



Relationship of Phosphorus Uptake with Its Fractions in Different Soil Parent Materials

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Authors' contributions

The research work was carried out in collaboration among all authors. All authors read and approved the manuscript.

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ABSTRACT

The objectives were to determine inorganic P fractions in selected parent material soils and to develop a relationship of various P fractions with P uptake by *Zea mays*. Experimental study was conducted at Soil Chemistry Laboratory, Department of Soil Science and Soil and Water Conservation, Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi, Pakistan, during February, 2013 to January, 2014. Triplicate soils were selected at three different level of development in each of loess, alluvium, shale residuum, and sandstone residuum, and surface and subsurface samples were taken. Samples were analyzed for pH, soil test P, total P, CaCO₃, dissolved and total organic carbon, dithionite extractable and amorphous iron. Soil P was fractionated into Ca₂-P, Ca₈-P, P adsorbed by Fe and Al, P occluded in iron oxides bodies, and apatite-P. Apatite-P was 33-71 %, and secondary phosphates i.e. occluded P, iron oxides surface adsorbed P and aluminum oxides surfaces adsorbed P ranged between 0.80 – 4.0 %, 2.65 – 14 % and 1.20 – 5.0 % of total P, respectively. Phosphorus uptake also differed significantly with soil parent material. The bioavailability of soil P fractions follow the order Ca₂-P > Org-P > Al-P > Fe-P > Ca₈-P > Occluded P > apatite-P. Dicalcium phosphates, iron adsorbed P, aluminum oxides adsorbed P and organic P control P bioavailability in *Zea mays*. Olsen P and occluded P gave better prediction for P uptake rather than Olsen P alone. This study will help to improve P fertilizer management and ultimately result in increase crop production.

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1. INTRODUCTION

Chemical forms of phosphorus (P) help understand P dynamics in soil. Soil solution P is the immediate source for crop plants. Level of P in soil solution is maintained by desorption and dissolution of solid-phase inorganic P, and by mineralization of soil organic compounds i.e. nucleic acids and phospholipids to soluble P [1,2]. Inorganic P forms are associated with calcium, iron, and aluminum to form various phosphate minerals, and adsorbed on the surfaces of iron and aluminum oxides. Organic and inorganic P fractions may play crucial role in plant-available P with soil types [3]. Olsen P is commonly used for assessment of bioavailable P and relationship of P forms with Olsen P shows that NaHCO_3 extracts all the water soluble P and some amount from the P attached on the surfaces of clay, organic matter, and on the surfaces of iron and aluminum oxides [4,5]. As Olsen P is extracted with NaHCO_3 which cannot remove P occluded in the fringes of goethite minerals but plant roots have capability to extract occluded P in severe P deficiency [6]. Phosphorus bioavailability may be better explained by relationship between P uptake and P fractions rather than Olsen P.

The soil P fractionation is important for investigation of soil P behavior and bioavailability. Several different types of sequential extraction schemes are available for different soil types [7-10]. Jiang and Gu [9] developed a P sequential extraction method for calcareous soils, and fractionated Ca-bound P into various fractions, namely $\text{Ca}_2\text{-P}$, $\text{Ca}_8\text{-P}$, and $\text{Ca}_{10}\text{-P}$. The $\text{Ca}_2\text{-P}$ is monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] and dicalcium phosphate ($\text{CaHPO}_4 \cdot n\text{H}_2\text{O}$) equivalents. The $\text{Ca}_8\text{-P}$ resembles with a group of phosphates with a chemical structure similar to octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot n\text{H}_2\text{O}$], which is less available than $\text{Ca}_2\text{-P}$ to plants. The $\text{Ca}_{10}\text{-P}$ corresponds to a group of phosphates with a chemical structure similar to apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and releases P upon weathering. Phosphorus adsorbed on the Al and Fe oxides surfaces (Al-P and Fe-P, respectively) and P occluded in iron oxides bodies (Occluded P) have been considered as other P fractions in addition to Ca-bound P pools.

