



Full Length Article

Dynamics of Phosphorus Pools in Subtropical Alkaline Soils

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Abstract

Knowledge about different phosphorus pools in the soil and their relationship with different soil properties is of immense significance for increasing phosphorus use-efficiency in agricultural systems. Fifteen soil series from the relevant agricultural fields were analysed for their phosphorus pools. The average size of different P pools (% of total P) in the soils was in order of, dHCl-P (63.7%) > cHCl-P_i (14.8%) > residual P (9.4%) > cHCl-P_o (3.8%) > $\text{NaHCO}_3\text{-P}_i$ (2.4%) > NaOH-P_i (2.0%) > $\text{NaHCO}_3\text{-P}_o$ (1.4%) > resin-P (1.3%) > NaOH-P_o (1.2%). Overall, the inorganic P pools comprised of 93.6% of total P in the soils and had highly significant positive correlation with soil pH and CaCO_3 content. The organic P constituted a small proportion (6.4%) of the total P and was positively correlated with the clay and organic C contents of the soils. The data indicated that organic P pool represents an important source of P in subtropical alkaline soil ecosystems. © 2014 Friends Science Publishers

Keywords: Calcareous soils; Inorganic P; Organic P; P pools

Introduction

Despite wide distribution of phosphorus (P) in nature, it is often a limited resource for crop production (Redel *et al.*, 2011). About 80 to 90% soils of arid and semiarid regions of the world like Pakistan are deficient in plant available phosphorus (NFDC, 2001). The P problem in alkaline calcareous soils is attributed to various adsorption and precipitation reactions of both the applied as well as indigenous soil P with Ca and/ or Fe and Al components (Khan and Joergensen, 2009). This demands application of large quantities of expensive inorganic P fertilizers for successful crop production putting extra economic burden on resource poor farmers of the developing countries like Pakistan. Moreover, diminishing P reserves with mining, and environmental hazards in the form of surface water eutrophication are the other problems associated with the over-use of inorganic P fertilizers (Barberis *et al.*, 1995). It is, thus, imperative to develop some practicable and cost effective P management strategies in order to increase P use efficiency and maintain soil fertility using the existing farmers resources (Gichangi *et al.*, 2009).

Plants take up P from the soil solution, which is replenished by various P pools in the soil (Mengel and Kirkby, 2001). Therefore, information regarding different P pools in soils and their relationship with available P and other soil properties is of potential significance to enhance P use efficiency in the soil-plant system (Mostashari *et al.*, 2008; Halajnia *et al.*, 2009). Lajtha and Schlesinger (1988)

indicated the importance of geochemical processes for P cycling in the semiarid calcareous soils. Ligand exchange between P and carbonate minerals restricts the P availability in alkaline soils, whereas phosphate precipitation with calcium determines the upper limit for P availability in the calcareous soils (Cross and Schlesinger, 2001). Organic anions may increase P availability in soil solution by competing P for adsorption sites on calcite grains (Reddy *et al.*, 2005) but semiarid soils usually lack appreciable levels of organic matter. Thus, while geochemical properties limit labile P pool, the biologically-available P (organic P) may contribute to P cycling and P availability in the semiarid alkaline calcareous soils.

Many researchers have focussed on inorganic P pools whereas the dynamics of more labile organic P pools have been, in general, ignored in the semiarid soils with low organic matter. This is particularly true for the semiarid, subtropical alkaline soils of Pakistan where so far no significant work on P fractions and their contribution to plant available P has been reported. Therefore, an effort has been made to quantify different organic and inorganic P pools in semiarid, alkaline soils of Potohar, Pakistan and determine their relationship with physico-chemical soil properties.

Materials and Methods

Background and Collection of Soil Samples

Representative surface soil samples (0-15 cm) of 15

prominent soil series (Argan, Balkassar, Basal, Chakwal, Dhumman, Domel, Guliana, Kahuta, Missa, Qutbal, Rajar, Rawalpindi, Satwal, Therpal and Tirnaul) were collected from agricultural fields of Potohar plateau of the Punjab province of Pakistan during September, 2008. The soils were developed from loess, alluvium and residuum parent materials and classified as *Ustochrepts* (Argan, Domel, Kahuta, Missa, Rawalpindi, Tirnaul), *Haplargids* (Balkassar, Chakwal, Dhumman), *Camborthids* (Basal, Therpal), *Haplustalf* (Guliana), *Ustorthents* (Qutbal), *Torriorthents* (Rajar) and *Chromusterts* (Satwal) according to USDA soil classification system (Ali, 1967; Zeb *et al.*, 1970; Choudhary and Khan, 1974). Among 15 soils, 3 (Guliana, Kahuta and Rawalpindi) were non-calcareous while remaining 12 soils varied between slightly and strongly calcareous. All the experimental sites were fallow at the time of sampling and contained moisture contents below field capacity. The mean annual temperature of the experimental area is 24.5°C and the mean annual rainfall is 750 mm, of which more than 70% is received in the months of July to September as monsoon rains. Major crops grown in the area are wheat, groundnut, oilseed rape, millet and maize. In general, soil management is poor and lacks use of modern technology because of less awareness and poor economic conditions of the farmers. Tillage is carried out usually with cultivators up to 12-15 cm soil depth whereas some farmers occasionally use mouldboard plough down to 20 cm depth. Being rain-fed area, use of inorganic fertilizers is not up to the mark and the application of organic manures is also limited (Mufti, 2011).

