Alfisol which may be due to its acidic pH. Available K content was medium to high. Maximum non exchangeable potassium was observed in Inceptisol which was 4-5 times higher than Alfisol and Vertisol. Texture of Alfisol, Inceptisol and Vertisol as observed from textural triangle was sandy clay loam, sandy loam and clay, respectively. The content and composition of crystalline clay minerals revealed that the major mineralogical composition for Alfisol was kaolinitic (76-81%) in both the fractions. Both Inceptisol fine clay and coarse clay were micaceous (71-76%). Vertisol fine clay was smectitic (60%), whereas coarse clay showed mixed smectite (35%)-mica (46%) mineralogy. Mica was present in all soils and fractions. Inceptisol contained vermiculite (13% in fine clay and 1% in coarse clay). Kaolinite content in Inceptisol and Vertisol was higher in coarser fraction than in the finer fraction.

Table 1. Physicochemical properties of initial soil samples

Parameter	Alfisol	Inceptisol	Vertisol
pH (1:2.5)	5.16	8.32	8.30
E.C. (dS m ⁻¹)	0.08	0.35	0.37
CEC cmol (p ⁺) kg ⁻¹	6.4	10.5	24.5
Oxidizable Org. C (%)	0.35	0.5	0.62
Mineralizable N (kg ha ⁻¹)	527.0	539.0	351.0
Available P (kg ha ⁻¹)	3.4	46.6	58.6
Ca-P (kg ha ⁻¹)	22.7	433.1	530.9
Non occluded Al and Fe-P (kg ha ⁻¹)	228.5	375.1	486.7
Available K (kg ha ⁻¹)	269.9	355.0	420.0
Non-exch. K(kg ha ⁻¹)	576.8	2494.2	561.1
Mechanical Analysis (%)	Sand: 64.3 Silt: 9.3 Clay: 26.4	Sand: 54.4 Silt: 31.8 Clay: 13.8	Sand: 11.2 Silt: 23.9 Clay: 64.9
Crystalline minerals in fine clay (%)	Kaolinite: 81 Mica: 19	Kaolinite: 11 Mica: 76 Vermiculite: 13	Kaolinite: 10 Mica: 30 Smectite: 60
Crystalline minerals in coarse clay (%)	Kaolinite: 76 Mica: 24	Kaolinite: 28 Mica: 71 Vermiculite: 1	Kaolinite: 19 Mica: 46 Smectite: 35

Short- range order (SRO) minerals content (%) in soil clay- humus complexes averaged over fertility and rhizospheric status (Table 2) indicated that, AFAS content was highest in Inceptisol followed by Vertisol and Alfisol for colloidal clay, whereas in Vertisol followed Alfisol and Inceptisol for non colloidal clay. Mean allophane plus imogolite content were maximum in Inceptisol colloidal clay-humus complex and Vertisol non colloidal clay-humus complex, whereas ferrihydrite, crystalline iron, poorly ordered iron and organically bound Fe in Alfisol. In both of the fractions of clay-humus complex, organically bound Al content was almost similar in Alfisol and Vertisol samples.

3.2. Phosphorus and potassium fractions

The difference of non occluded Al-Fe-P content (Figure 1a) of Alfisol, in between non-rhizosphere and rhizosphere were 18, 15.3 and 12.4 mg kg⁻¹ for depleted, original and fertilized fertility status, respectively. These values revealed that plants meet their P requirement from non occluded Al-Fe-P pool when P supply was limited. However, no such trend was observed in Inceptisol and Vertisol. The experimental result (Figure 1a) revealed that, non occluded Al and Fe-P decreased over cropping. Calcium-P (Figure 1b) was the dominant P-fraction in soil and maximum in Inceptisol, but much lower in

Alfisol. Maize rhizosphere contained less Ca-P than non-rhizosphere, however no significant changes were observed in Ca-P content when different fertility statuses were considered. Available P (Figure 1c) was decreased in rhizosphere soil, lowest in 'depleted×rhizosphere' and maximum in Vertisol. Available K content (Figure 2a) was much high in Vertisol followed by Inceptisol and Alfisol. It was increased in 'depleted×rhizosphere' in comparison

to 'depleted×non-rhizosphere' in Vertisol, which might have come from non-exchangeable pool and decreased due to cropping in case of original and fertilized fertility status. The maximum non-exchangeable potassium (Figure 2b) was observed in Inceptisol which was 4-5 times higher than Alfisol and Vertisol. Non-exchangeable K fraction was lesser in maize rhizosphere than non-rhizosphere, except in Vertisol.