Indus River tributaries alluvium, loess deposits, and sandstone and shale residuum are the four morphological units that host the most soils of

Pothwar plateau (Pakistan) where different source rocks have contributed sediments and can be taken as different soil parent materials [11]. Soil P fraction and basic soil characteristics vary due to different source rock and level of development within parent material. Stepwise multiple regressions can be performed to evaluate the degree of association of soil P fractions with plant P uptake. Several studies show the use of stepwise multiple regressions to evaluate the relationship between soil test P and other P fractions [4,5,12]. Studying the relationships between soil P fractions and available P through plant growth experiments would be a very useful way for the assessment of the P pools that are more available to plant roots. The objective of this study was to determine the inorganic P fractions in selected soils of different parent material and to develop a relationship of various P fractions which represents better P uptake estimation by *Zea mays*.

2. MATERIALS AND METHODS

2.1 Soil Sampling and Characterization

Soils were selected to represent range of clay, CaCO_3 and free Fe oxides contents created due to variation in source of parent material and weathering (Table 1). The soils were taken from four parent materials occurring on the Pothwar Plateau (Pakistan). For each of the selected soil in parent materials, triplicate surface and subsurface horizon samples at distant locations were taken and, air dried, and crushed to pass through a 2 mm sieve. Each sample was analyzed for texture, pH, CaCO_3 , Olsen-P, sodium dithionite extractable iron and aluminum, and total and dissolved organic carbon. The soil particle size distribution was determined after dispersion in $(\text{NaPO}_3)_6$ and pH of saturated soil paste. Soil CaCO_3 was determined by acetic acid (CH_3COOH) consumption [13]. Phosphorus was extracted with 0.5 M sodium bicarbonate (NaHCO_3) solution pH 8.5, and measured colorimetrically for Olsen test P [14]. Total organic carbon (TOC) was determined by wet digestion in potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) [15]. Dissolved organic carbon (DOC) was extracted with potassium sulfate (K_2SO_4) and determined by consumption of $\text{K}_2\text{Cr}_2\text{O}_7$ [16]. Soil iron oxide was dissolved with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) in NaHCO_3 buffer solution. Iron and aluminum in the extract were measured by an atomic

absorption spectroscopy, and expressed as Fe_d and Al_d , respectively [17]. Amorphous Fe was determined for each soil sample by extracting soil in acidified $(NH_4)_2C_2O_4 \cdot H_2O$ solution [18].

Table 1. Selected soil series with USDA classification

Parent material	Soil series	USDA classification
Alluvium	Shahdra	Typic Ustifluvents
	Argan	Fluventic Haplustepts
	Gujranwala	Typic Haplustalfs
Loess	Rajar	Typic Ustorthents
	Rawalpindi	Udic Haplustepts
	Chakwal	Typic Haplustalfs
Shale	Ghoragali	Typic Udorthents
	Tirnul	Typic Haplustepts
	Murree	Typic Hapludolls
Sandstone	Qazian	Lithic Ustipsamments
	Balkasar	Typic Haplustalfs
	Kahuta	Udic Haplustalfs

2.2 Sequential Extraction of Soil Phosphorus

Jiang and Gu [9] fractionation scheme modified by Samadi and Glikes [4] used for P fractionation (Table 2). Separately, total P was determined by

digestion in perchloric acid ($HClO_4$). Organic P fraction was estimated by the difference in the sum of inorganic P and total P. Each extraction step in Table 2 was end with centrifugation at 2500 rpm for 10 min and P assay in supernatant determined by using spectrometer following the procedure of Murphy and Riley [19].

2.3 Assessment of Bioavailable Phosphorus

Uniform-weight maize (*Zea mays*) seeds were sown in plastic pot containing one kg sieved soil from the surface (Ap/A) and subsurface (Bw/BA) horizons of each replicate of each soil. Potassium, zinc, iron, sulfur and boron were applied as fertilizer at sowing and nitrogen was applied in three splits. No phosphorus was applied. The seedlings were thinned to two plants per pot one week after germination. The pot soil moisture was maintained near field capacity during the growth of the plants. Twenty eight day old plants were harvested, oven dried at $65^\circ C$, and weighed for biomass. Plant material was digested in nitric acid and hydrogen peroxide before analysis for P content [20].