The soil samples (1.5 kg) were taken from four different locations of each selected site using soil auger. All the soil samples were air-dried, passed through a 2-mm sieve and analysed for different P fractions. Grinding of soil samples might cause over estimation of labile P pools by exposing the phosphorus held in the internal structure of crystalline minerals (Cross and Schlesinger, 2001). Thus, un-ground soil samples were used for P fractionation.

Soil Analysis

Particle size distribution was carried out by hydrometer method after dispersion with sodium hexametaphosphate (Gee and Bauder, 1986). Water holding capacity was determined by preparing a saturated soil paste (Anderson and Ingram, 1993). Water holding capacity (WHC) was determined after 24 h drying at 105°C. Soil pH and electrical conductivity were determined in 1:2.5 (w/w) soil:water suspensions (Anderson and Ingram, 1993). For the measurement of cation exchange capacity, sodium from samples was replaced with ammonium acetate solution and measured on the flame photometer (Hinga *et al.*, 1980). Olsen P was measured at 882 nm using spectrophotometer (UV-1700, Shimadzu, Japan) after extraction with 0.5 M NaHCO₃ adjusted to pH 8.5 (Olsen and Sommers, 1982) and colour development by Murphy and Riley (1962)

method. Total organic carbon (TOC) was determined by Walkley-Black method (Nelson and Sommers, 1982) and calcium carbonate (CaCO₃) was measured by acid neutralization (Ryan *et al.*, 2001). For the determination of total N, P, K, Ca and Mg, 0.2 g soil samples were digested with 4.4 mL digestion mixture containing selenium powder, lithium sulphate, hydrogen per oxide (30%) and sulphuric acid at 360°C for at least 2 h (until colorless). In the clear digest, N and P contents were measured colorimetrically using spectrophotometer (UV-1700, Shimadzu, Japan) at 665 and 882 nm wavelengths, respectively (Anderson and Ingram, 1993). Total Ca and Mg were measured in the digest with atomic absorption spectrometer (GBC 932 plus), whereas total K was determined using flame photometer (PFP7, Jenway, England).

P Fractionation (Sequential Extraction)

Soil samples were subjected to sequential P fractionation using a modified Hedley fractionation method (Hedley *et al.*, 1982) as described by Tiessen and Moir (1993). Air-dried samples of 0.5 g (oven dry basis) soil were placed in 50 mL centrifuge tubes and horizontally shaken for 16 h at room temperature at 175 rev min⁻¹ with 1 resin strip (6×2 cm, anion-exchange resin) in 30 mL deionised H₂O. The P adsorbed by resin strip was recovered in 30 mL of elution solution (0.1 M NaCl + HCl) after shaking for 2 h and inorganic P in the eluents was determined (Kouno *et al.*, 1995). The suspension was centrifuged for 10 min at 8000 rpm and the supernatant discarded. The soil residues left in the centrifuge tubes were then sequentially extracted with 30 mL each of 0.5 M NaHCO₃ (pH 8.5), 0.1 M NaOH and 6M HCl after 16 h shaking (end to end) at room temperature at 175 rev min⁻¹. The suspensions were centrifuged at 8000 rpm for 15 min and filtered with Whatman No. 42. A portion of NaHCO₃ and NaOH extracts was acidified to precipitate extracted organic matter and the supernatant was analysed for inorganic P (P_i). Another portion of NaHCO₃ and NaOH extracts was digested with acidified ammonium persulphate in an autoclave at 120 kPa and 121°C (60 min for NaHCO₃ and 90 min for NaOH extract) and analysed for total P (P_t) (Greenberg *et al.*, 1992). For the determination of concentrated HCl-P (6HCl-P), the soil residues (obtained after 6HCl extraction) were heated for 10 min in 10 mL 6HCl at 80°C in a water bath. Then 5 mL 6HCl was added and centrifuged, and P content measured in HCl solution after adjusting pH to 1.5. Total P (P_t) in 6HCl fraction was measured by digesting 5 mL of the 6HCl solution in acidified ammonium per sulphate for 60 min in an autoclave at 120 kPa and 121°C. The organic P (P_o) in NaHCO₃, NaOH and 6HCl extracts was obtained as the difference between P_t and P_i of respective extracts. Finally, the residual P in soil samples was determined after digestion with H₂SO₄-H₂O₂. The P concentration in all extracts and digestion solutions was determined colorimetrically at 882 nm (Murphy and Riley, 1962).

Statistical Analysis

The results are presented as arithmetic means of 15 soil series showing variability of various experimental sites as expressed on an oven dry weight basis (24 h at 105°C). Arithmetic means, minimum and maximum values and coefficients of variation (CV) of different soil parameters were estimated by using Microsoft Excel Package (Office-2007). This package was also used for plotting graphs and drawing figures. Regression and correlation analysis were carried out using mean values to see interrelation between different P fractions and soil physical and chemical properties. Confidence interval (CI) of different P fractions was measured by Statistica 9.0.

Results

Physico-chemical Properties of Soil

Texture of the soils varied between sandy loam and clay loam with dominance of silt loam (Table 1). Sand, silt and clay contents varied from 5-71%, 16-74% and 11-43 % with mean values of 30%, 48% and 22%, respectively. Water holding capacity ranged from 23-36% with mean value of 28%.