Table 2. Content of short -range order (SRO) minerals (%) in soil clay and clay humus complexes averaged over fertility and rhizospheric status

SRO minerals (%)	Formula	Colloidal			Non-colloidal		
		Alfisol	Inceptisol	Vertisol	Alfisol	Inceptisol	Vertisol
AFAS	(%Si _n O ₂ + %Al _n 2O ₃ + %Fe _n 2O ₃)/ 0.9	12.28-14.92 (13.25)	15.83-19.35 (18.06)	15.11-18.37 (16.25)	8.27-10.78 (9.23)	6.08-8.58 (7.23)	11.23-14.95 (12.87)
Allophane+i mogolite	% Si _o × 7.1	1.06-2.88 (1.73)	2.65-7.13 (4.15)	2.10-3.60 (2.60)	1.17-2.52 (1.70)	4.44-5.93 (5.00)	4.45-6.12 (5.43)
Ferrihydrite	% Fe _o × 1.7	0.63-0.73 (0.66)	0.48-0.63 (0.53)	0.38-0.43 (0.40)	0.69-0.75 (0.72)	0.44-0.50 (0.47)	0.50-0.53 (0.52)
Crystalline Fe	Fe _d -Fe _o (%)	5.61-9.15 (7.39)	1.57-1.93 (1.79)	1.74-2.61 (2.08)	7.24-9.46 (8.35)	1.93-2.18 (2.06)	1.84-2.68 (2.40)
Poorly ordered Fe	Fe _o -Fe _p (%)	0.19-0.34 (0.25)	0.15-0.25 (0.18)	0.08-0.14 (0.11)	0.21-0.31 (0.26)	0.09-0.17 (0.13)	0.16-0.21 (0.18)
Organically bound Al	Al _p (%)	1.05-1.70 (1.42)	0.77-1.41 (1.20)	0.99-1.91 (1.46)	1.17-1.65 (1.33)	0.86-1.76 (1.25)	0.76-1.68 (1.33)
Organically bound Fe	Fe _p (%)	0.09-0.19 (0.14)	0.11-0.15 (0.13)	0.10-0.15 (0.12)	0.11-0.21 (0.16)	0.11-0.17 (0.15)	0.11-0.15 (0.13)

Data mentioned within parenthesis indicates the mean value and the value outside of parenthesis indicates the range. (n= NaOH extractable, o= oxalate extractable, d= CBD extractable, p= pyrophosphate extractable)

3.3. Phosphorus and potassium uptake in rhizospheric soil samples

The mean phosphorus uptake by root was maximum in fertilized fertility status and significantly higher in Inceptisol than Vertisol and Alfisol. All the three combinations of fertilized fertility status with soils were found to be superior to the other combinations (Figure 3a). Shoot phosphorus uptake showed similar trend

like root uptake when fertility status was concerned, but highest phosphorus uptake was observed in Vertisol, followed by Inceptisol and Alfisol. Among different combinations, highest phosphorus uptake value was observed in 'fertilized×Vertisol' (Figure 3a).

The mean root potassium uptake in depleted and original fertility statuses was significantly higher than fertilized fertility status and in Inceptisol than Alfisol

