

Sequential extraction of Phosphorous fractions in calcareous soils amended with P-fertilizers

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Abstract: Phosphorous is relatively immobile in calcareous soil and moves very little from the site of its application. When fertilizer P is added to calcareous soil, part of it goes to soil solution which may be either taken up by crops or precipitates, while more than 80 per cent of added P gets fixed. P is mainly bound to adsorption surfaces at low concentration, where as it is mainly precipitated as Ca-phosphate at higher concentrations in calcareous soils. With this background, an attempt has been made to know the transformation of added Phosphorus in selected calcareous soils. The profile samples of three calcareous soils developed from different parent materials were collected. An incubation study was conducted to know the extent of release or transformation of different forms of phosphorus in the soil after the addition of fertilizers, DAP and KH₂PO₄. The incubated sample was subsampled repeatedly at different time intervals to determine the P fractions. Applied phosphorous transformed mostly into Pedogenic Ca-P followed by reductant-soluble P in all the three soils. In brown soil and black soil, the order of occurrence of inorganic fractions was: lithogenic apatite> reductant-soluble P> residual P> Al- and Fe- bound P. In case of red soil, however, the lithogenic apatite fraction was lesser than the residual P fraction. This may be attributed to the calcareous nature of these soils.

Key words: P-fertilizers, P-fractions, calcareous soil

INTRODUCTION

Phosphorus (P) is the tenth most abundant element in the earth's crust. The amount of P present in soil is sufficient to meet the requirement of the crops, if it is available in full amounts, but large proportion remains in fixed form and not available to plant. The transformation of added P into different insoluble forms and their availability in soils depend upon the properties of soils and sources of P. P is relatively immobile in calcareous soil and moves very little from the site of its application. When fertilizer P is added to calcareous soil, part of it goes to soil solution which may be either taken up by crops or precipitates, while more than 80 per cent of added P gets fixed (Leytem and Mikkelsen, 2005). The high pH level results in unavailability of phosphate due to the formation of unavailable calcium phosphates as apatite. In calcareous soils, considerable part of the applied P is precipitated as dicalcium phosphate (DCP) which subsequently transforms into octacalcium phosphate. Efficiency of fertilizer P in calcareous soils remains

low (Delgado *et al.*, 2002).When fertilizer P is added, a part of it goes to soil solution and taken up by crops, while the rest either precipitates or goes to exchange sites and is adsorbed on sorption complex in the soil. The apparent recovery of applied P in soil is very less (15-20 per cent) indicating transformation into very sparingly soluble forms. These sparingly soluble forms control the P concentration in soil solution for a long period of time. The uptake of P by plants is indirectly governed by the solubility of these compounds.

P fractionation is an applicable technique to determine the P status of soils and to study the chemistry and genesis of soil (Chang and Jackson, 1957). Accurately characterizing P form is a prerequisite to develop effective remediation strategies to minimize the adverse environment impact. Principles of the fractionation methods are to displace PO_4^{-P} from its sorption sites through anion competition, to alter the adsorption surface, or to dissolve compounds containing P. The most easily desorbed and labile compounds are removed first

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with dilute reagents and the strength of the extractant increases stepwise, in order to separate more strongly bound P forms. In calcareous soils, P is mainly bound to adsorption surfaces at low concentration, where as it is mainly precipitated as Ca-phosphate at higher concentrations. With this background, an attempt has been made to know the transformation of added Phosphorus in selected calcareous soils. The objectives of the study were to evaluate the status of P fractions in calcareous soils from agricultural fields and to investigate the relationship between soil properties and inorganic P fractions.

MATERIAL AND METHODS

Collection of soil samples

The profile samples of three calcareous soils developed from different parent materials were collected. A calcareous black soil, developed from Deccan traps, was sampled from uplands of Kaulagi village, 13 km East of Bijapur district on Gulberga highway. A brown soil in vicinity of this black soil and from where the top black soil had been completely eroded was sampled. This brown soil was also found to be calcareous. Another red soil which was also calcareous with lime nodules and developed from granite was also sampled from foot slopes of Nandibanda reserved forest, 5 km south-west of Mariyammanahalli in Hospet taluk (Plate. 1, 2, & 3).