All the soils were alkaline in nature having pH in the range of 7.2-8.3 with an average of 8.0 (Table 2). Electrical conductivity of the soils varied between 0.07 to 0.60 dS m⁻¹ with mean value of 0.17 dS m⁻¹ which indicated that none of these was salt-affected. Cation exchange capacity of the soils was in the range of 9.0 to 19.2 cmol kg⁻¹ having mean value of 14.1 cmol kg⁻¹. Calcium carbonate varied extensively in soils (0.2-17.6%) with an average of 7.9% to be classified into non-calcareous/ slightly calcareous to strongly calcareous. Soil organic carbon ranged between 1.5 to 10.1 mg g⁻¹ soil with average value of 5.0 mg g⁻¹ soil. The mean concentrations of total N and K were 0.5 and 14.3 mg g⁻¹ varying in the range of 0.2 to 0.9 and 9.1 to 19.8 mg g⁻¹ soil, respectively. Bioavailable P determined as 0.5 M NaHCO₃ extractable P ranged from 2.2 to 19.7 µg g⁻¹ soil with average value of 6.4 µg g⁻¹ soil. It was 1.3 % of total P which indicated that soils of Potohar are deficient in plant available P. Total P content of the soils ranged from 178-653 µg g⁻¹ having mean value of 495 µg g⁻¹ soil, being lower in non-calcareous compared to the calcareous soils. The average amounts of total Ca and Mg were 8.9 and 9.5 mg g⁻¹ varying between 0.8 to 25.4 and 5.7 to 14.3 mg g⁻¹ soil, respectively.

Phosphorus Pools in Soil

The average size of different P pools in the soils increased in the order: NaOH-extractable P_o (1.2%) < resin P (1.3%) < NaHCO₃-extractable P_o (1.4%) < NaOH-extractable P_i (2.0%) < NaHCO₃-extractable P_i (2.4%) < $\frac{1}{2}$ HCl-extractable P_o (3.8%) < residual P (9.4%) < $\frac{1}{2}$ HCl-extractable P_i (14.8%) < $\frac{1}{4}$ HCl-extractable P (63.7%). The labile P fractions (resin-P, NaHCO₃-P_i and NaHCO₃-P_o)

Table 1: Physical properties of Potohar soils

Soil Series	Sand	Silt	Clay	WHC
			(%)	
Argan	61	28	11	25
Balkassar	65	22	13	24
Basal	11	60	29	32
Chakwal	20	54	26	30
Dhumman	54	30	16	24
Domel	10	72	19	28
Guliana	5	63	32	36
Kahuta	71	16	14	24
Missa	7	74	19	29
Qutbal	12	62	26	29
Rajar	22	62	16	25
Rawalpindi	8	70	21	30
Satwal	14	42	43	31
Therpal	61	26	13	23
Tirmaul	30	38	32	32
Mean	30	48	22	28

accounted for 5.1%, whereas hydroxide fraction constituted 3.1% of the total P. The largest P fraction was Ca-associated $\frac{1}{4}$ HCl-P which comprised of 63.7% of the total P pool. The highly stable and recalcitrant P forms including $\frac{1}{2}$ HCl-P_i, $\frac{1}{2}$ HCl-P_o and residual-P contributed 28% to the total P pool. Organic fractions as a whole made up a small portion of the total P pool comprising 6.4% only, while the remaining 93.6% constituted by various inorganic fractions.

The absolute concentration of resin P varied between 2.2 to 17.6 µg g⁻¹ with an average content of 6.4 µg g⁻¹ soils (Table 3). The average content of 0.5 M NaHCO₃ extractable P_i and P_o were 11.9 and 6.9 µg g⁻¹ varying in the range of 3.6-29.4 and 2.3-17.1 µg g⁻¹ soil, respectively. The amounts of 0.1 M NaOH extractable P_i and P_o ranged from 3.5-24.6 and 1.9-12.6 µg g⁻¹ with average of 9.7 and 5.9 µg g⁻¹ soils, respectively. The dominant and relatively stable fraction $\frac{1}{4}$ HCl (1.0 M) extractable P ranged from 74.5 to 437.4 µg g⁻¹ with an average of 315.6 µg g⁻¹ soil. The average contents of $\frac{1}{2}$ HCl extractable P_i and P_o were 73.5 and 18.9 µg g⁻¹ varying in the range of 37.2-128.9 and 4.9-31.1 µg g⁻¹ soil, respectively. Residual P was in the range of 29.5 to 63.2 µg g⁻¹ with an average of 46.4 µg g⁻¹ soil. The confidence intervals for different P pools in soils given in Table 3 indicated 95% probability of mean being in between the range given against each.

Correlation between P Pools and Soil Properties

The labile P pool (resin-P, NaHCO₃-P_i, NaHCO₃-P_o) exhibited significant positive correlation with Olsen P in soil. The $\frac{1}{4}$ HCl-P showed highly significant positive correlation ($P < 0.01$) with soil pH and CaCO₃ contents, while the correlation between NaOH-P_i and soil pH was negative. All organic P pools were significantly ($P < 0.05$) positively related to the clay and organic carbon (SOC) contents of soil (Table 4). Similarly, highly stable $\frac{1}{2}$ HCl-P_i, $\frac{1}{2}$ HCl-P_o and residual-P pools were negatively related to the sand contents and positively related to the silt and clay contents.

