Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 1952-1962

ASIAN JOURNAL OF CHEMISTRY

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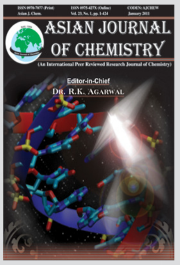

Phosphorus Forms in the Indus River Alluvial and Loess, Shale and Limestone Derived Residual Soils

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(*Received*: 2 April 2010; *Accepted*: 10 January 2011) AJC-9462

Phosphorus (P) fractionation helps to understand the soil processes related to its agronomic efficiency and contribution to environmental quality. Distribution of P in various forms in the slightly weathered calcareous soils of the Indus plain (Pakistan) has not been investigated which limits understanding of long-term P chemistry trends. Several alluvial and residual soils were sampled at genetic horizon depths and the soil inorganic P forms were sequentially extracted by the Jiang and Gu scheme along with their mineral and chemical parameters. Two highly weathered soils from Germany were included for comparison. Apatite was 500-600 mg kg^{-1} in the alluvial soils, 200-300 mg kg^{-1} in the loess and shale derived soils and a major contributor to total P. With strong loss of apatite from the surface, the highly weathered soils had almost equal contribution to total from the pools: (a) P desorbed from and released by iron oxide dissolution, (b) occurring as apatite and (c) occurring as organic-P. The dicalcium phosphate and octacalcium phosphate accumulated in surface horizon of the fertilized alluvial soils and below 75 cm in strongly structured silty clay and massive loamy sand soils. NaOH-Na_2CO_3 appeared to be an ineffective treatment for desorbing P from the well crystallized goethite found in the alluvial soils. CBD and extractable iron (Fe_d), oxalate extractable iron (Fe_o) and aluminum (Al_o), goethite (Gt), dissolved organic carbon (DOC), $CaCO_3$ and clay kaolinite explained 75-99 % of variability in the soil P forms. This study demonstrates role of soil parent material, weathering and land use in distribution of soil P forms and their relationships to soil-test P.

Key Words: Soil phosphorus fractionation, Calcareous soils, Iron oxide adsorbed- and occluded-P, Soil P form predictive equations.

INTRODUCTION

Soils are deficient in plant available phosphorus (P) in many agro-climatic regions, and P fertilizer has become a necessary input for commercial crop production. Soil P chemistry has been investigated extensively in highly weathered or acidic soils for agronomic efficiency[1,2] and, lately, for environmental impact[3,4]. Analogous studies on calcareous soils are scarce where P deficiency is equally widespread, and the inorganic fertilizer P use efficiency is low[5]. Bioavailable P pool in soil is affected by several edaphic conditions and management practices as well as by the distribution of various soil P forms through interactive mechanisms of mobility and transfer functions[6].

Identification of soil P forms helps assess natural P reserves and the fate of applied P[7,8]. In calcareous soils the forms of P have been determined mostly for surface samples[9-11] and in potted soil after fertilizer application[12]. Phosphorus forms were determined for samples taken from fixed depths[4] and for samples taken from selected horizons[13]. Comparison of P forms in soils differing in pedological origin and profile distribution is lacking in these studies. Phosphorus forms in complete profile were examined for soils rich in pedogenic carbonate[14].

Sequential extraction by selective dissolution has been extensively carried out to characterize soil inorganic P forms[15,16]. Hadley and co-workers[7,17] developed a sequential extraction scheme to characterize labile and more stable inorganic and organic P. In other cases the fractionation scheme of Chang and Jackson[15] was used without or with some modifications[13,18,19]. Formation of CaF_2 in NH_4F extraction in case of calcareous samples was reported as a cause of underestimation of non-occluded Fe and Al-P and an overestimation of acid-extractable Ca-P[20]. Later modifications[16,21-23] in the Chang and Jackson[15] scheme improved P extractability in calcareous soils but yet these methods were not sensitive to the specific P compounds in calcareous soils. A new fractionation scheme for calcareous soils through which inorganic P could be fractioned into 6 groups: dicalcium phosphate (Ca_2-P), octacalcium phosphate (Ca_8-P), phosphate adsorbed on iron oxides (Fe-P), iron oxide occluded phosphate (Occl-P), aluminium phosphate (Al-P) and P as apatite (Ca_{10}-P) was suggested[21]. This scheme has been used successfully for alluvial calcareous soils[24], calcareous soils from north China[9], fertilized calcareous soils[10] and highly calcareous soils[11].

The Indus plain supports extensive crop production in South Asia where more than 95 % soils are deficient in bioavailable P and applied P efficiency is as low[5] as 15 %. Distribution of P forms in the slightly weathered calcareous soils is less well understood. The objectives were (i) to determine distribution of P forms in soil in relation to parent material in the Indus plain and (ii) to determine relationships between inorganic P forms and the soil minerals and chemical parameters.

EXPERIMENTAL

Soil description: Nine soils from four different landscape positions and three climatic regimes were included in this study: (1) Five pedons (Fig. 1) formed in the subrecent and recent mixed alluvium derived from the Himalayan mountains by the Indus river and its tributaries (Shahdara, Sultanpur, Pacca and Pitafi soil series) and one in an intermountain alluvium (piedmont) derived mainly from local limestone and calcareous red shale (Peshawar series) all occurring in arid and semi-arid region; (2) One pedon developed in Pleistocene loess plain in a sub-humid area and under rainfed crop production (Guliana soil series) and (3) one pedon derived from residuum of interbedded Siwalk sandstone and shale on ridge-and-trough upland in a humid climate (Murree soil series): (4) Two pedons representing "Parabraunerde" from Baden Wurttemberg, Germany: one developed in glacial loess at Weingarten and another one developed in Upper Muschelkalk colluvium at Osterburken were also included as high weathered soils. The Murree soil and both the Parabrouderde were under permanent pine forest. US soil classification, parent material and selected characteristics are presented in Table-1.

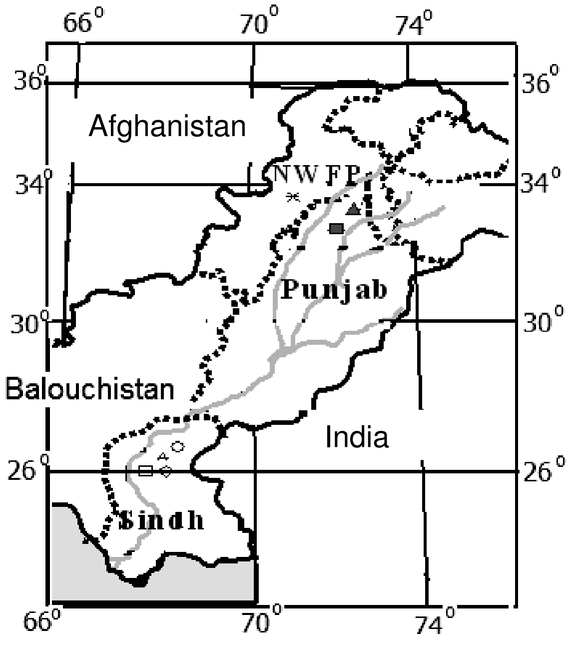


Fig. 1. Scheme of the sampling sites in Pakistan: □ Shahdara, ○ Pacca, △ Sultanpur, ◊ Pitafi, ⁎ Peshawar, ▲ Murree, ■ Guliana soil series

Soil sampling and preparation: At each site the soil was exposed and samples were taken from upper four soil horizons (Table-1) except that the litter layer (0-4 cm) was excluded in case of the two German soils under pine forest. The samples were air-dried and ground to pass through a 2-mm sieve.

Soil characterization: Soils were analyzed for pH and electrical conductivity (1:2 soil water suspension), $CaCO_3$ (neutralization with excess acid), organic matter (OM) by wet digestion[25], soil test P by extraction with 0.5 M sodium bicarbonate ($NaHCO_3$) solution[26], citrate bicarbonate dithionite extractable iron (Fe_d) and aluminum (Al_d) and oxalate extractable iron (Fe_o) and aluminum (Al_o)[27]. Crystalline iron oxide (Fe_{crys}) was calculated by the difference in Fe_d and Fe_o.