Table 2. Extraction steps for the inorganic P fractions by Jiang and Gu, [9] and Samadi and Gilkes [4]

Step	Extraction procedure	Extracted P form (and notation)
1	One gram soil added in 50 mL 0.25 M $NaHCO_3$ (pH 7.5) solution and shaken for 1 h.	Surface complex of P on calcite or discrete dicalcium phosphate (Ca_2 -P)
2	Residue washed twice with 95% alcohol, added 50 mL 0.5 M NH_4CH_3COO (pH 4.2), left soaking for 4 h and shaken for 1 h.	Octacalcium phosphate (Ca_8 -P)
3	Residue washed twice with saturated NaCl, added 50 mL 0.5 M NH_4F , shaken (orbital) for 1 h.	Amorphous aluminum P (Al-P)
4	Residue washed twice with saturated NaCl, added 1:1 ratio of 0.1 M NaOH and 0.1 M Na_2CO_3 solution (pH 8.2), shaken for 2 h, left unshaken for 16 h and shaken again for 2 h.	P adsorbed on surface of iron oxides (Fe-P)
5	Residue washed twice saturated with NaCl, added 40 mL 0.3 N Na-citrate plus 1 g Na-dithionate and heating at $80^\circ C$ for 15 min.	P incorporated, trapped into iron oxide coatings, or amorphous iron oxide P (Occl-P)
6	Residue added with 50 mL 0.5 M H_2SO_4 , and shaken for 1 h.	Hydroxylapatite (Ca_{10} -P)

2.4 Statistical Analysis

The data were transformed using Box-Cox transformation. Multiple regression analysis was carried out to develop empirical equation to develop relationship between P uptake and soil P fractions using SAS version 9 [21].

3. RESULTS AND DISCUSSION

3.1 Basic Characteristics and P Fractions of Soils

The selected soils widely varied in the chemical properties that affect P uptake and in P fractions (Table 3). The soils at relatively higher stage of development (Alfisols and Mollisols) were decalcified, low pH, high oxalate and dithionite extractable iron as compared to soil at early stage of development (Entisols) were calcareous, high pH, and were low in oxalate and dithionite extractable iron. The shale derived soils had greater extractable iron due to lithogenic hematite [12]. Total and dissolved organic carbon content also varied with soil development within parent material. Almost all soils were deficient in soil test P (Olsen P) and ranged between 3.25 to 9.20mg kg⁻¹.

Soil P fractions varied with soil development in parent materials and apatite-P was the largest P fraction between 33 to 71 % of total P (Fig. 1). Apatite-P decreased while organic P increased with soil development. Apatite P decrease with soil development was higher in the loess and alluvium than shale and sandstone parent materials. The Chakwal (Udic Haplustalfs) and Rawalpindi (Udic Haplustepts) differ slightly in development as compared to Rajar (Typic Ustorthents). The Kahuta (Udic Haplustalfs) was lesser than Balkasar (Typic Haplustalfs) followed by Qazian (Lithic Ustipsamments), while in shale Murree (Typic Hapludolls) and Tirnul (Udic Haplustepts) were similar but lower than Ghoragali (Typic Udorthents) in apatite-P content. Apatite is the dominant form of P in many parent materials at early stage of soil development [22]. Apatite decreased from 503 mg kg⁻¹ in least weathered greywacke to 3 mg kg⁻¹ in strongly weathered greywacke [23]. Almost all P in unweathered greywacke (sandstone) and mica schist was in the form of apatite [24]. Apatite P was 70 % in weathered soil and almost 95% in less weathered soil of total P developed on basalt [25]. Soil developed on loess toposequence showed apatite P depletion with weathering [26].