Table 2: Chemical properties of Potohar soils

Soil Series	pH _{1,2,5}	EC _{1,2,5} dS m ⁻¹	CEC cmol kg ⁻¹	CaCO ₃ %	SOC mg g ⁻¹	Total N mg g ⁻¹	Olsen P µg g ⁻¹	Total K mg g ⁻¹	Total Ca mg g ⁻¹	Total Mg mg g ⁻¹
Argan	8.1	0.12	9.0	12.4	7.3	0.7	15.7	9.8	12.3	9.2
Balkassar	8.2	0.13	10.7	9.2	2.8	0.3	2.9	12.0	6.2	11.3
Basal	8.2	0.13	17.5	9.7	2.7	0.3	2.3	16.9	3.6	13.2
Chakwal	7.8	0.17	18.5	1.0	5.0	0.4	6.0	16.1	0.8	9.5
Dhumman	8.0	0.13	13.8	6.0	3.5	0.3	3.3	10.7	4.7	9.8
Domel	8.2	0.12	12.7	11.5	4.0	0.4	6.2	15.5	16.7	8.4
Guliana	7.8	0.08	19.2	0.3	9.3	0.9	4.6	19.8	2.3	9.1
Kahuta	7.8	0.07	12.6	0.2	3.4	0.3	3.1	9.1	2.8	6.3
Missa	8.2	0.13	14.1	13.2	4.7	0.4	4.1	17.0	10.8	9.8
Qutbal	8.3	0.12	11.6	17.6	3.7	0.5	2.2	15.5	24.4	10.4
Rajar	8.0	0.60	11.8	13.8	1.5	0.2	3.5	16.6	12.3	14.3
Rawalpindi	7.2	0.17	14.7	0.3	5.8	0.5	6.8	15.6	1.2	5.7
Satwal	8.0	0.24	18.2	3.2	7.5	0.8	19.7	14.6	3.3	9.3
Therpal	8.3	0.10	11.4	3.8	3.8	0.4	5.3	11.3	7.2	8.8
Tirnaul	8.2	0.20	16.4	16.8	10.1	0.7	9.6	13.5	25.4	7.6
Mean	8.0	0.17	14.1	7.9	5.0	0.5	6.4	14.3	8.9	9.5
Minimum	7.2	0.07	9.0	0.2	1.5	0.2	2.2	9.1	0.8	5.7
Maximum	8.3	0.60	19.2	17.6	10.1	0.9	19.7	19.8	25.4	14.3
CV (± %)	0.20	0.62	1.2	5.2	2.4	5.4	2.5	1.6	3.9	2.8

CV = coefficient of variation between replicates (n = 4), SOC = soil organic carbon, CEC = cation exchange capacity

Table 3: Different P pools in the Potohar soils

Soil Series	Resin P	NaHCO ₃ -P		NaOH-P		dHCl-P	dHCl-P		Residual P
		P _i	P _o	P _i	P _o		P _i	P _o	
						(µg g ⁻¹ soil)			
Argan	14.1	25.4	6.0	12.8	7.7	377.4	57.8	12.8	38.2
Balkassar	10.1	5.5	5.2	3.5	1.9	429.4	54.9	10.4	46.2
Basal	3.1	5.4	4.9	5.9	3.4	346.8	117.0	18.5	52.2
Chakwal	6.3	6.7	5.7	8.6	5.8	272.3	62.2	23.4	45.4
Dhumman	6.4	5.1	7.6	5.0	4.2	287.3	48.8	19.7	41.8
Domel	5.5	12.8	2.3	5.6	5.6	367.5	81.4	21.9	55.6
Guliana	2.5	3.6	9.3	13.7	12.6	122.2	128.9	29.4	60.5
Kahuta	2.2	5.9	9.2	8.1	3.9	74.5	37.2	7.1	29.7
Missa	3.3	12.4	5.8	7.7	6.7	409.8	86.5	21.5	63.2
Qutbal	3.2	9.2	3.8	4.7	5.4	435.5	68.6	18.1	52.2
Rajar	3.0	11.4	2.4	7.0	3.9	424.9	76.0	4.9	29.5
Rawalpindi	2.5	14.7	4.7	24.6	6.5	137.0	102.4	21.9	46.9
Satwal	17.6	29.4	17.1	16.4	8.9	437.4	61.8	28.9	35.5
Therpal	7.2	9.1	8.2	7.2	2.2	345.9	40.7	14.0	37.3
Tirnaul	8.5	21.2	10.8	15.0	9.2	265.9	77.7	31.1	61.2
Mean	6.4	11.9	6.9	9.7	5.9	315.6	73.5	18.9	46.4
CV (± %)	5.1	7.2	4.5	6.5	4.6	2.5	4.7	8.4	4.6
CI (95%)	3.8-8.9	7.5-16.2	4.8-8.9	6.5-12.9	4.3-7.5	248.8-382.4	58.7-88.2	14.5-23.3	40.3-52.5

CV = coefficient of variation between replicates (n = 4), CI = confidence interval at 95 % level

Table 4: Correlations (Pearson) between P pools and physico-chemical properties of soils