Each soil sample was separately treated to remove $CaCO_3$ by 1 N NaOAc buffered to pH 5 at 75 ºC for 0.5 h and soil organic matter by H_2O_2 at 70-80 ºC. The clay (< 2 mm) was separated from the treated soil suspension and analyzed for mineral composition by X-ray diffraction[28]. Soil clay smectite and vermiculite were quantified by the difference in Ca/Mg and K/NH_4 cation exchange capacities and kaolinite by thermogravimetry. Iron oxides present in soils were determined by X-ray diffraction before and after pre-concentration treatments[29] using cyclic voltammetry[30] and viewing under a transmission electron microscope. The methodology adopted for iron oxide characterization was given earlier[31].

Sequential extraction of phosphorus: Inorganic P forms were sequentially extracted as per protocols[32] detailed in Table-2. Duplicate one g soil sample was treated sequentially with 0.25 M $NaHCO_3$ (pH 7.5) for extracting dicalcium phosphate (Ca_2-P), 0.5 M NH_4CH_3COO (pH 4.2) for octacalcium phosphate (Ca_8-P), 0.5 NH_4-F (pH 8.2) for amorphous aluminum oxide adsorbed P (Al-P), 1:1 mixture of 0.1 M NaOH and 0.1 M Na_2CO_3 for P adsorbed on surface of iron oxides (Fe-P), 0.3 M Na-citrate and Na-dithionate for P occluded in iron oxide particles and coatings (Occl-P) and, finally, digesting the residue in 0.5 M H_2SO_4 for apatite (Ca_{10}-P) content. Separately, the soil samples were digested in 60 % $HClO_4$ for total P content[33]. Phosphorus in each extraction was assayed by inductively coupled plasma optical emission spectrometer (ICP-OES) using respective extracting solutions as matrix for the P standard solution. Organic P was calculated by the difference between total P and the sum of inorganic P fractions.

Statistical analysis: The soil parameters were transformed using standard Box and Cox generalized power transformation[34] before analysis of variance by SAS[35]. Soil means (mean over the horizons) were tested by Duncan multiple range test for soil type effect. Further, stepwise regression analysis (forward selection) based on maximizing r^2 generated empirical model relating the P fractions with the soil properties. In the regression analysis "soil" was taken as an independent character variable resulting in different intercepts for individual soil or group of soils when "soil" as variable was significant. Predictive accuracy of the statistical models was tested using Mallows C_p statistics where C_p for a model containing p explanatory variables was defined as:

$$C_p = \frac{RSS_p}{\sigma^2} + 2p - n$$

TABLE-1
SOILS' US CLASSIFICATION[52], LOCATION, PARENT MATERIAL AND IMPORTANT SOIL CHARACTERISTICS

Soil classification/site location	Selected characteristics (g kg^{-1})
Shahdara, coarse-loamy, mixed, aridic hyperthermic Ustic Torrifluvent: deep well drained soil developed in recent level river plains at 25°24'14"N 68°29'39"E	Ap (0-16 cm) pH[$] 8.3 2.5Y 6/2[†] SiL[‡], $CaCO_3$ 48 C1 (16-32 cm) pH 8.4 2.5Y 5/2 SiL, $CaCO_3$ 98 C2 (32-63 cm) pH 8.0 2.5Y 4/2 vfSL, $CaCO_3$ 103 C3 (63-78 cm) pH 8.3 10YR 4/2 vfSL, $CaCO_3$ 98
Sultanpur, fine-loamy, mixed, aridic hyperthermic Fluventic Haplocambid: deep well drained soil developed in subrecent alluvial level plain t 25°24'59"N 68°29'21"E	Ap (0-13 cm) pH 8.3 10YR 4/3 SiL, $CaCO_3$ 130 Bw1 (13-39 cm) pH 8.2 10YR 4/3 SiL, $CaCO_3$ 118 Bw2 (39-62 cm) pH 8.1 10YR 5/3 fSL, $CaCO_3$ 50 2C1 (62-81 cm) pH 8.2 10YR 4/3 SiL, $CaCO_3$ 75
Pacca, fine-silty, mixed, aridic hyperthermic Fluventic Haplocambid: deep imperfectly drained soil in Subrecent level to nearly level broad in-filled alluvial basins at 25°25'30"N 68°31'04"E	Ap (0-15 cm) pH 8.6 2.5Y 5/2 SiL, $CaCO_3$ 46 Bat (15-32 cm) pH 8.3 10YR 4/2 SiC, $CaCO_3$ 60 Bt1 (32-53 cm) pH 8.2 2.5Y 4/2 SiL, $CaCO_3$ 70 Bt2 (53-92 cm) pH 8.8 2.5Y 3/2 SiC, $CaCO_3$ 140
Pitafi, fine-silty, mixed, aridic hyperthermic, Typic Haplosalid: deep, mod well drained, calcareous, gypsiferous, saline soil in Subrecent floodplains at 25°24'32"N 68°23'43"E	Ap (0-15 cm) pH 7.9 10YR 4/3 CL, $CaCO_3$ 80 Ayz (15-41 cm) pH 8.0 10YR 4/3 SiC, $CaCO_3$ 95 Bwy1 (41-57 cm) pH 8.3 10YR 4/3 SiC, $CaCO_3$ 250 Bwy2 (63-111 cm) pH 8.1 10YR 4/3 SiC, $CaCO_3$ 130
Peshawar, fine-silty, mixed, hyperthermic Haplocalcidic Haplustept: deep mod. well drained, calcareous soil in limestone/shale sandstone piedmont alluvial plain at 34°00'44"N 71°30'47"E	Ap (0-11 cm) pH 7.5 7.5YR 5/4 SiCL, $CaCO_3$ 195 Bt1 (11-43 cm) pH 7.3 7.5YR 6/4 SiCL, $CaCO_3$ 186 Bt2 (43-66 cm) pH 7.4 7.5YR 6/4 SiCL, $CaCO_3$ 198 2Btb (66-98 cm) pH 7.4 7.5YR 6/4 SiCL, $CaCO_3$ 203
Murree, loamy, mixed, udic mesic/thermic Typic Hapludoll: deep, well drained, slightly to noncalcareous on hill slopes of red shale and sandstone at 33°56'05"N 73°26'00"E	A (0-11 cm) pH 7.5 5YR 3/2 SiCL, $CaCO_3$ 30 Bt1 (11-30 cm) pH 7.8 5YR 3/3 C, $CaCO_3$ 30 Bt2 (30-52 cm) pH 7.4 5YR 3/3 C, $CaCO_3$ 12 2Bt3 (52-58 cm) pH 7.7 5YR 3/2 CL, $CaCO_3$ 10
Guliana, fine-silty, mixed, ustic hyperthermic Typic Haplustalf: deep, mod. well drained, decalcified soil in nearly level/slightly depressions loess plain at 33°33'40"N 72°38'34"E	Ap (0-12 cm) pH 7.6 10YR 5/4 SiL, $CaCO_3$ 12 Batc (12-25 cm) pH 7.2 10YR 5/4 SiL, $CaCO_3$ 3 Btc1 (25-56 cm) pH 7.8 10YR 3/3 SiCL, $CaCO_3$ 2 Btc2 (56-83 cm) pH 7.5 10YR 4/3 CL, $CaCO_3$ 6
Osterburken, clayey, udic mesic/thermic Typic Hapludalf : deep well drained soil in Muschelkalk colluvial foothill at 49°26'38"N and 9° 29'37"E	Bv (4-25 cm) pH 4.7 7.5YR 4/4 SiCL, $CaCO_3$ 3 Bt (25-50 cm) pH 6.0 7.5YR 3/4 SiC, CaCO3 4 C (>50 cm) pH 7.7 7.5YR 4/6 SiCL, $CaCO_3$ 57
Weingarten, fine-silty, udic mesic/ thermic Lithic Hapludalf: deep, well drained soil limestone and glacial loess on hillslopes 49°02'13"N 8°31'25"E	Bv (4-25 cm) pH 4.5 7.5YR 3/4 SiL, $CaCO_3$ 5 Bt (25-45 cm) pH 5.9 10YR 5/5 SiCL, $CaCO_3$ 5 C (>45 cm) pH 7.1 10YR 6/5 SiCL, $CaCO_3$ 250

[$] pH 1:2 soil water extract; [†] moist color; [‡] definition of soil texture classes: SiL, silt loam; vfSL, very fine sand loam; SiC, silty clay; CL, clay loam; SiCL, silty clay loam.