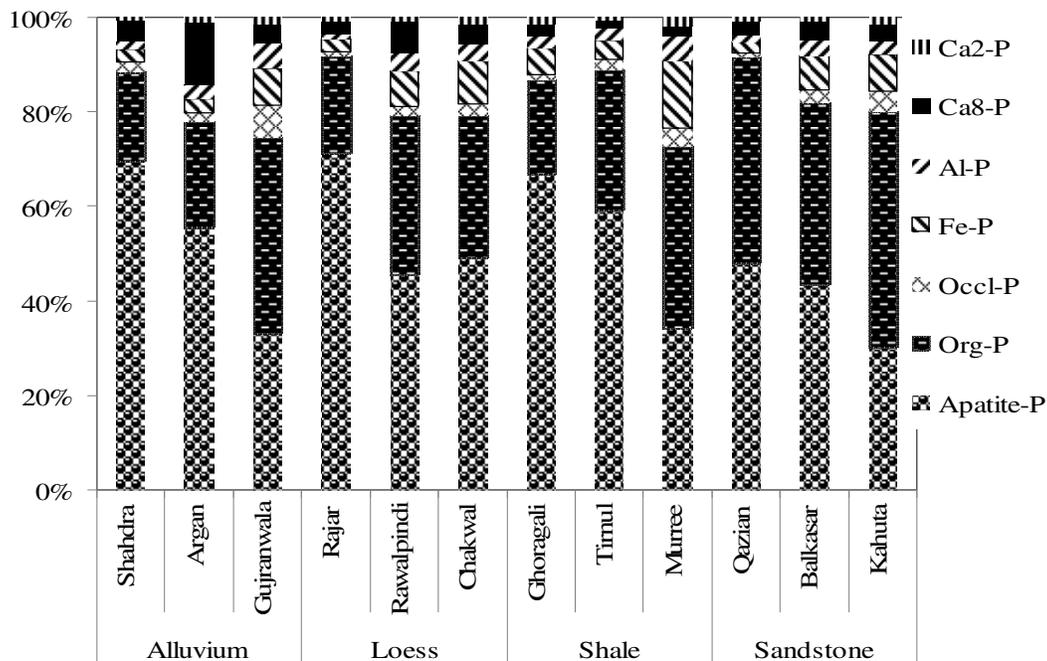


Fig. 1. Percent phosphorus fractions of total P in soils derived from different parent materials

Table 3. Soil basic properties in soils derived from different parent materials

PM	Soil Series	pH	Clay	CaCO ₃	Fe _d	Fe _o	TOC	DOC	Olsen-P
			----- g 100 g ⁻¹ -----	----- g kg ⁻¹ -----	----- mg kg ⁻¹ -----				
Alluvium	Shahdra	7.70 _(0.52)	19 _(1.91)	13.95 _(0.78)	10.55 _(0.02)	0.30 _(0.04)	3.10 _(0.61)	39 _(0.67)	4.25 _(1.15)
	Argan	7.70 _(2.63)	25 _(1.25)	7.05 _(1.73)	9.00 _(0.02)	0.40 _(0.13)	3.55 _(0.65)	40 _(0.56)	9.15 _(2.80)
	Gujranwala	7.30 _(3.20)	21 _(1.21)	0.95 _(2.90)	12.80 _(0.02)	0.65 _(0.13)	3.15 _(0.76)	51 _(0.55)	5.75 _(0.70)
Loess	Rajar	8.00 _(3.31)	23 _(1.17)	16.40 _(2.57)	7.70 _(0.03)	0.55 _(0.13)	3.15 _(0.76)	48 _(0.56)	6.80 _(2.0)
	Rawalpindi	7.25 _(2.97)	23 _(1.61)	0.90 _(2.89)	9.40 _(0.06)	0.95 _(0.12)	4.40 _(0.72)	63 _(0.48)	8.65 _(2.15)
	Chakwal	7.50 _(2.39)	34 _(1.55)	1.10 _(2.40)	9.55 _(0.07)	0.75 _(0.10)	3.95 _(0.36)	38 _(0.47)	5.85 _(0.85)
Shale	Ghoragali	7.30 _(0.18)	31 _(1.69)	14.85 _(1.98)	16.45 _(0.07)	0.70 _(0.06)	9.70 _(0.35)	72 _(0.08)	9.20 _(2.65)
	Tirnul	7.45 _(0.19)	34 _(2.23)	11.75 _(2.59)	17.35 _(0.07)	0.30 _(0.10)	3.20 _(0.35)	41 _(0.21)	3.25 _(0.65)
	Murree	6.40 _(0.19)	30 _(2.41)	1.00 _(2.59)	21.35 _(0.05)	1.95 _(0.10)	10.75 _(0.31)	83 _(0.25)	6.50 _(1.55)
Sandstone	Qazian	7.60 _(0.03)	13 _(2.93)	9.50 _(2.83)	4.85 _(0.04)	0.30 _(0.14)	2.95 _(0.22)	39 _(0.30)	4.15 _(0.45)
	Balkasar	7.65 _(0.03)	26 _(2.64)	1.60 _(1.61)	7.90 _(0.04)	0.50 _(0.13)	4.50 _(0.24)	79 _(0.28)	4.20 _(1.0)
	Kahuta	6.90 _(0.09)	21 _(2.95)	0.60 _(1.46)	8.15 _(0.06)	0.60 _(0.12)	3.20 _(0.19)	42 _(0.29)	6.05 _(0.95)