Property	Resin-P	NaHCO ₃ -P _i	NaHCO ₃ -P _o	NaOH-P _i	NaOH-P _o	dHCl-P	dHCl-P _i	dHCl-P _o	Residual-P
Sand							-0.78**	-0.59*	-0.57*
Silt							0.75**		0.55*
Clay			0.59*		0.62*			0.79**	
pH				-0.71**		0.72**			
CaCO ₃						0.66**			
SOC		0.53*	0.59*	0.68**	0.89**			0.76**	
Total N		0.54*	0.61*	0.65**	0.89**			0.69**	
Total P						0.93**			
Olsen P	0.85**	0.92**	0.63*	0.56*					
Total Mg				-0.57*		0.65**			

*, ** Significant at 5% and 1% levels of probability, respectively

Discussion

Among different P fractions in soil, resin P and bicarbonate

extractable P (P_i and P_o) pools are collectively considered as bio-available or labile P (Sui et al., 1999). The labile pool was lowest proportionally and accounted for 5.1%

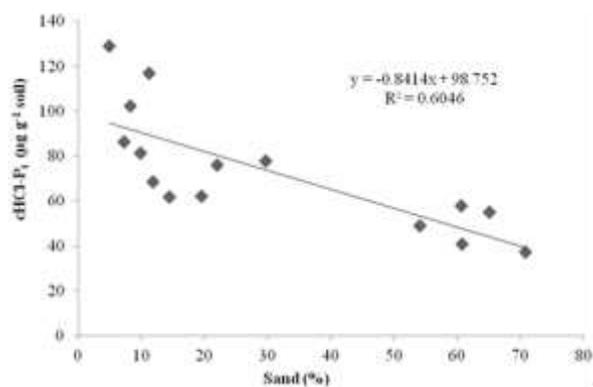


Fig. 1: Correlation between sand contents and ${}_{\text{d}}\text{HCl-P}_i$ in soil

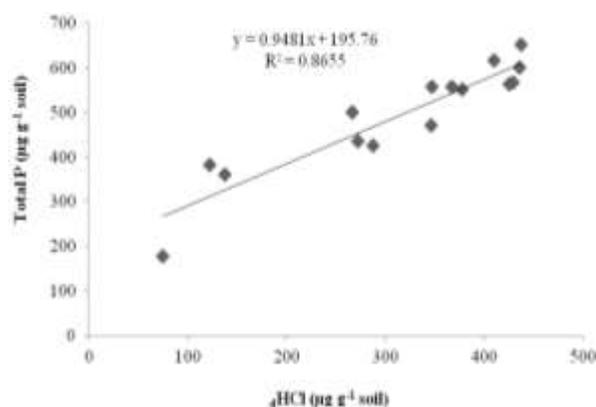


Fig. 2: Correlation between total P and ${}_{\text{d}}\text{HCl-P}_i$ in soil

of the total P in the soils. In general, sandy loam soils had higher concentrations of resin P compared to the silt loam or silty clay loam soils. Thus, the contents of resin P were linked to the particle size distribution in the soils. More resin P in the sandy soils is attributed to the low P-fixing capacity of such soils. As most P-fixing compounds are associated with the fine soil fractions thus, phosphorus fixation tends to be higher in the soils having high clay contents (Brady and Weil, 2008).

The bicarbonate extractable P_i ($\text{NaHCO}_3\text{-P}_i$) corresponds to the P sorbed on the surfaces of soil colloids and is considered as the easily available P to crop plants (Reddy *et al.*, 2005). In the present study, bicarbonate extractable P_i accounted for 2.4% of total P in the soils, and is quite similar to the findings of Lajtha and Schlesinger (1988) and Tiessen and Moir (1993). There was a significant positive correlation between $\text{NaHCO}_3\text{-P}_i$ and the organic carbon contents in the soils because organic soil components, particularly those containing P may release phosphorus to the $\text{NaHCO}_3\text{-P}_i$ pool through mineralization (Cassagne *et al.*, 2000). The results are in agreement with Wang *et al.* (2008).

The $\text{NaHCO}_3\text{-P}_o$ defines the P associated with easily

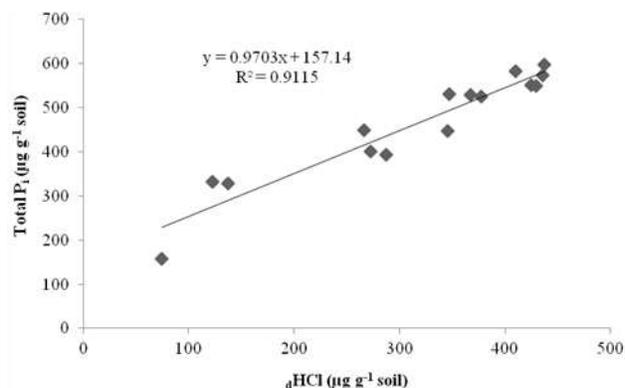


Fig. 3: Correlation between total P_i and ${}_{\text{d}}\text{HCl-P}_i$ in soil

mineralisable organic soil components (Bolan, 1991). This fraction was 1.4% of the total soil P within the ranges reported by others (Cross and Schlesinger, 2001; Scherer and Sharma, 2002). Generally, the soils having higher organic C have higher values of labile P fraction. This is because of the direct relationship between organic C and microbial biomass P contents in the soil, the major part of which becomes part of the $\text{NaHCO}_3\text{-P}_o$ fraction in the soil after microbial turnover (Wang *et al.*, 2008). The contents of CaCO_3 and total Ca could be the other factors affecting the $\text{NaHCO}_3\text{-P}_o$ pool in soils as this P pool was lower in the soils having high CaCO_3 and Ca contents (Cross and Schlesinger, 2001). The soils with higher concentrations of CaCO_3 and total Ca usually have higher pH values. Thus, a negative correlation between $\text{NaHCO}_3\text{-P}_o$ and soil pH has also been observed in the present study which conforms the findings of Wang *et al.* (2006).