TABLE-2
EXTRACTION PROTOCOL FOR FRACTIONATION OF THE INORGANIC SOIL P FORMS[32]

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_4-F, shaken for 1 h orbital.	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 16 h and shaken again for 2 h.	P adsorbed on surface of iron oxides (Fe-P)
5	Residue washed twice with saturated NaCl, added 40 mL 0.3 M Na-citrate plus 1 g Na-dithionate and heating at 80 °C for 15 min.	P incorporated, trapped into iron oxide coatings, or P incorporated in iron oxide (Occl-P)
6	Residue added with 50 mL 0.5 M H_2SO_4 and shaken for 1 h.	Hydroxylapatite (Ca_{10}-P)

[†] Each extraction ended with centrifugation at 2500 rpm for 10 min and P assay in supernatant by ICP. [††] Are P forms perceived to be extracted and parentheses contain abbreviated form for respective fraction.

where RSS_p = residual sum of squares for the model, p number of explanatory variables and σ^2 the root-mean-squared-error. A regression model was selected when C_p was the minimum or negative[35]. Measures of pair-wise association was determined by Pearson coefficient, r^2, along with probability > r^2 for all the soil parameters.

RESULTS AND DISCUSSION

Soil characteristics: The alluvial soils were relatively light textured except the Pacca soil. As Pacca soil occurs in broad basins in the fluvial plain, it had silty clay texture. As these soils are weakly differentiated, alkaline, irregular distribution of $CaCO_3$ in the soil matrix, low organic matter and low Fe$_d$ content were the main features (Table-3). The loess derived Guliana soil was silty clay loam/silty clay, decalcified through 90 cm depth, and exhibited an increase in Fe$_d$ and Al$_d$ content with depth suggesting relatively intense *in situ* weathering. The Murree soil, which developed in residuum from interbeded shale/sand under a coniferous forest, was silt loam containing 10-24 g OM kg^{-1} soil and slightly calcareous (Table-3). It contained Fe$_d$ greater than any other soil due to its shale parent material rather than pedogensis. The two Parabrounerde, relatively more weathered soils, were silty clay loam and had acidic surface soil decalcified to 50 cm depth. Decalcification and leaching of bases occurred under pluvial conditions in the German soils. Compared to 6-9 g Fe$_d$ kg^{-1} in the alluvial soil, the Parabrounerde and Guliana had 10-23.2 g kg^{-1} soil. Al$_d$ was also greater in these soils than that of the alluvial and the shale-derived soils (Table-3). Oxalate extractable iron (Fe$_o$) and Al$_o$ were, respectively lesser than Fe$_d$ and Al$_d$ in all soils, yet, the weathered soils had relatively greater proportion than the alluvial soils. The Parabrounerde showed an increase in Fe$_d$ content with depth while the alluvial soils had an irregular distribution in the respective profiles. Most of the free iron oxide appeared to be crystalline as reported for calcareous soils from south-western Australia[10].

Furthermore, Fe$_d$ and Al$_d$ were highly correlated (r^2 0.71, < 0.0001) suggesting that Al dissolved by CBD may be substituted for Fe in soil iron oxide. Similarly, Fe$_o$ and Al$_o$ were also

TABLE-3
SOME SELECTED PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS

Horizon	Depth	EC	OM	Olsen-P	Smectite	Kaolinite	Fe$_d$	Fe$_o$	Al$_d$	Al$_o$
Shahdara, coarse-loamy, mixed, aridic hyperthermic Ustic Torrifluvent										
	cm	dS m^{-1}	g kg^{-1}	mg kg^{-1}	g kg^{-1} clay		g kg^{-1} soil			
Ap	0-16	0.4	11.0	8.50	19.0	19.1	6.7	0.28	0.88	0.38
C1	16-32	0.3	5.0	2.37	18.6	18.0	7.1	0.42	0.67	0.38
C2	32-63	0.2	3.0	1.68	17.0	19.3	3.6	0.07	0.30	0.11
C3	63-78	0.2	3.0	2.30	16.9	18.5	5.2	0.21	0.41	0.20
Sultanpur, fine-loamy, mixed, aridic hyperthermic Fluventic Haplocambid										
Ap	0-13	0.9	25.0	27.44	17.1	17.9	6.3	0.28	0.47	0.34
Bw1	13-39	1.6	8.0	2.99	21.8	17.5	6.9	0.28	0.58	0.41
Bw2	39-62	2.6	6.0	1.37	16.6	18.2	8.2	0.49	0.52	0.52
2C1	62-81	1.9	4.0	6.17	18.6	18.4	6.1	0.28	0.53	0.25
Pacca, fine-silty, mixed, aridic hyperthermic Fluventic Haplocambid										
Ap	0-15	8.6	20.0	30.77	16.7	17.3	7.8	0.35	0.63	0.60
Bat	15-32	8.3	8.0	6.73	17.2	17.1	7.0	0.42	0.62	0.74
Bt1	32-53	8.2	6.0	4.3	15.9	18.3	5.9	0.42	0.55	0.70
Bt2	53-92	8.8	6.0	4.2	18.6	17.9	8.2	0.28	0.65	0.63
Pitafi, fine-silty, mixed, aridic hyperthermic, Typic Haplosalid										
Ap	0-15	59.0	10.0	11.90	21.5	17.9	3.6	0.49	0.47	0.77
Ayz	15-41	11.5	7.0	10.84	19.0	18.3	9.3	0.56	0.68	0.56
Bwy1	41-57	5.6	4.0	8.35	20.5	17.6	9.3	0.42	0.70	0.47
Bwy2	63-111	3.9	2.0	4.49	18.8	18.1	7.2	0.28	0.50	0.27
Peshawar, fine-silty, mixed, hyperthermic Haplocalcidic Haplustept										
Ap	0-11	0.6	21.0	16.07	15.3	20.6	10.5	0.28	0.64	0.60
Bt1	11-43	0.3	10.0	11.20	14.9	20.3	10.6	0.42	0.75	0.74
Bt2	43-66	0.3	8.0	10.09	16.2	19.5	9.9	0.42	0.67	0.70
2Btb	66-98	0.3	10.0	13.46	18.1	18.9	9.0	0.28	0.58	0.63
Murree, loamy, mixed, udic mesic/thermic Typic Hapludoll										
A	0-11	0.2	22.1	8.40	13.7	25.4	13.2	0.21	0.61	0.62
Bt1	11-30	0.2	23.6	4.48	18.3	25.0	14.4	0.49	0.63	0.60
Bt2	30-52	0.1	11.1	3.36	10.8	25.3	15.4	0.63	0.74	0.70
2Bt3	52-58	0.1	21.5	3.92	16.4	24.7	16.5	0.70	0.83	0.84
Guliana, fine-silty, mixed, ustic hyperthermic Typic Haplustalf										
Ap	0-12	2.4	12.0	11.48	19.6	32.1	10.3	0.28	1.35	0.71
Batc	12-25	0.2	4.5	5.60	19.3	32.4	11.1	0.28	1.45	0.72
Btc1	25-56	0.2	7.7	2.94	15.5	29.3	13.5	0.42	2.28	1.13
Btc2	56-83	0.3	6.0	10.64	28.9	27.4	13.6	0.28	2.37	0.98
Prb-Ostb, clayey, udic mesic/thermic Typic Hapludalf										
Bv	4-25	0.1	11.6	6.72	18.2	15.5	12.9	1.40	2.30	1.46
Bt	25-50	0.1	4.8	16.00	22.9	16.0	23.2	1.33	3.27	1.84
C	>50	0.3	5.9	7.50	16.6	13.6	20.0	0.77	2.34	1.10
Prb-Wein, fine-silty, udic mesic/thermic Lithic Hapludalf										
Bv	4-25	0.1	10.7	5.0	14.4	16.6	9.8	1.33	1.95	1.28
Bt	25-45	0.2	8.4	5.5	17.1	17.7	16.7	1.12	2.37	1.31
C	>45	3.2	6.9	5.5	18.4	17.4	20.0	0.21	1.31	0.55

Ca$_{ex}$: Exchangeable calcium; OM: organic matter; EC: electrical conductivity; Fe$_d$: citrate bicarbonate dithionite extractable iron; Fe$_o$: oxalate extractable iron; Al$_d$: citrate bicarbonate dithionite extractable aluminium; Al$_o$: oxalate extractable aluminum.