CaCO₃; calcium carbonate, Fe_d; dithionite extractable iron, Fe_o; oxalate extractable iron, TOC; total organic carbon, DOC; dissolved organic carbon, Olsen P; the number in parenthesis are standard errors

Secondary phosphates i.e. occluded P, iron oxides surface adsorbed P and aluminum oxides surfaces adsorbed P was the small fraction of total P. Occluded P ranged 0.80 – 4.0 %, iron oxides surface adsorbed P was 2.65 – 14 % and P adsorbed on aluminum oxides surfaces was 1.20 – 5.0 % of total P. Secondary phosphates increased with soil development in all parent materials except iron oxides surface adsorbed P was higher in Ghoragali, the soil at early stage of development (Entisols) than Tirnul (Inceptisols) is due to higher contents of oxalate extractable iron oxides in Ghoragali soil. Organic P was also the major fraction of total P and was 20 to 49 % of total P. Soil P occurs as apatite at the early stage of soil development and with weathering primary P mineral decreases giving rise to phosphorus other forms i.e. organic P, occluded P under adaphic and biotic processes. Soluble P released from primary mineral is taken up by biota or become organic P reservoir and/or adsorbed onto the surface of secondary minerals in soils to become non-occluded P [27]. The aluminum and iron adsorbed P is slowly converted to occluded with advance weathering, and non occluded P is physically encapsulated or surrounded by iron and aluminum oxides [28,29].

3.2 Phosphorus Uptake and Its Relation with Phosphorus Fraction

Phosphorus uptake was calculated from the measured concentration and plant biomass. The increase in P uptake with soil development differed within the parent material (Fig. 2). Phosphorus uptake increased with soil development in alluvial soils while P uptake was high in soils at intermediate stage of development in loess soils. High P uptake in Rawalpindi soil may be due to high iron oxides and organic matter sorbed P. Phosphorus uptake was lower in intermediate stage of development than soils at early and relatively higher level of development in shale and sandstone derived soils. High P uptake in Murree and Ghoragali soils is due to high organic P. Phosphate diesters i.e. nucleic acids and phospholipids are easily mineralizable and are important source of P for biota [2].

Phosphorus uptake by the maize plants significantly correlated with labile P fractions, Olsen P and organic P (Fig. 3). The bioavailability of soil P fraction follow the order