NaOH-P (P_i and P_o) is considered to be the P associated with the surface of amorphous and some crystalline Fe and Al minerals and is perhaps available in intermediate term (Cross and Schlesinger, 2001). In present investigation, this P fraction constituted 3.1% of the total P, with 1.9 and 1.2% contributions as the NaOH-P_i and NaOH-P_o , respectively. The above values are within the ranges reported by Roberts *et al.* (1985) and Cross and Schlesinger (2001) for Mollisols and Aridisols. In contrast, the values were much lower than those reported for acidic soils by Cassagne *et al.* (2000). The variability among soils was mainly associated with the soil pH as usually the higher amounts of NaOH-P_i were found in soils having lower pH values. A strong positive correlation between NaOH-P_o and organic C content in the soils supports the previous conclusion drawn by Wang *et al.* (2008). The NaOH extracts P mainly from organic components and some amorphous aluminum-containing compounds in soil (Cassagne *et al.*, 2000) i.e., the P associated with humic acids or chemisorbed to the surfaces of Fe and Al compounds. The products of microbial decomposition of organic materials might solubilise some of the sorbed or recalcitrant P in soil causing an increase in organic P

associated with the humic substances (Reddy *et al.*, 2005).

The amount of dHCl-P was highest among all P fractions, which indicated the influence of geochemical properties on P cycling dominated by high concentrations of CaCO_3 minerals (Cross and Schlesinger, 2001). This implies that a large proportion of inorganic P in the soils existed in association with calcium carbonate (Wang *et al.*, 2008). Among 15 soils under study, three non-calcareous soils had significantly lower concentration of dHCl-P (37.3%) compared to the other 12 calcareous soils (67.5%). These findings are in agreement with Yang *et al.* (2002) who reported existence of more than 65% of total P in dHCl-P pool in calcareous soils. The principle behind this relationship is most probably the precipitation of P with Ca ions as dicalcium phosphate as well as surface precipitation on solid CaCO_3 (Mackay *et al.*, 1986).

The concentrated HCl derives P_i and P_o occluded in Al and Fe minerals and from apatite (Tiessen and Moir, 1993). This fraction accounted for 18.6% of the total P with 14.8 and 3.8% contributions as the cHCl-P_i and cHCl-P_o , respectively in the present set of soils. These contributions were similar to those reported by Cross and Schlesinger (2001) in Aridisols. The higher concentrations of cHCl-P_i were found in fine textured soils compared to those in coarse textured soils which indicated the influence of particle size distribution. Wang *et al.* (2008) reported a strong positive correlation of cHCl-P_i with silt and clay contents and the negative correlation with sand contents in semiarid wetland soils from Northeast China which is in line with our findings. Regression analysis revealed that 60% variability in this fraction among the soils was because of sand content (Fig. 1). The cHCl-P_o is thought to be derived from particulate organic matter that is unextractable with the alkali but may become readily bioavailable after decomposition (Tiessen and Moir, 1993). Usually, fine textured soils with high organic C contents have more particulate organic matter and thus more cHCl-P_o (Anderson, 1988). Also the Fe and Al minerals in which cHCl-P_o is occluded are more abundant in fine textured soils.

Residual P is highly stable part of total P pool and is available to plants in long-term only (Cross and Schlesinger, 1995). The residual P had highly significant negative correlation with sand content and significant positive correlation with silt contents which demonstrated that residual P comprises high molecular weight organic compounds (humus) and originates from Fe and Al compounds. These results are consistent with the previous work of Wang *et al.* (2008) where strong positive correlations of residual P with silt and clay and negative correlation with sand contents in four semiarid wetland soils of China have been reported.

The total P (sum of all organic and inorganic P fractions) in the soils under investigation varied from 0.02-0.07%, which was within the range (0.02-0.15%) reported for total P in soils by Mengal and Kirkby (2001) and Ahmad

et al. (2006). There was significant positive correlation of total P with pH and CaCO_3 in the soils. This may be due to the fact that dHCl-P fraction dominated the total P with 64% contribution in the soils reported herein. Regression analysis showed that dHCl fraction accounted for 86% variability in the total P in the soils under study (Fig. 2). Thus all factors which control variability in dHCl-P pool also controlled the variability in total P.

The total P_i was 93.6% of the total P, and had highly significant positive correlation with dHCl-P , which showed the strong contribution of dHCl-P to the total P_i in soils under study. The regression analysis indicated that dHCl-P accounts for 91% variability in total P_i in the soils (Fig. 3). Thus, the factors, which control dHCl fraction in the soil also controlled total P_i in these soils. Strong positive relationship between total P_i and pH, CaCO_3 and total Mg contents in soil supported this interpretation. However, these observations are entirely different from the findings reported for acidic soils in previous studies in which hydroxide fraction dominated the total P_i (Cassagne *et al.*, 2000).