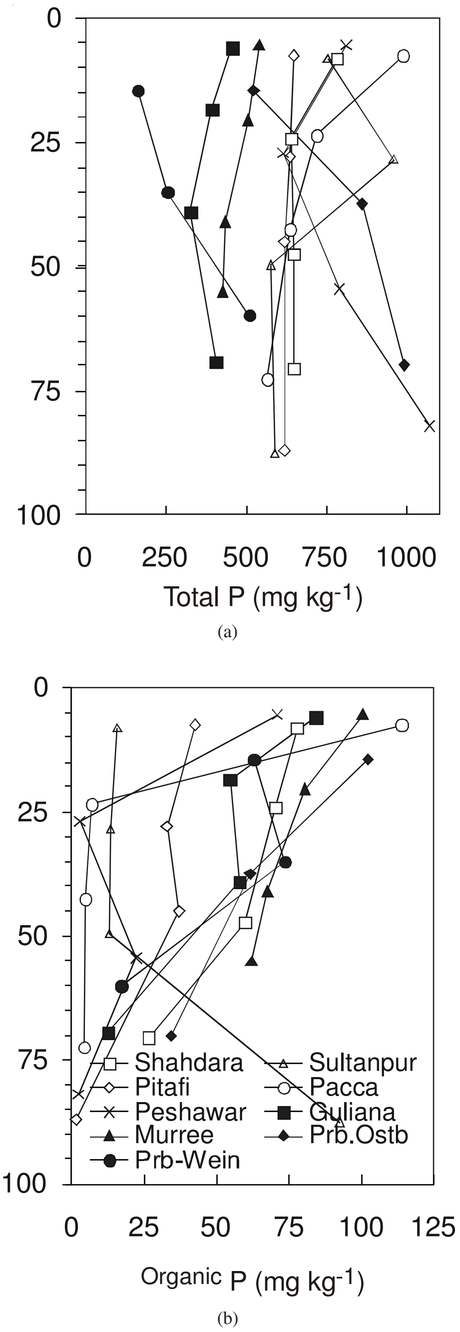
highly correlated (r^2 0.85, < 0.0001) again suggesting a common source. A similar correlation has been reported[10]. Oxalate extractable aluminium may be present as amorphous or Al-organic matter complex rather than free oxide[10].

The soil clays had mixed mineral composition (X-ray diffraction data not presented). The alluvial soil clays were composed mostly of mica, smectite and kaolinite, where smectite ranged from 7-22 % and kaolinite from 17-19 %. The Murree and Peshawar soil clays were mainly composed of vermiculite, mica and kaolinite with small amount of chlorite. Smectite content in these soils was less than that of alluvial soils and kaolinite content was greater. The clay from Parabrounerde from Ostburken exhibited no expansion in Mg-saturated 14 Å peak upon gylcolation indicating dominance of vermiculite. The Parabrounerde had low kaolinite contents in the clay fraction probably due to high silica leaching under humid climate. Well crystallized multidomainic goethite was identified in the clays from the alluvial soils[31].

Total phosphorus: Total soil P in the samples ranged from 163-1050 mg kg^{-1}. The alluvial soils *viz*., Sultanpur, Pacca, Pitafi, Shahdara and Peshawar contained greater total P than the loess derived Guliana and the shale derived Murree soil; and had total P either slightly increased towards the surface (*e.g*., Pacca soil) or uniformly distributed in the four upper horizons (Fig. 2a). Total P in Muschulkalk derived Parabrounerde from Osterburken was similar to that of alluvial soils. Total P in glacial loess derived Parabrounerde from Weingarten matched to the shale and loess derived soils. But in both German soils P loss had occurred at the surface.

Empirically, soil Fe_d, Fe_o and organic matter explained 93 % variation in total P content in the soils with $p > F < 0.001$ on each parameter estimate in the regression equation. L total P = 18.44 - 7.95LFe_o + 2.16LpH + 0.17LOM + 0.18LGt_s for all the alluvial soils. The bold face L denotes Box and Cox power transformation *e.g*., LOM = $[((OM + 11)^{0.00015}) - 1)/0.00015]$ or OM = $[((LOM0.00015 + 1)^{(1/0.00015)}) - 11]$. The intercept for Guliana (17.89), Murree (18.28), Parabrounerde from Weingarten (18.09) and for Parabrounerde from Osterburken (19.33) was significantly less than for the alluvial soils. The parameter estimates for Fe_o had negative sign and pH had positive. Fe_o may be taken as proxy indicator for soil weathering as it was greater in the weathered soils which had less apatite.

Organic phosphorus: Organic P varied widely between 5 and 115 mg P kg^{-1} soil and was 3.0-23.7 % of total soil P (Table-4). Organic P was greater in the Parabrounerde and Murree (under indigenous vegetation covers) and in the Guliana (occurring in subhumid climate) than in the irrigated arable alluvial soils conforming to previous findings[19,36]. The Parabrounerde, Murree and Guliana soils also had increased organic P towards the surface as opposed to cultivated alluvial soils (Fig. 2b). Increased organic P toward the surface was consistent with higher organic matter accumulation in the surface layers[19,37]. The exception that the Sultanpur 2C1 horizon (below 75 cm) had high organic P may be related to the sediments rather than a pedological phenomenon as the profile is the least homogenised. Overall organic P is a small portion of total P[4,38,39]. Organic P was more strongly related to DOC (r^2 0.55, p 0.002) than total soil organic matter (r^2 0.43, p 0.01). The sum of Al-P and organic P was even more closely related to DOC (r^2 0.70, $p < 0.0001$) and soil organic matter (r^2 0.64, $p < 0.0001$) and non-significantly to the Al_d and Al_o content[19]. When regressed stepwise the following relation explained 80 % variation in the organic P pool: LOrg-P = -110.25 + 2.02LDOC + 32.48LFe_o + 13.30LpH - 6.46LAl_o - 0.87Lclay + 2.73Lkaolinite for all the soils with the exception that the intercept for the Murree was -111.02, for Pacca -111.00 and for Sultanpur -111.25.



(a)

(b)

Fig. 2. Quantitative distribution of (a) total P and (b) organic-P form in the pedons suggesting greater total in the alluvial soils (Shahdara, Sultanpur, Pacca, Pitafi and Peshawar) than the shale and loess soils and loss of total P in the Parabrounerde

Inorganic phosphorus forms: Quantitative distribution of inorganic P forms, their pairwise correlation with other soil parameters and multiple regression models are presented. The sequence presentation is from non-labile to most labile P form.

TABLE-4
CONTRIBUTION OF VARIOUS P FRACTIONS (MEAN OF ALL HORIZONS) AS PER CENT OF SUM OF INORGANIC FRACTIONS (ΣIP), AND TOTAL SOIL P (TP) IN CASE OF ORGANIC P FRACTION IN THE PEDONS

Soil	Ca_2-P:ΣIP	Ca_8-P: ΣIP	Al-P:ΣIP	Fe-P:ΣIP	Occl-P:ΣIP	Apatite:ΣIP	Org-P:TP
				(%)			
Sultanpur	1.00a	1.02b	3.17ba	0.76b	12.20bcd	81.85a	5.37bc
Shahdara	1.26a	1.00b	1.58b	0.65b	7.62cd	87.90a	8.56bc
Pacca	0.90a	1.13b	7.85a	1.06b	13.90bc	75.15ba	3.48c
Pitafi	1.55a	0.86b	1.24b	0.09b	12.40bcd	83.85a	4.50bc
Peshawer	1.13a	0.89b	4.30ba	0.87b	13.43bc	79.40a	3.04c
Murree	1.95a	1.61b	2.84ba	20.24a	4.57d	68.80acb	16.21ba
Guliana	5.42a	1.62b	4.50ba	16.24a	18.17ba	54.04bcd	13.31bac
Prb-wein	3.56a	3.36a	1.37b	20.40a	24.45a	46.85dc	23.66a
Prb-Ost	4.45a	1.11b	6.03ba	30.12a	24.9a	33.40d	11.60bc