$Ca_2\text{-P} > \text{Org-P} > \text{Al-P} > \text{Fe-P} > Ca_8\text{-P} > \text{Occluded P} > \text{apatite-P}$. Phosphorus uptake exponentially increased with dicalcium phosphate and correlated significantly with $Ca_2\text{-P}$ (r 0.83; $p \geq 0.0001$). Dicalcium phosphate is mainly water extractable can be easily taken up by plants [9]. Samadi [30] reported that dicalcium P fraction is highly correlated with plant P uptake. Phosphorus uptake also significantly correlated with organic P (r 0.51; $p \geq 0.0001$). Nucleic acids and phospholipids are easily weatherable and are important source of P for biota [1,2]. Phosphorus uptake also positively correlated with Al-P and Fe-P (r 0.50; $p \geq 0.0001$; r 0.50; $p \geq 0.0001$). Phosphorus desorbed from aluminum and iron oxide surface can be taken by plants. The availability of soil P to plants depends on the replenishment of labile phosphorus from other P fractions [31]. Plant P uptake poorly correlated with occluded P and apatite-P. Apatite is resistant mineral and apatite-P cannot be taken up by plant and p entrapped in iron oxides bodies is also difficult to extract by plant.

We used stepwise multiple regression analysis for the prediction of P uptake from the Olsen P and the P fractions. From stepwise multiple regressions Olsen P was still better predictor of P uptake (Table 4). The $Ca_2\text{-P}$ with organic P gave better prediction of P uptake than Olsen P alone. Phosphorus uptake increased exponentially with increase in Olsen P (r 0.86). Olsen P is extracted with 0.5 M $NaHCO_3$ at pH 8.5 and mainly extracted all the $Ca_2\text{-P}$ and some fraction of $Ca_8\text{-P}$, Al-P and Fe-P but cannot extract the occluded P. In sever phosphorus deficiency plant roots can also extract P occluded in iron oxides bodies as Olsen P with occluded P also gave better P prediction than Olsen P alone. This confirms the results of Shen and Co. [6] that when P is severely deficient, the plants are able to access the sparingly soluble pools such as phosphates adsorbed on iron and aluminum oxides and Occluded P.

Table 4. Regression relations for predicting P uptake

Parameter	Equation	r^2
P-uptake	$Y=3.59+0.188\text{Olsen P}$	0.55
	$Y=3.011+0.211Ca_2P+0.04$ organic P	0.58
	$Y=3.21+0.029$ occluded P+0.196Olsen P	0.58