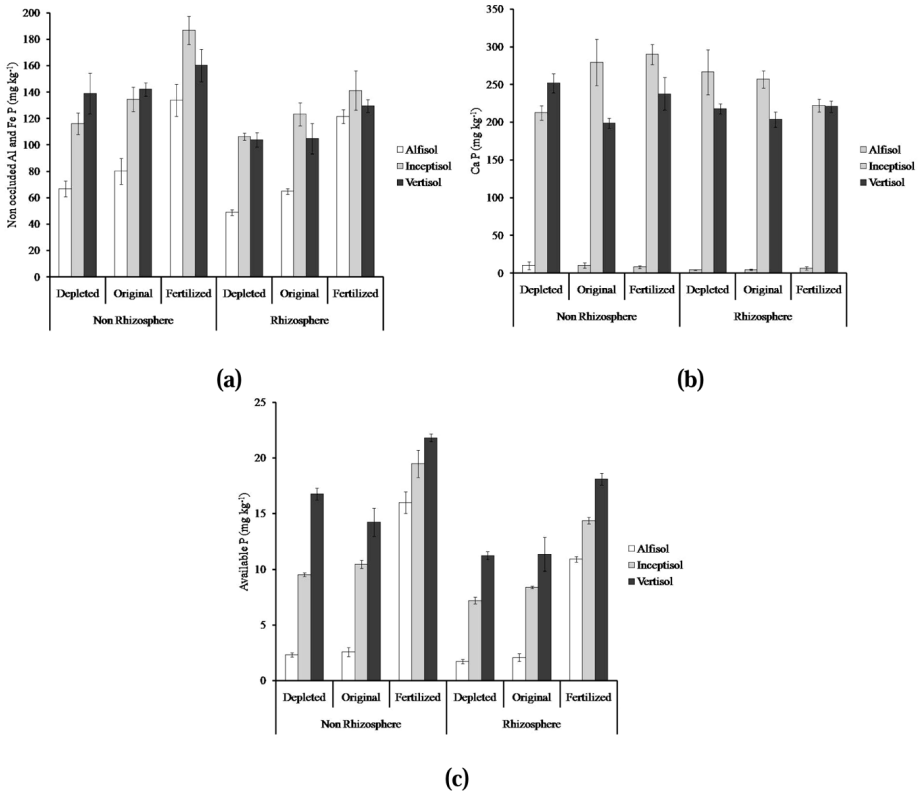


Figure 1. Different fractions of soil phosphorus in three soils after harvesting of maize: (a) non occluded aluminium and iron P (b) calcium P and, (c) available P

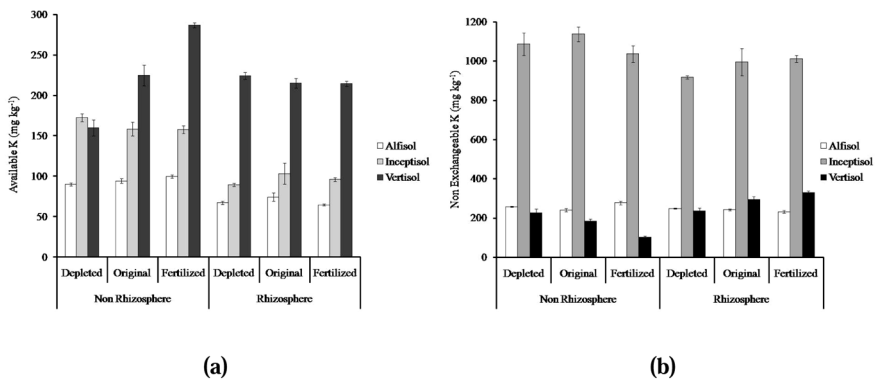


Figure 2. Different fractions of soil potassium in three soils: (a) available potassium (b) non exchangeable potassium

Vertisol. ‘Depleted×Alfisol’ showed significantly lesser uptake than other combinations (Figure 3b). Mean potassium uptake by shoot was significantly higher in fertilized soil and Vertisol. The fertilized fertility status in combination with different soils showed the maximum potassium uptake (Figure 3b).

3.4. P and K fixation with colloidal clay-humus complex

Mean P fixation was highest in depleted fertility status and Alfisol (Table 3). Maximum mean P fixation was observed in non-rhizosphere and among the treatment combinations; ‘Alfisol×non-rhizosphere’ and ‘Inceptisol×non-rhizosphere’ showed superiority over others (Table 3). ‘Depleted×non-rhizosphere’ fixed P

at highest quantity as compare to other combinations (Table 3).

Mean K fixation was highest in depleted fertility status followed by original and fertilized fertility statuses. Among the soils, it was significantly higher in Vertisol, followed by Inceptisol and Alfisol. ‘Depleted×Vertisol’ fixed maximum amount of potassium among the all combinations (Table 4). Mean K fixation was higher in rhizosphere as compare to non-rhizosphere. Among the combinations, ‘Vertisol×rhizosphere’ fixed maximum amount of K, whereas lowest amount of fixation was observed in ‘Alfisol×non-rhizosphere’ (Table 4). ‘Depleted×rhizosphere’ fixed significantly higher amount of potassium than other combinations (Table 4).