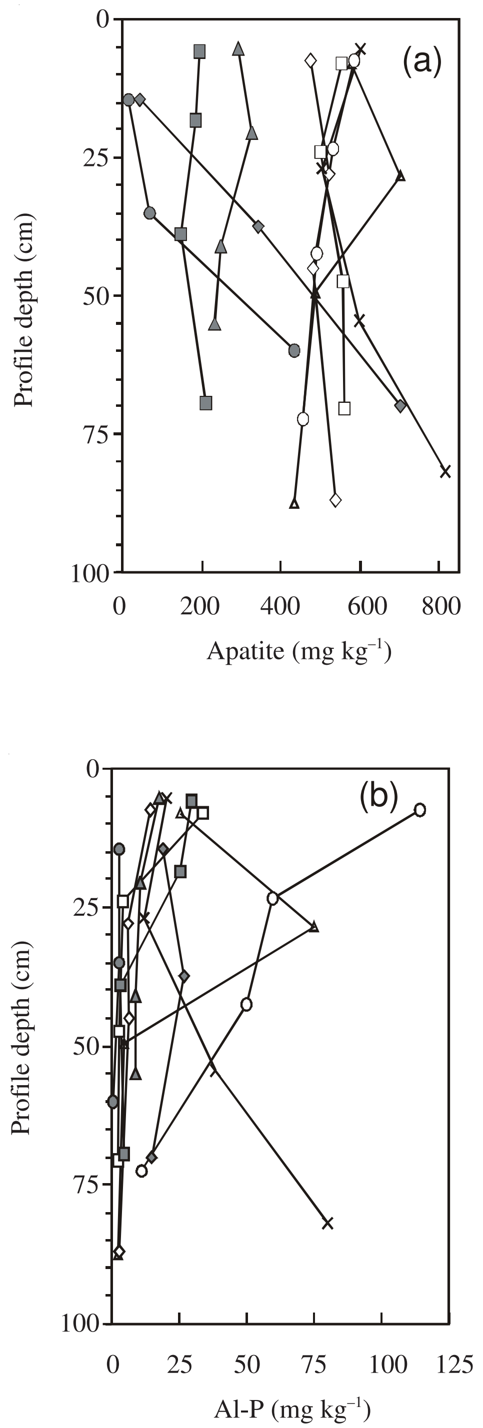
The multiple regression models have value to understand the processes rather than as predictive tools.

Apatite (Ca_{10}-P): Equivalent apatite P in the data set ranged from 43-800 mg kg^{-1} and was dominant contributor to sum of inorganic P forms (7-95 %, mean 68.5 %). Apatite in the alluvial soils including Peshawar was in the range of 500-600 mg kg^{-1} and was almost uniformly distributed (Fig. 3a). The shale derived Murree soil and loess derived Guliana soil had apatite in the range between 200-300 mg kg^{-1}. In both the Parabrounerde apatite increased with depth from few tens of mg at the surface to 700 mg kg^{-1} in the lower profile. The loss of apatite from surface layers of both Parabrounerde soils may be related to intensive weathering in pluvial climatic conditions.

Apatite-pH and apatite-$CaCO_3$ pairwise correlations were significant (*p* 0.001) with Pearson coefficient (r^2) 0.68 and 0.66, respectively. This is in line with the perception that high pH (less H^+)-controlled by presence of $CaCO_3$-protects apatite against weathering[40]. Comparatively, lower concentration of hydroxyapatite in acidic soils than in neutral to slightly alkaline soils have been reported[13]. Interestingly, only three soil parameters, *viz.*, soil Fe_o, $CaCO_3$ and clay kaolinite explained 90 % (*p* 0.0001) variations in apatite in the samples. Apatite = 1128.8 - 372.3Fe_o - 26.9kaolinite + 0.4$CaCO_3$ for all the soils except Parabrounerde from Weingarten which had significantly lesser intercept (954.2) than other soils. Soil Fe_o and kaolinite had negative sign and $CaCO_3$ had positive sign in the regression equation indicating that apatite was well protected by the presence of $CaCO_3$.

Apatite was the dominant contributor to total P and the sum of inorganic P fractions (ΣIP) *e.g.*, apatite contributed 75-88 % P to ΣIP in Shahdara, Sultanpur, Pitafi, Peshawar and Pacca series (Table-4) and 54-68 % in case of the shale derived Murree and loess derived Guliana soils. Based on all data points except from the Parabrounerde ΣIP = 100.4 + 1.07apatite; r^2 0.90). ΣIP in case of Parabrounerde consisted of equal amounts Fe-P/Occl-P, Org-P and apatite.

Apatite is derived from parent material and therefore, a difference in lithology created inherent levels of apatite in these soils. The fact that even surface of alluvial soils (exposed to weathering) had greater apatite than the subsurface of loess derived Guliana or the shale derived Murree soils suggests an obvious control of lithology. Parabrounerde might have had initially high apatite and loss of apatite occurred under intense weathering and created the distribution trend within



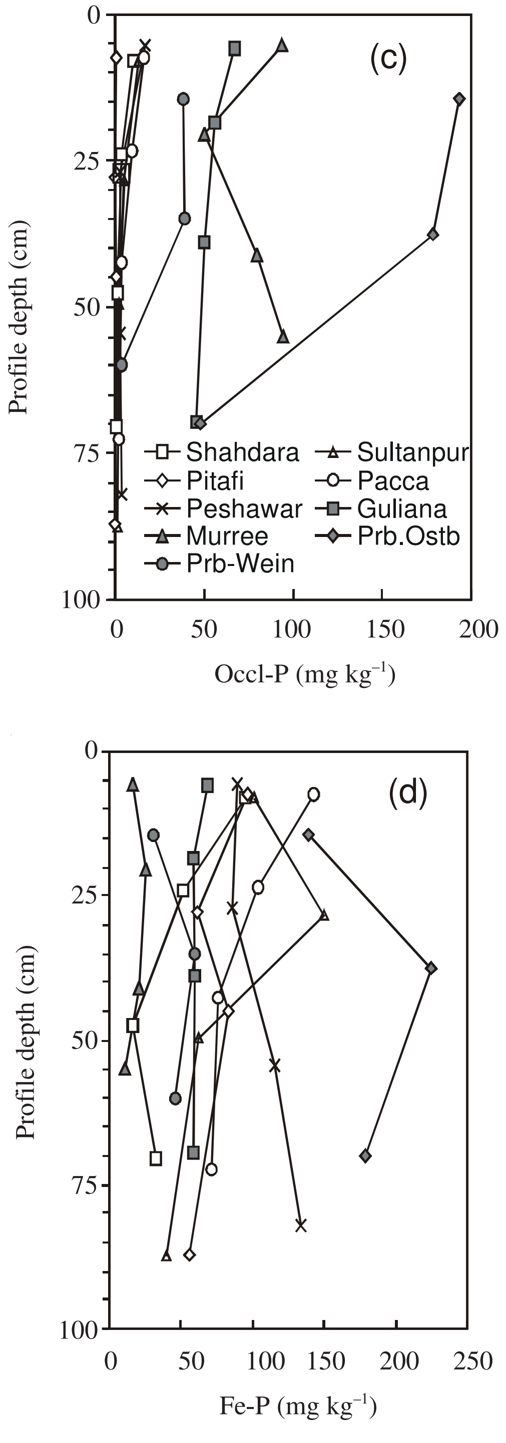


Fig. 3. Quantitative distribution various P forms in the soil profiles: (a) apatite or Ca_{10}-P, (b) aluminum-P, (c) P desorbed from iron oxide surfaces or Fe-P and (d) P released by dissolution of iron oxide or Occl-P

the level of their apatite content. Apatite has been reported to be the dominant form of inorganic P fractions through many studies[9,14,41]. Probably addition of fresh mineral matter with irrigation increased apatite in Pacca, Pitafi and Shahdara soils. Addition of fresh micaceous minerals through river-diverted irrigation has been reported[42].

Aluminium phosphorus: The P fraction extracted by NH_4-F, referred as Al-P, ranged from 2.3-115 mg kg^{-1} soil (Fig. 3b) and accounted for 0.06-14.6 % inorganic P (only mean value given in Table-4). Pacca soil had the highest mean profile Al-P. Peshawar, Parabrounerde from Osterburken and Sultanpur had mean profile Al-P statistically similar to the Pacca profile mean. The lowest mean profile Al-P was in Parabrounerde from Weingarten that was also similar to Shahdara, Pitafi, Guliana and Murree soils' profile. Aluminum P appeared to be independent of soil parent material in this study. Pacca soil profile had Al-P increased towards the surface while in Peshawar soil it increased with depth (Fig. 3b). Al-P correlated well with dissolved organic carbon (r^2 0.56, p 0.002) and soil organic matter content (r^2 0.51, p 0.002). The relation with Al_d and Al_o was non-significant as reported[43] yet correlation with Al-P and Olsen-P was significant (r^2 0.56, p 0.0003).