The total P_o was 6.4% of the total P and was mainly associated with the particle size distribution and organic C contents in the soils. The cHCl-P_o was the major component of total P_o in the soils with its 59.8% share, whereas the contributions of $\text{NaHCO}_3\text{-P}_o$ and NaOH-P_o were 21.7% and 18.5%, respectively. These results corroborate the findings of Wang *et al.* (2008) who reported the predominance of cHCl-P_o in total organic P pool with 45-68% contributions. The total P_o had highly significant positive correlation with clay and organic C content of the soils which advocated the role of soil mineralogy in soil fertility with respect to P availability. The biologically available P (proportion of $\text{NaHCO}_3\text{-P}_o$ in labile P) was 29.5% of the labile P indicating the importance and role of biological processes in P cycling in the soils having low organic matter content (Cross and Schlesinger, 2001).

Olsen P (non-sequentially extractable $\text{NaHCO}_3\text{-P}_i$) was 1.28% of the total P and had highly significant positive correlation with sequentially extracted $\text{NaHCO}_3\text{-P}_i$ as expected but the concentrations of sequentially extracted $\text{NaHCO}_3\text{-P}_i$ were 0.8 to 4.1 folds higher than Olsen P. This can be explained by variation in soil to extractant ratio, and the shaking periods employed in the extractions (Reddy *et al.*, 2005). In sequential extraction, soil to extractant ratio and shaking times were 1:60 and 16 h respectively, whereas in case of Olsen P extraction, these were 1:20 and 30 min respectively. Previous work indicated that concentration of NaHCO_3 -extractable P increased by decreasing the soil to extractant ratio and increasing the shaking time (Reddy *et al.*, 2005).

The present study concludes that dHCl-P pool was dominant with 64% proportion of the total P in the present set of soils and had highly significant positive correlation with soil pH and CaCO_3 contents. Overall, the size of organic P pool was smaller (6.4% of the total P) in the soils and had significant positive correlation with organic C

and clay contents in the soils. The inorganic P pool constituted 93.6% of the total P in the soils and had highly significant positive correlation with soil pH and CaCO₃ contents. The labile P pool (resin-P, NaHCO₃-P_i and NaHCO₃-P_o) had significant positive correlation with Olsen P in the soils.