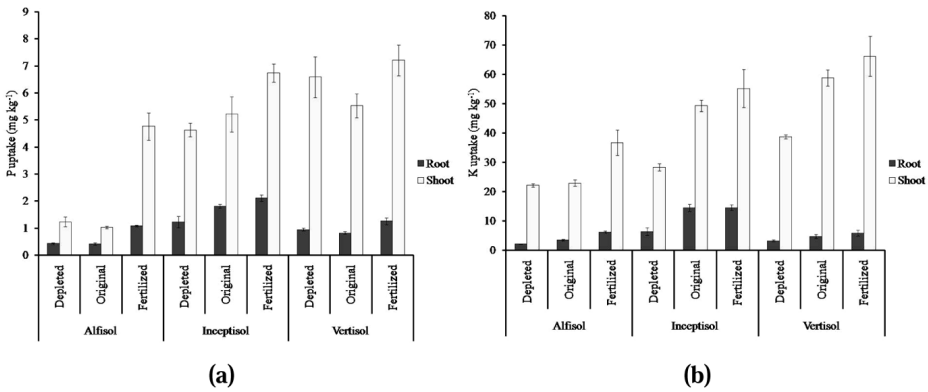


Figure 3. Uptake of (a) phosphorus and (b) potassium by root and shoot in three dissimilar soils

3.5. P and K fixation with non colloidal clay-humus complex

Unlike colloidal clay-humus complex, mean P fixation was highest with original fertility status followed by depleted and fertilized fertility statuses. Alfisol fixed significantly higher amount of P than Vertisol and Inceptisol. Among the different combinations, ‘original×Alfisol’ showed the highest fixation (Table 5).

Mean fixation of P was higher in non-rhizosphere than rhizosphere and among the combinations ‘Alfisol× non-rhizosphere’ showed superiority over others (Table 5). ‘Original×non-rhizosphere’ fixed P at highest quantity as compare to other combinations (Table 5).

Mean K fixation was highest with depleted fertility status followed by original and fertilized fertility statuses. Among the soils, Vertisol fixed more K as compare to Inceptisol and Alfisol. Among the

different combinations, highest fixation was recorded in ‘depleted×Vertisol’ (Table 6). Rhizosphere fixed more K than non-rhizosphere (Table 6). Among all combinations, ‘depleted×rhizosphere’ fixed more K than others (Table 6).

3.6. Relationship with fixation capacity

Phosphorus fixation in colloidal clay-humus complex showed significant and positive correlation with kaolinite content, ferrihydrite, crystalline iron, and poorly ordered iron, but negatively correlated with organically bound aluminum. Potassium fixation in colloidal clay- humus complex showed significant and positive correlation with AFAS content (data not shown).

Phosphorus fixation in non colloidal clay-humus complex showed significant positive correlation with allophane content, kaolinite content, ferrihydrite, crystalline aluminum, crystalline iron and poorly ordered iron. Potassium fixation in non colloidal clay- humus complex was significantly negatively correlated with kaolinite content, ferrihydrite, crystalline aluminum, crystalline iron and poorly ordered iron. K fixation in colloidal clay- humus complex showed positive and significant correlation with AFAS content (data not shown).

The relationship can be expressed in terms of equations (Eqn. 1-8) by considering phosphorus and potassium fixation capacity as a dependent variable and crystalline minerals, nano-minerals and oxides as independent variables.

Table 3. Effect of soil, fertility status and rhizospheric status on P fixation (%) in colloidal clay humus complex

Fertility Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Depleted	63.23 a	59.23 b	37.75 d	53.41 A
Original	59.87 b	52.07 c	26.90 f	46.28 B
Fertilized	53.05 c	36.33 d	30.95 e	40.11 C
Mean	58.72 A	49.21 B	31.87 C	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.38	Fertility Status(F)= 1.38		S×F= 2.39
Rhizospheric Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Non Rhizosphere	60.31 a	61.44 a	35.83 c	52.53 A
Rhizosphere	57.12 b	36.98 c	27.90 d	40.67 B
Mean	58.72 A	49.21 B	31.87 C	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.38	Rhiz. Status (RH)= 1.13		S×RH=1.96
Rhizospheric Status	Fertility Status			Mean
	Depleted	Original	Fertilized	
Non Rhizosphere	58.39 a	52.67 b	46.53 c	52.53 A
Rhizosphere	48.42 c	39.89 d	33.69 e	40.67 B
Mean	53.41 A	46.28 B	40.11 C	
LSD (<i>P</i> = 0.05)	Fert. Status(F)= 1.38	Rhiz. Status (RH)= 1.13		F × RH= 1.96

Means followed by the same capital letter or interactions followed by same small letter in each row or column are not significantly different at 0.05 level of probability by LSD range test.