Phosphorus desorbed from iron oxides (Fe-P): The P fraction extracted with NaOH-Na_2CO_3, referred as Fe-P, ranged from 0.3-193 mg kg^{-1} (Fig. 3c) and 0.04-47 % to ΣIP. In the alluvial soils, Fe-P was 10-17 mg kg^{-1} soil in the surface and below the method detection limit (< 0.1 mg L^{-1}) in the subsurface horizons. The more ferruginous profiles (Parabrounerde from Osterburken) contained significantly greater Fe-P values (140 mg kg^{-1}) than the alluvial soils including Peshawar and consequently, the contribution of Fe-P to ΣIP was significantly greater than the alluvial soils (Table-4). Fe-P increased towards the surface in Parabrounerde and within the 2-20 mg kg^{-1} range, also increased toward the surface in the alluvial soils. The Murree had Fe-P in the range of 50-95 mg kg^{-1} greater than the 46-67 mg kg^{-1} values of the Guliana and had inconsistent depth trend ascribed to lesser profile development under accelerated colluvial deposition and erosion in the mountain slopes.

Phosphorus desorbed from iron oxides correlated positively with several soil parameters. The strongest correlation was with dissolved organic carbon (r^2 0.82, p 0.0001) followed by Fe_o (r^2 0.70, p 0.0001), Al_d (r^2 0.61, p 0.0001), Al_o (r^2 0.67, p 0.0001) and soil organic matter (r^2 0.67, p 0.0001). Significant negative correlation was with soil $CaCO_3$ (r^2 0.50, p 0.002). The reaction between phosphate and surfaces of Fe and Al oxides is typical of acid soils[17]. In calcareous system such as these soils Fe and Al oxides may exist as either discrete components or as coatings on other soil particles. Stronger correlation of Fe-P with oxalate extractable Fe and Al than CBD extractable Fe and Al suggested role of large surface area of soil oxides[37].

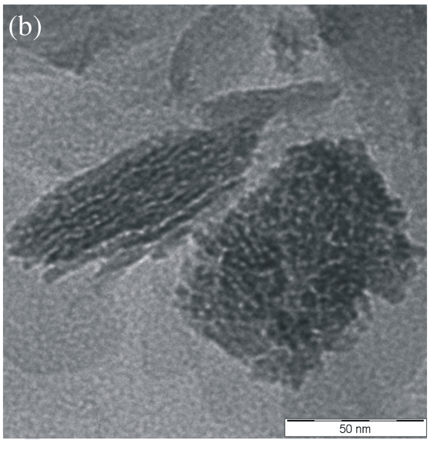
The soil DOC, Fe_o and Al_d jointly explained 99 % variation in P desorbed from iron oxides (tested for multicolinearity): $\text{Fe-P} = 5.08 + 1.05\text{DOC} - 7.54\text{Fe}_o - 5.50\text{Al}_d$ for all the alluvial soils. The regression parameter "soil" was source of variability and consequently intercept for the soils with high total extractable iron was significantly greater than the soil with low total extractable iron *e.g.*, 194.3 for Parabrounerde from Osterburken, 44.24 for the Parabrounerde from Weingarten, 65.20 for the Murree and 62.70 for the Guliana soil. The lower intercept for the alluvial soil may be due to low desorption by the chemical used as discussed later.

Phosphorus released by dissolution of Fe oxides (Occl-P): Phosphorus released by dissolution of Fe oxides ranged from 11-225 mg kg^{-1} soil (Fig. 3d). The highest value was in Parabrounerde from Osterburken Bt horizon and lowest in

Murree 2Bt3 horizon. It accounted for 2.7-33 % of ΣIP (mean given in Table-4). Occl-P and ΣIP were positively correlated (r^2 0.83 $p < 0.0001$). The contribution of Occl-P to the ΣIP was significantly greater in both the Parabrounerde, Guliana and Murree soils than in all the alluvial soils. Occl-P values for the alluvial soils are similar to those reported for fertilized calcareous soils[44].

Phosphorus released by dissolution of Fe oxides increased with depth in the Peshawar soil, increased towards surface in Shahdara, Sultanpur and Pacca soils and remained uniformly distributed in all other soils (Fig. 3d). Although the P form is ascribed to release by dissolution of iron oxides with Na-dithionite treatment, the relationship with soil goethite or Fe_d was not strong. Rather, it had significant positive relationship with DOC (r^2 0.71, $p < 0.0001$), clay kaolinite (r^2 0.58, $p < 0.0003$) and soil Al_o (r^2 0.51, $p < 0.001$). Contribution of Occl-P to ΣIP was highest in the Parabrounerde and Guliana soils (14-33 %). Occl-P contribution in the alluvial soils was 8-14 % and in Murree only 3-6 %. Small share of Occl-P to ΣIP in the Murree beside its twice as much Fe_d and Fe_o due to shale parent material highlights the significance of crystal nature of iron oxides[45]. Soil DOC, Fe_o, Al_d, $CaCO_3$ and exchangeable Ca explained 0.84 % variability in Occl-P (tested for multicollinearity). LOccl-P was $-30.61 + 0.831LDOC + 5.78LFe_o + 3.39LAl_d + 0.25LCaCO_3 + 3.61LCa_{ex}$ for all except Parabrounerde from Weingarten and the Murree soils where the intercept was 31.79 and -31.67, respectively. The bold face L denotes Cox Box power transformation *e.g.*, $LFe_o = [((Fe_o + 11)^{0.00015}) - 1)/0.00015]$ and $Fe_o = [((LFe_o0.00015 + 1)^{(1/0.00015)}) - 11]$.

The study also suggested that NaOH-Na_2CO_3 treatment is probably ineffective for complete displacement of P from well crystalline goethite particles found in the alluvial soils. The alluvial soils had several times greater P released by dissolution of iron oxide than P desorbed while Parabrounerde had equal distribution of both the P forms and reverse was true for Murree and Guliana soils (Fig. 3c-d). Apparently, P cannot be occluded unless initially adsorbed on the surfaces, therefore, greater Occl-P should associate with greater Fe-P. As goethite in the alluvial soils was multidomainic with v-shape grooved edges (Fig. 4) and the grooved edges have stronger P adsorbing sites[46] which may have protected P being displaced during the mild NaOH-Na_2CO_3 treatment. A complete dissolution of goethite by CBD released the trapped P.



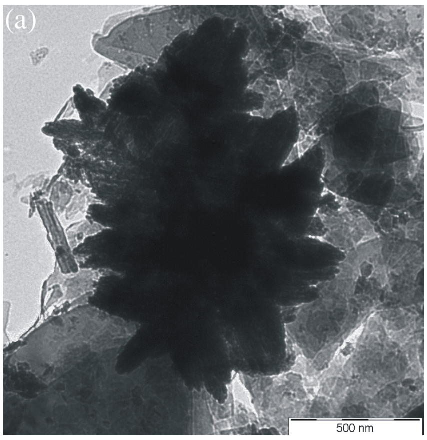


Fig. 4. Transmission electron micrographs showing the morphology of soil goethite: (a) well crystalline goethite particle as thick twined laths with structurally controlled terminations into v-shaped groove edges and (b) comparatively smaller less crystalline particles, one showing monodomainic-serrated laths and other poorly developed lattice fringes and serrated edges. Goethite in the alluvial soils were characteristically after the particle shown in this figure in (a) and goethite in the Murree, Guliana, Prb-Wein and Prb-Ostb mostly resembled with b

Iron co-extracted with P with 0.3 M Na-citrate and Na-dithionite (step-5 in Table-2) ranged from 6000-10000 mg kg^{-1} soil compared to 60-700 mg kg^{-1} of that co-extracted with 0.1 M NaOH and 0.1 M Na_2CO_3 (step-4) (Fig. 5). Generally, there was no correlation between Fe and P released in these two extractions, neither there was any relation between these two Fe fractions; however, Fe:P ratio in the extracts of step-4 and step-5 varied with the source of parent material. In the loess derived Guliana soil Fe of step-5 ranged from 6000-9000 mg kg^{-1} and that of step-4 from 100-1000 mg kg^{-1} but P was almost equal (60 mg kg^{-1}) in both the extractions (Fig. 5a), in the alluvial soils (*e.g.*, Pacca; Fig. 5b) Fe in the step-4 and step-5 was approximately the same as in the Guliana soil but P was 85-145 mg kg^{-1} in step-5 and only 2-16 mg kg^{-1} in step-4 (Fig. 5b) and an opposite trend was noted in the Murree soil, *i.e.*, with approximately the same Fe distribution in step-4 and step-5 (as in Guliana and Pacca soils), it had three to four times more P in step-4 than the step-5 (Fig. 5c). The shale derived Murree had hematite and less well crystallized goethite suggesting a strong effect of crystallinity and nature of iron oxides on the amount of P extracted in step 4 and step 5.