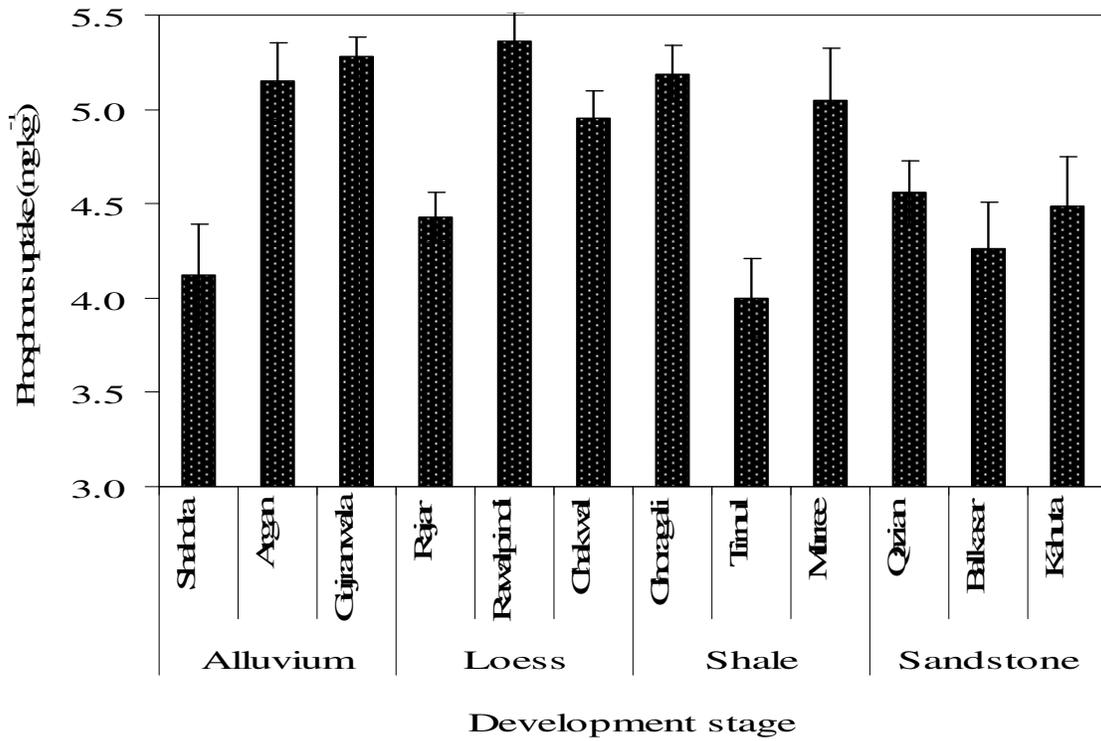


Fig. 2. Phosphorus uptake variation with soil development in soils derived from the parent materials; error bars shows the standard error

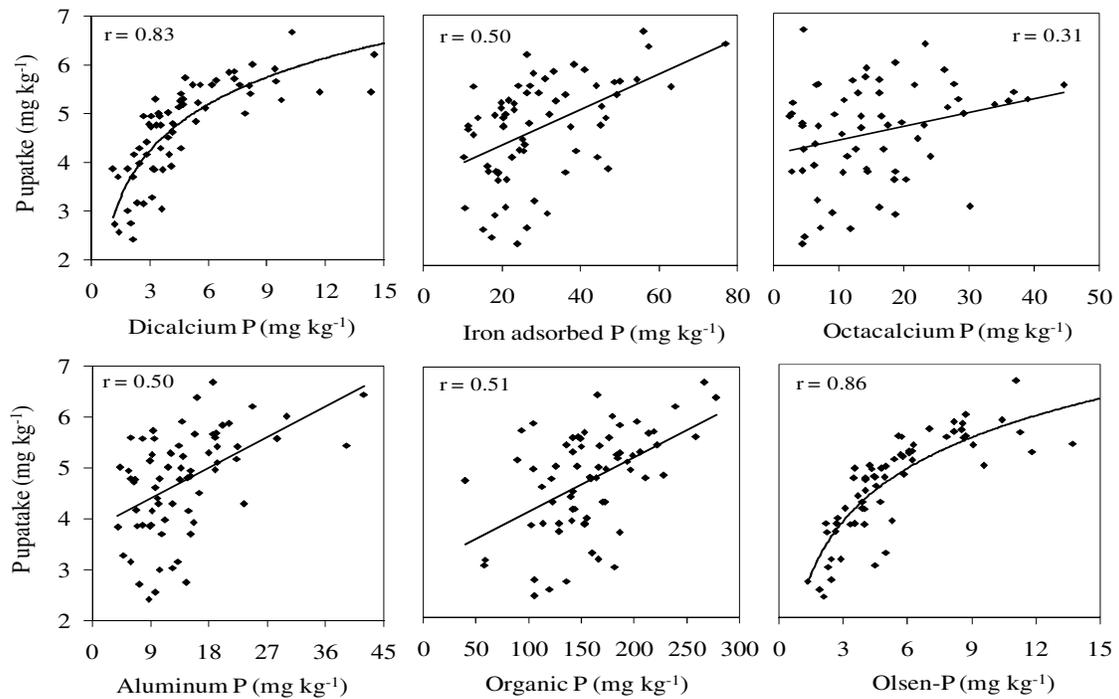


Fig. 3. Relationship of p uptake in maize with various P fractions' and Olsen P

4. CONCLUSION

Labile P fractions, secondary phosphates and apatite-P varied with soil development within parent materials. Phosphorus resembles with dicalcium phosphates, aluminum oxides and iron oxides surface adsorbed P and organic P correlated significantly with P uptake by *Zea mays*. From stepwise multiple regressions it is concluded that Olsen P with occluded P gave prediction for P uptake than Olsen P alone. Phosphorus uptake differed significantly with soil development (class) with parent material. Phosphorus uptake increased with soil development in alluvial soils while P uptake was highest at intermediate stage of development in loess. Phosphorus uptake remained similar with soil development in sandstone while was lowest in soil at intermediate stage of development in shale derived soils.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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