Table 4. Effect of soil, fertility status and rhizospheric status on K fixation (%) in colloidal clay -humus complex

Fertility Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Depleted	21.80 d	32.82 b	37.12 a	30.58 A
Original	14.25 f	23.52 cd	35.05 ab	24.27 B
Fertilized	10.48 g	18.03 e	25.53 c	18.02 C
Mean	15.51 C	24.79 B	32.57 A	
LSD ($P=0.05$)	Soil (S)= 1.86	Fertility Status(F)= 1.86		S×F= 3.22
Rhizospheric Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Non Rhizosphere	9.05 d	21.26 c	30.39 b	20.23 B
Rhizosphere	21.97 c	28.32 b	34.74 a	28.34 A
Mean	15.51 C	24.79 B	32.57 A	
LSD ($P=0.05$)	Soil (S)= 1.86	Rhiz. Status (RH)= 1.52		S×RH= 2.63
Rhizospheric Status	Soil			Mean
	Depleted	Original	Fertilized	
Non Rhizosphere	26.61 b	19.96 c	14.13 d	20.23 B
Rhizosphere	34.54 a	28.59 b	21.90 c	28.34 A
Mean	30.58 A	24.27 B	18.02 C	
LSD ($P=0.05$)	Fert. Status(F)= 1.86	Rhiz. Status (RH)= 1.52		F × RH= 2.63

Means followed by the same capital letter or interactions followed by same small letter in each row or column are not significantly different at 0.05 level of probability by LSD range test.

Table 5. Effect of soil, fertility status and rhizospheric status on P fixation (%) in non colloidal clay- humus complex

Fertility Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Depleted	75.98 a	45.10 e	45.27 e	55.45 A
Original	70.37 b	44.88 e	45.30 e	53.52 B
Fertilized	55.42 d	38.90 f	57.78 c	50.70 C
Mean	67.26 A	42.96 C	49.45 B	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.15		Fertility Status(F)= 1.15	S×F= 1.99
Rhizospheric Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Non Rhizosphere	72.82 a	46.07 d	43.90 e	54.26 A
Rhizosphere	61.69 b	39.86 f	55.00 c	52.18 B
Mean	67.26 A	42.96 C	49.45 B	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.15		Rhiz. Status (RH)= 0.94	S×RH= 1.62
Rhizospheric Status	Fertility Status			Mean
	Depleted	Original	Fertilized	
Non Rhizosphere	56.66 a	52.69 c	53.44 bc	54.26 A
Rhizosphere	54.24 bc	54.34 b	47.96 d	52.18 B
Mean	55.45 A	53.52 B	50.70 C	
LSD (<i>P</i> = 0.05)	Fert. Status(F)= 1.15		Rhiz. Status (RH)= 0.94	F × RH= 1.62

Means followed by the same capital letter or interactions followed by same small letter in each row or column are not significantly different at 0.05 level of probability by LSD range test.

Table 6. Effect of soil, fertility status and rhizospheric status on K fixation (%) in non colloidal clay- humus complex

Fertility Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Depleted	16.57 f	32.17 c	44.38 a	31.04 A
Original	19.37 e	27.90 d	34.95 b	27.41 B
Fertilized	16.73 ef	26.27 d	34.50 bc	25.83 C
Mean	17.56 C	28.78 B	37.94 A	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.57	Fertility Status(F)= 1.57		S×F= 2.72

Rhizospheric Status	Soil			Mean
	Alfisol	Inceptisol	Vertisol	
Non Rhizosphere	14.40 e	29.50 c	35.89 b	26.60 B
Rhizosphere	20.71 d	28.06 c	40.00 a	29.59 A
Mean	17.56 C	28.78 B	37.94 A	
LSD (<i>P</i> = 0.05)	Soil (S)= 1.57	Rhiz. Status (RH)= 1.28		S×RH= 2.22

Rhizospheric Status	Fertility Status			Mean
	Depleted	Original	Fertilized	
Non Rhizosphere	29.94 ab	26.32 c	23.52 d	26.60 B
Rhizosphere	32.13 a	28.49 bc	28.14 bc	29.59 A
Mean	31.04 A	27.41 B	25.83 C	
LSD (<i>P</i> = 0.05)	Fert Status(F)= 1.57	Rhiz. Status (RH)= 1.28		F × RH= 2.22

Means followed by the same capital letter or interactions followed by same small letter in each row or column are not significantly different at 0.05 level of probability by LSD range test.