Ca_8-P and Ca_2-P: octacalcium phosphate in these soils varied in a narrow range of 3.7-13.3 mg kg^{-1} and was only 0.64-5.9 % of ΣIP (Fig. 6a, Table-4). The surface of arable soils (Shahdara, Sultanpur, Pacca and Peshawar soils) had greater Ca_8-P while in other profiles Ca_8-P was uniformly distributed. The arable soils' surface had less Ca_2-P than Ca_8-P. Dicalcium phosphate ranged from 0.6-20 mg kg^{-1} except the one highest value of 70 mg kg^{-1} for the Guliana Btc2 horizon (Fig. 6b). Ca_2-P was 0.09-17.7 % of ΣIP. The contribution of Ca_2-P to the inorganic P fractions did not vary with soil type (Table-4). Ca_2-P in most soils was greater at the surface than the underlying 20-50 cm profile and, except for the Parabrounerde, the subsoil had Ca_2-P increased over the value of surface layer. Exceptionally high Ca_2-P in the Guliana (70 mg kg^{-1}, plotted outside the Fig. 6b) ascribed to preferential flow of surface applied P accumulation at Btc2 depth level. Phosphorus is generally considered as an

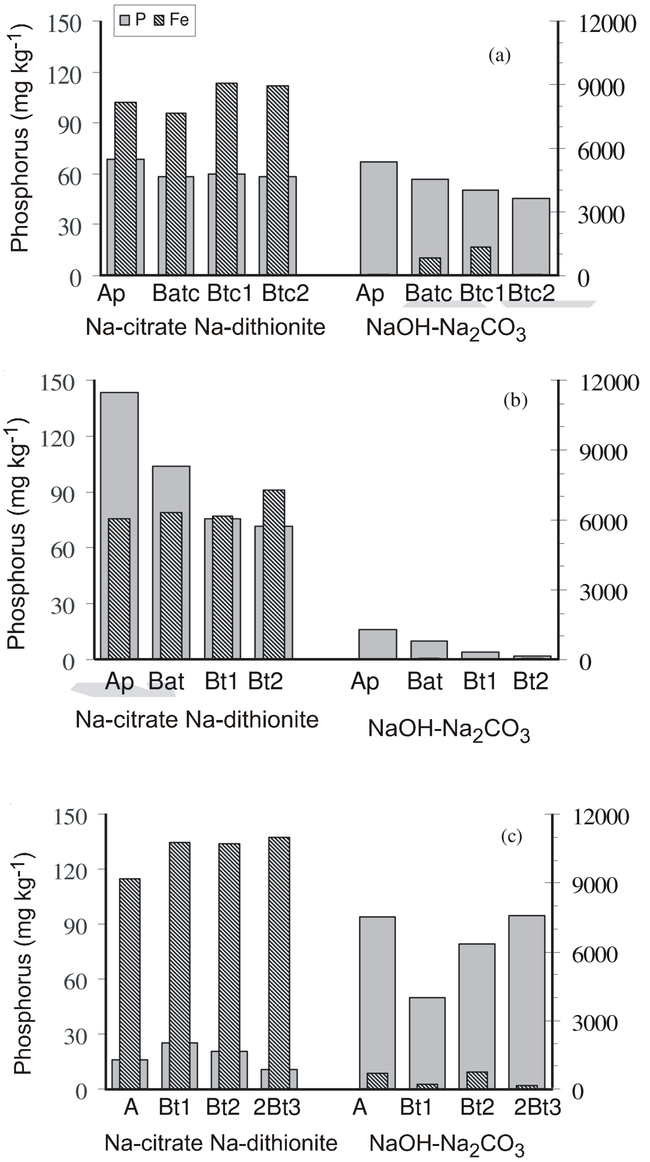
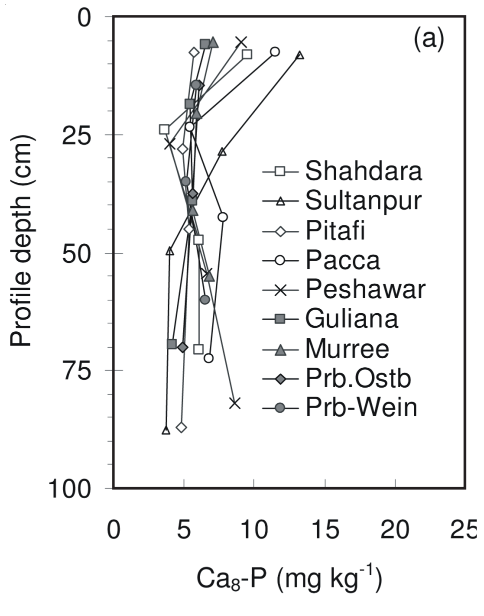


Fig. 5. Distribution of P and the Fe co-extracted in NaOH-Na_2CO_3 (step 4, Table-2) and Na-citrate Na-dithionite (step 5, Table-2): (a) Guliana soil, (b) Pacca soil and (c) Murree soil



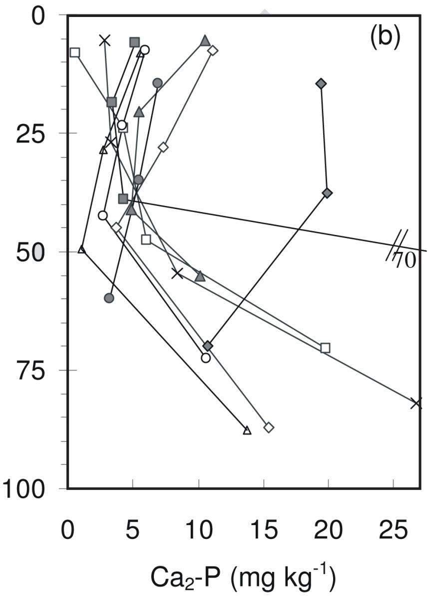


Fig. 6. Quantitative distribution of the P forms in the profiles: (a) NH_4-acetate extractable (Ca_8-P) and (b) Na-bicarbonate extractable P (Ca_2-P). NB in the Guliana profile Ca_2-P in the Btc2 horizon was 70 mg kg^{-1}

immobile element yet preferential flow through strong prismatic silty clay structural units has been demonstrated[47]. The light textured soils (*e.g.*, Shahdara and Sultanpur) also had greater Ca_2-P below 75 cm depth.

Ca_8-P had significant positive relationship with soil OM (r^2 0.71, $p < 0.001$) and Olsen P (r^2 0.68, $p < 0.001$). A significant correlation between Olsen P and Ca_2-P (r^2 0.63 p 0.05) and non-significant with Ca_8-P has been reported[44]. The relationship between Olsen P and Ca_2-P fraction should be expected as both the P forms are determined by $NaHCO_3$ extraction but there seems an analytical artifact here. For Olsen P $NaHCO_3$ concentration was 0.5 M and pH was 8.5 whereas for Ca_2-P $NaHCO_3$ concentration was 0.25 M and pH was 7.5. Explanation lies in the fact that the solubility of Ca_2-P increases with increasing concentration of $NaHCO_3$ when pH of the extracting medium is 8.548. Olsen P was greater than both Ca_2-P and Ca_8-P fractions. The best regression model for predicting Ca_8-P had r^2 of 0.72 ($p < 0.0001$). $Ca_8\text{-P} = 11.91 + 0.32LOM - 1.136LAl_o + 2.98LFe_o$ for all soils except that intercepts for Murree was 11.814, for Parabrounerde from Weingarten 12.145, Parabrounerde from Osterburken 12.256, Pacca 12.005 and for Sultanpur 11.950. The best regression model for Ca_2-P had r^2 0.71 ($p < 0.0001$) and $Ca_2\text{-P} = 42.20 - 12.47LFe_o - 3.18LpH + 6.07LAl_o + 3.51LAl_d - 0.35LGt_s - 6.88\ Lkaolinite + 0.25LCaCO_3$ where L is the Cox Box transformation factor on the parameters. Intercept for Guliana was 44.746 and for the Murree 43.691.