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References

- Ahmad, W., Rahmatullah, M.A. Gill and T. Aziz, 2006. Bioavailability of inorganic phosphorus fractions in calcareous soils estimated by Neubauer technique, iron-impregnated filter paper, and chemical tests. *Comm. Soil Sci. Plant Anal.*, 37: 1185–1193
- Ali, M.A., 1967. *Reconnaissance Soil Survey of the Rawalpindi Area*. Directorate of Soil Survey, West Pakistan, Lahore
- Anderson, D.W., 1988. The effect of parent material and soil development on nutrient cycling in temperate ecosystems. *Biogeochemistry*, 5: 71–97
- Anderson, J.M. and J.S.I. Ingram, 1993. *Tropical Soil Biology and Fertility*. CAB International, Wallingford, UK
- Barberis, E., F.A. Marsan, R. Scalenghe, A. Lammers, U. Schwertmann, A.C. Edwards, R. Maguire, M.J. Wilson, A. Delgado and J. Torrent, 1995. European soils overfertilized with phosphorus: Part 1. Basic properties. *Nutr. Cycl. Agroecosys.*, 45: 199–207
- Brady, N.C., and R.R. Weil, 2008. *The Nature and Properties of Soils*, 14th edition. Prentice Hall, Upper Saddle River, New Jersey, USA
- Bolan, N.S., 1991. A critical review of the role of mycorrhizal fungi in uptake of phosphorus by plants. *Plant Soil*, 134: 189–207
- Cassagne, N., M. Remaury, T. Gauquelin and A. Fabre, 2000. Forms and profile distribution of soil phosphorus in alpine Inceptisols and Spodosols (Pyrenees, France). *Geoderma*, 95: 161–172
- Choudhary, M.R. and A. Khan, 1974. *Soil Series Key and Soil Classification*. Directorate of Soil Survey, West Pakistan, Lahore
- Cross, A.F. and W.H. Schlesinger, 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma*, 64: 197–214
- Cross, A.F. and W.H. Schlesinger, 2001. Biological and geochemical controls on phosphorus fractions in semiarid soils. *Biogeochemistry*, 52: 155–172
- Gee, G.W. and J.W. Bauder, 1986. Particle size analysis. In: *Methods of Soil Analysis*, pp: 383–411. Klute A. (ed.). American Society of Agronomy, No. 9, Madison, Wisconsin, USA
- Gichangi, E.M., P.N.S. Mkeni and P.C. Brookes, 2009. Effects of goat manure and inorganic phosphate addition on soil inorganic and microbial biomass phosphorus fractions under laboratory incubation conditions. *Soil Sci. Plant Nutr.*, 55: 764–771
- Greenberg, A.E., L.S. Clesceri and A.D. Eaton, 1992. *Standard Methods for the Examination of Water and Waste Water*. American Public Health Association, Washington, DC, USA
- Halajnia, A., G.H. Haghnia, A. Fotovat and R. Khorasani, 2009. Phosphorus fractions in calcareous soils amended with P fertilizer and cattle manure. *Geoderma*, 150: 209–213
- Hedley, M.J., J.W.B. Stewart and B.S. Chauhan, 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Amer. J.*, 46: 970–976
- Hinga, G., F.N. Muchena and C.M. Njihia, 1980. *Physical and Chemical Methods of Soil Analysis*. National Agricultural Research Laboratories, Nairobi, Ministry of Agriculture, Kenya
- Khan, K.S. and R.G. Joergensen, 2009. Changes in microbial biomass and P fractions in biogenic household waste compost amended with inorganic P fertilizers. *Bioresour. Technol.*, 100: 303–309
- Kouno, K., Y. Tuchiya and T. Ando, 1995. Measurement of soil microbial biomass phosphorus by an anion exchange membrane method. *Soil Biol. Biochem.*, 27: 1353–1357
- Lajtha, K. and W.H. Schlesinger, 1988. The biogeochemistry of phosphorus cycling and phosphorus availability along a desert soil chronosequence. *Ecology*, 69: 24–39
- Mackay, A.D., J.K. Syers, R.W. Tillman and P.E.H. Gregg, 1986. A simple model to describe the dissolution of phosphate rock in soil. *Soil Sci. Soc. Amer. J.*, 50: 291–296
- Mengel, K. and E.A. Kirkby, 2001. *Principles of Plant Nutrition*, 5th edition. Kluwer Academic Publishers, London
- Mostashari, M., M. Muazardalan, N. Karimian, H.M. Hosseini and H. Rezaei, 2008. Phosphorus Fractions of Selected Calcareous Soils of Qazvin Province and their Relationships with Soil Characteristics. *Amer.-Eurasian J. Agric. Environ. Sci.*, 3: 547–553
- Mufti, S., 2011. An epidemiological study of bovine fasciolosis in Pothwar region, Pakistan. *Ph.D. Thesis*, Department of Zoology, Faculty of Sciences, Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi, Pakistan
- Murphy, J. and J.P. Riley, 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chem. Acta*, 27: 31–36
- Nelson, D.W., and L.E. Sommers, 1982. Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis*, Part 2, pp: 539–579. Page, A.L., R.H. Miller and D.R. Keeney (eds.). Chemical and microbiological properties. American Society of Agronomy, Madison, Wisconsin, USA
- NFDC, 2001. *Balanced Fertilization through Phosphate Promotion*. Project terminal report, National Fertilizer Development Centre, Islamabad, Pakistan
- Olsen, S.R. and L.E. Sommers, 1982. Phosphorus. In: *Methods of Soil Analysis*, Part 2, pp: 403–430. Page, A.L. (ed.). Chemical and microbiological properties. American Society of Agronomy, Madison, Wisconsin, USA
- Reddy, D.D., S.A. Rao and M. Singh, 2005. Changes in P fractions and sorption in an Alfisol following crop residues application. *J. Plant Nutr. Soil Sci.*, 168: 241–247
- Redel, Y.D., M. Escudey, M. Alvear, J. Conrad and F. Borie, 2011. Effects of tillage and crop rotation on chemical phosphorus forms and some related biological activities in a Chilean Ultisol. *Soil Use Manage.*, 27: 221–228
- Roberts, T.L., J.W.B. Stewart and J.R. Bettany, 1985. The influence of topography on the distribution of organic and inorganic soil phosphorus across a narrow environmental gradient. *Can. J. Soil Sci.*, 65: 651–665
- Ryan, J., G. Estefan and A. Rashid, 2001. *Soil and Plant Analysis Laboratory Manual*, 2nd edition. Jointly published by International Center for Agricultural Research in the Dry Areas and National Agricultural Research Centre (NARC), Islamabad, Pakistan.
- Scherer, H.W. and S.P. Sharma, 2002. Phosphorus fractions and phosphorus delivery potential of a luvisol derived from loess amended with organic materials. *Biol. Fert. Soils*, 35: 414–419
- Sui, Y., M.L. Thompson and C. Shang, 1999. Fractionation of phosphorus in a Mollisol amended with biosolids. *Soil Sci. Soc. Amer. J.*, 63: 1174–1180
- Tiessen, H. and J.O. Moir, 1993. Characterization of available P by sequential fractionation. In: *Soil Sampling and Methods of Analysis*, pp: 75–86. Carter, M.R. (ed.). Lewis Publishers, Boca Raton, Florida, USA
- Wang, G.P., Z.L. Zhai, J.D. Wang and J.B. Yu, 2006. Soil phosphorus forms and their variations in depression and riparian fresh water wetlands (Sanjiang Plain, Northeast China). *Geoderma*, 132: 59–74
- Wang, G.P., Z.L. Zhai, J.S. Liu and J.D. Wang, 2008. Forms and profile distribution of soil phosphorus in four wetlands across gradients of sand desertification in Northeast China. *Geoderma*, 145: 59–74
- Yang, J.E., J.A. Jones, H.J. Kim and J.S. Jacobsen, 2002. Soil inorganic phosphorus fractions and Olsen-P in phosphorus-responsive calcareous soils: Effects of fertilizer amount and incubation time. *Commun. Soil Sci. Plant Anal.*, 33: 855–871
- Zeb, A., A.D. Choudhary, M. Afzal and M.R. Choudhary, 1970. *Reconnaissance Soil Survey of the Campbellpur*. Directorate of Soil Survey, Lahore, West Pakistan

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