For colloidal clay humus complex

$$PFIX = 51.516^{**} + 3.315 KAHA^{**} - 1.085 ALIM - 24.775 FERRI + 2.369 CRYFE - 4.608 ORAL - 70.171 ORFE$$

(Method: Enter, $R^2=0.601^{**}$).....(Eqn. 1)

$$PFIX = 24.926^{**} + 2.656 KAHA^{**} + 1.94 CRYFE^{**}$$

(Method: Stepwise, $R^2=0.543^{**}$)..... (Eqn. 2)

$$KFIX = 37.353^{**} - 0.856 KAHA - 3.937 ALIM^{**} + 16.944 FERRI - 4.102 CRYFE^{**} - 1.655 ORAL + 85.981 ORFE^{**}$$

(Method: Enter, $R^2=0.772^{**}$) (Eqn. 3)

$$KFIX = 51.285^{**} - 49.369 POFE^{**} - 2.517 CRYFE^{**} - 3.064 ALIM^{**}$$

(Method: Stepwise, $R^2=0.737^{**}$) (Eqn. 4)

For non colloidal clay humus complex

$$PFIX = 37.854 - 1.655 AFAS - 2.552 KAHA^{**} + 0.078 ALIM + 71.188 FERRI^{*} + 2.072 CRYFE - 9.065 ORAL + 5.371 ORFE$$

(Method: Enter, $R^2=0.643^{**}$)..... (Eqn. 5)

$$PFIX = 11.165 + 93.062 FERRI^{**} - 8.499 ORAL^{**}$$

(Method: Stepwise, $R^2=0.601^{**}$) (Eqn. 6)

$$KFIX = 20.268^{*} - 2.368 KAHA - 1.012 ALIM^{**} + 16.987 FERRI - 0.851 CRYFE - 4.069 ORAL + 48.786 ORFE^{*}$$

(Method: Enter, $R^2=0.805^{**}$) (Eqn. 7)

$$KFIX = 27.473^{**} - 2.32 KAHA^{**} + 1.077 ALIM^{**}$$

(Method: Stepwise, $R^2=0.780^{**}$)(Eqn. 8)

(PFIX= phosphorus fixation capacity; KFIX= potassium fixation capacity; AFAS= amorphous ferri-alumino silicate; FERRI= ferrihydrite; CRYFE= crystalline iron; ORAL= organically bound aluminum; ORFE= organically bound iron; KAHA= kaolinite + halloysite; ALIM= allophane + imogolite; POFE= poorly ordered iron)

4. Discussion

4.1. Phosphorus and potassium fractions

Phosphorus is considered as the most limiting nutrients. Variable charged minerals *viz.*, Fe and Al hydrous oxides and/or allophane bind with P and render it unavailable to plant uptake, although the total level may be high. Non-occluded Al-P and Fe-P content were lesser in rhizosphere than non-rhizosphere, which suggests under depleted condition soil solution P concentration may be maintained by this pool. Both the available P and Al-Fe-P were decreased over cropping. Similarly a study revealed that, all soil P fractions including residual P in the rhizosphere soil declined following 60-day growth of either wheat or chickpea and the decreases were greater in soils with a history of high P application than low P (Vu *et al.*, 2008). Rivaie *et al.* (2008) observed that the rate of increase of the concentrations of the P fractions was highest for P associated with Fe and Al oxides and allophane when triple superphosphate was applied and highest for calcium phosphates or apatite-type P minerals or P occluded in Fe oxides when phosphate rock was applied.

Available K was found to be increased in Vertisol rhizosphere which may come from non-exchangeable pool and can be validated with the work of Srinivasarao *et al.* (2007). However, marked depletion of K^+ in the soil solution is not always necessary for the release of interlayer K from the rhizosphere (Moritsuka *et al.*, 2004). Inceptisol have highest non-exchangeable potassium than others. The non-exchangeable K is a source of potassium in some soils and can be released to provide a significant portion of the K removed by crops during the growing season (Rahmatullah *et al.*, 1994).

4.2. Phosphorus and potassium uptake

The mean phosphorus uptake by root and shoot were much high in fertilized soil. Average P uptake in maize is $18.6 \text{ kg P ha}^{-1}$ (Havlin *et al.*, 1999) and this is around 44 per cent of the applied fertilizer to maize (Jalali,

2007). The mean P uptake in both root and shoot were lower in Alfisol, which may be due to more fixation of P in Al and Fe oxides. The mean potassium uptakes by root in depleted and original soils were more, which may be due to conversion of non-exchangeable K to available K under such conditions, which favored the uptake process. Among the three soils, Inceptisol recorded highest mean potassium uptake than Alfisol and Vertisol. More fixations and less K uptake in Vertisol may be attributed to presence of smectitic clay minerals (Raheb and Heidari, 2012).