Relation between phosphorus forms and Olsen-P: Finally, it is of interest to find relationships between the soil P forms and the Olsen-P (soil test-P). Apatite (and ΣIP) had only marginal relation with Olsen-P (Fig. 7a-b). The arable alluvial soils with high apatite throughout the profile had high Olsen-P at the surface but low in the subsurface horizon. Since both Ca_2-P and Olsen-P are extracted by $NaHCO_3$, a positive relationship was reported[12]. However, in this study the relationship was marginal (Fig. 7c) but a significant positive

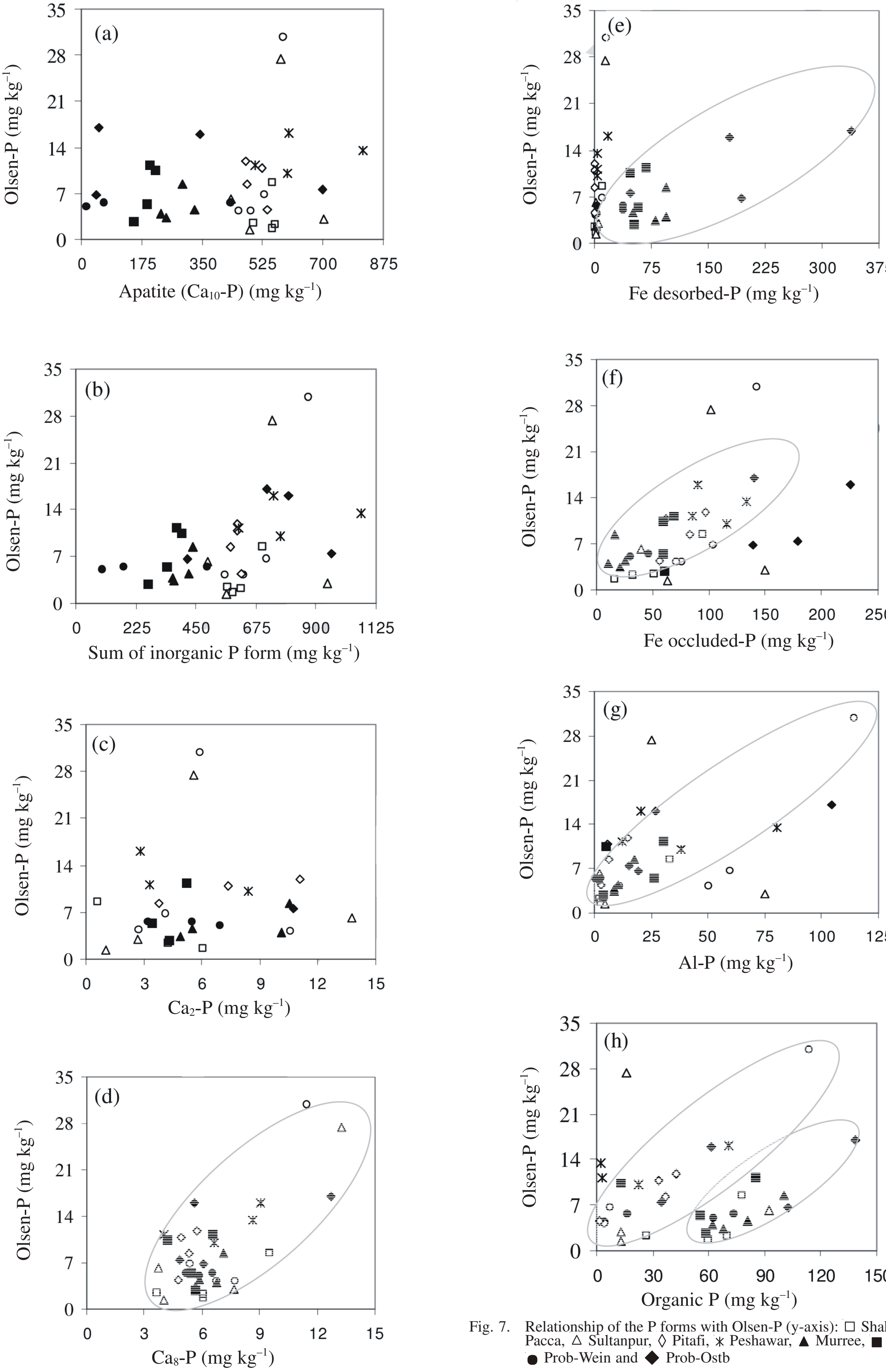


Fig. 7. Relationship of the P forms with Olsen-P (y-axis): □ Shahdara, ○ Pacca, △ Sultanpur, ◇ Pitafi, ⁎ Peshawar, ▲ Murree, ■ Guliana, ● Prob-Wein and ◆ Prob-Ostb

relation (r^2 0.61) was found between Ca_8-P and Olsen-P (Fig. 7d) which may suggest Ca_8-P formation subsequent to fertilizer P application rather rapidly as reported for highly calcareous[10]. Ca_2-P and Ca_8-P are intermediate products during precipitation before the apatite is formed[32]. Further, Fe-P correlated well with Olsen-P but only in the soils with poorly developed crystalline goethite, *viz.*, Guliana, Murree and both the Parabrounerde and not in alluvial soils (Fig. 7e). We think non-significant relation was due to incomplete desorption from the multi-domainic goethite in the alluvial soils. As the weathered residual soils contained mostly monodomainic serrated laths of goethite incomplete desorption was not a factor. Occluded P fraction correlated with Olsen-P better than Fe-P fraction (Fig. 7f) except that the Parabrounerde from Osterburken had different slope and spread in the Sultanpur was high. Organic-P *vs.* Olsen-P had two slopes because the sub-surface samples, which had less organic P, may not necessarily have lesser Olsen P caused by leaching as in case of the well structured Guliana and the sandy Shahdara and Sultanpur soils. Minor effect of fertilization and significant effect of land use on soil organic P forms were reported[8,36]. Lastly, Ca_2-P and Ca_8-P did not correlate with soil $CaCO_3$ (data not depicted) suggesting that P recovered as Ca_2-P and Ca_8-P fractions may have existed as discrete crystals[44] or the effect of solid phase $CaCO_3$ are masked by dominant effect of iron oxides. Ca_8-P is a product of gradual accumulation and subsequent transformation of Ca_2-P[48]. It transforms to Ca_2-P under P depletion[24]. Ca_2-P fraction is completely water soluble and is readily taken up by plants[9].

Conclusion

Overall, the dominant inorganic P fraction in the alluvial soils was apatite, proportionate contribution of Ca_2-P, Ca_8-P and Ca_{10}-P, Fe-P varied in the soils. The highly weathered Muschelkalk and the glacial loess derived soils from Germany exhibited loss of apatite and had almost equal contribution from iron oxide P (both adsorbed and occluded), apatite and organic-P pools. The shale and loess derived soil had less apatite and greater P adsorbed and iron oxides occluded P than in the alluvial soils. The contribution of P occluded in iron oxides in the alluvial soils was 8-14 % which is generally greater than the Ca_2-P and Ca_8-P fractions. The study also suggests accumulation P as Ca_8-P in the cultivated soils and leaching of Ca_2-P in the well structured and in the coarse textured soils. Olsen-P had poor correlation with Ca-P fractions. Therefore, the mechanisms and/or factors influencing the forms of P in soil are diverse and not essentially the same for all soils.

ACKNOWLEDGEMENTS

This contribution is based on PhD dissertation "Role of Fe-oxides for predicting phosphorus sorption in calcareous soils" submitted to Institute of Mineralogy and Geochemistry, University of Karlsruhe (TH), Karlsruhe D-76128. Germany, 2008, ISSN: 1618-2677. The authors thank Dr. Zsolt Berner, Mr. Peter Schaupp, Ms. Gesine Preuß, Mrs. Claudia Mössner and Mrs. Cornelia Haug from Institute of Geochemisty and Mineralogy, University of Karlruhe for their assistance in the experiment and analyses. This study was supported by partial financial support from Higher Education Commission, Islamabad, Pakistan.

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