4.3. Phosphorus and potassium fixation

In colloidal and non colloidal clay-humus complex, mean P fixation was highest with depleted and original fertility status, respectively. However in both the cases, fixation in fertilized soil is less. The reason behind this phenomenon can be explained by AFAS and allophane content of colloidal clay-humus complex. Mean AFAS content (%) in colloidal clay-humus complex of depleted and original fertility status was significantly higher than fertilized fertility status (data not shown).

Invariably, in both the clays mean P fixation was highest in Alfisol. P fixation in Alfisol occurs due to formation of insoluble Al or Fe phosphate by free oxides of iron and aluminum and also may be due to presence of SROs *viz.*, ferrihydrite, crystalline Fe and poorly ordered Fe which might fix phosphate through ligand exchange on the OH-Al species on the surfaces (Vacca *et al.*, 2003). Phosphorus fixation in allophanic soils was considered to occur only on the active surface of allophane and imogolite. Fixation mechanisms in these soils include chemi-adsorption and displacement of structural silicon (Parfitt, 1990). Phosphate can also be fixed in phyllosilicate like kaolinite, however this process highly depends on soil reaction. Matsuyama *et al.* (1998) reported that phosphate adsorption in synthetic allophane is stronger at higher Al/Si ratios. Maximum P fixation capacity of Alfisol may be attributed to its highest Al/Si ratio.

In both the clays, mean P fixation was highest in non-rhizosphere, which may be due to unavailability of secreted LMWOAs, rendering the more P to be in fixed form. Actually, excretion of organic acids, enzymes and protons by roots play a major role in the P nutrition of various crops (Raghothama, 1999). Mechanism of increasing availability of P by root exudates under P stress condition was widely studied such as the competition of phosphate and organic anions for similar adsorption sites can increase the concentration of P in the soil solution (Staunton and Leprince, 1996)

Mean K fixation was highest with depleted fertility status, Vertisol and rhizosphere for both colloidal and non colloidal clays. Potassium fixation mainly depends on interlayer spacing, unsatisfied charge on the minerals and the radius of hydration sphere. Potassium fixation is relatively higher in Vertisol due to the presence of high smectitic group of minerals; however the role of amorphous material cannot be ignored. There have been several reports of soils derived from volcanic materials having a strong K⁺ retention (Escudey *et al.*, 1997).

4.4. Relationship with fixation capacity

The major phosphate absorbent sites are free oxides (CBD extractable), short-range order minerals (SRO) along with active components (like Al³⁺, Fe³⁺) in the exchange complex, therefore the allophane content (for non colloidal clay- humus complex), kaolinite content, ferrihydrite, crystalline iron, and poorly ordered iron showed positive correlation with P fixation capacity in both the clay- humus fractions, however showed negative correlation with organically bound aluminum in colloidal clay -humus complex, which may be due to the hindering effect of organic matter in P fixation. In general, organic matter in soils decrease P sorption by the anion replacement of H₂PO₄⁻ on adsorption sites and the coating of Fe/Al oxides by humus to form a protective cover and reduce P sorption (Havlin *et al.*, 1999). Potassium fixation in both colloidal and non colloidal clay- humus complex showed positive significant correlation with AFAS content. Potassium

is fixed by the channels in the amorphous mineral acting as a molecular sieve (Van Reeuwijk and De Villiers, 1968). Phosphorus fixation largely depends on kaolinite+halloysite, crystalline iron, ferrihydrite and organically bound aluminum, whereas K fixation on allophane+imogolite, crystalline iron, kaolinite + halloysite and poorly ordered iron as evidenced in stepwise regression equations.

5. Conclusions

From the above experiment the following conclusions may be drawn: (a) Short-range order (SRO) minerals are involved in P and K fixation. However, some other factors like active Al and Fe, crystalline phyllosilicates may also working simultaneously in the natural system. (b) Not only the soil constituents but also some management practices like fertilizer application and rhizospheric effect can alter the P and K fixation capacity of clay -humus complex in various ways due to differential presence of SRO minerals.

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