Analyzing physico-chemical properties of soils

The soil samples were analyzed for clay, saturation percentage, organic carbon, free Fe-oxide, alkaline earth carbonate, CEC, exchangeable cations, available and other fractions of P, pH and EC using standard procedures (Jackson, 1958).

Laboratory experiment

An incubation study was conducted to know the extent of release or transformation of different forms of phosphorus in the soil after the addition of fertilizers, DAP and KH₂PO₄ The fertilizers, 124 mg of DAP or 42.75 mg of KH₂PO₄ were finally powdered and thoroughly mixed with 500 g soil samples. The amount of fertilizers added was equivalent to100 kg $P_{2}O_{z}$ per ha considering Cotton as the crop that needs maximum P among most crops of this region. A calculated amount of water was added and thoroughly mixed to bring the sample to saturation. The saturated condition of the sample was maintained during the course of incubation. The incubated sample was subsampled repeatedly at different time intervals to determine the P fractions. The subsamples were drawn on 0, 1, 2, 4, 7, 12, 18, 28 and 42 days of incubation.

Sequential extraction of P fractions

The soil phosphorus was sequentially fractionated using the fractionation technique (table.1) modified and developed by J. M. Ruiz, A. Delgado and J. Torrent (Ruiz *et al.*, 1997) *viz*. 0.1 M NaOH + 1M NaCl extractable P (Al and Fe phosphates), 0.27 M Nacitrate + 0.11 NaHCO₃ extractable P (Soluble Ca phosphates), 0.25M Na citrate extractable P (Pedogenic Ca phosphate), 0.2M Na citrate+0.05M ascorbate extractable P (mild reductant soluble P), 0.27M Na citrate-0.11M NaHCO₃-0.12M Na dithionite (CBD) extractable P (Reductant soluble P), 1M NaOAc extractable P (Residual Pedogenic Ca phosphates) and 1M HCl extractable P (Lithogenic apatite).

RESULTS

Physico- chemical Properties of Soils

The three calcareous soils developed from different parent materials were analysed for pH, EC, OC, CEC, exchangeable bases, alkaline-earth carbonates, available P and free oxides of Fe as represented in Table 2. The selected soils were alkaline. Black soil had pH of 8.2 in the surface and 8.3 in subsurface horizon. The brown and red soils had pH of 8.1 in both surface and subsurface horizons. The electrical conductivity of the soil solution of these calcareous soils was low. The sub- surface horizons always had less organic carbon content than surface horizon. The lowest organic carbon content was observed in red soil horizons. Exchangeable (Ca+ Mg) of surface and sub- surface horizons were 74.8 and 81.1 cmol (p⁺)

	Sequential	extractio	on of phosphorous fr	actions in calcareous soils	
Step	Extractant	pH	Shaking time (h)	P forms extracted	Abbreviations
1	0.1 M NaOH + 1M NaCl	-	16	Al- and Fe-bound P	NaOH-P
2	0.27 M Na- citrate + 0.11 NaHCO ₃	6-7	16	P readsorbed in the previous step: labile pedogenic Ca-rich phosphate	CB-P
3	0.25M Na citrate	6	16	Pedogenic Ca-P, much of the NaOH extractable P forms, if not dissolved	C1-P
4	0.25M Na citrate	6-7	8	Same as the previous step	C2-P
5	0.2M Na citrate+0.05M ascorbate	6	16	P occluded in poorly crystalline Fe-oxides	CAs-P
6	0.27M Na citrate-0.11M NaHCO ₃ -0.12M Na dithionite (CBD)	-	16	Various forms of P occluded in crystalline Fe-oxides	CBD-P
7	1M NaOAc	4	6	Ca-P excluding lithogenic apatite	NaOAc-P
8	1M HCl	-	16	Mostly lithogenic apatite	HCl-P

Table 1	
Sequential extraction of phosphorous fractions in calcareous se	oils

Table 2
Physico-chemical properties of selected calcareous soils

			J =		··· r · r							
Soils	Depth (cm)	рН (1:2.5)	EC (1:2.5)	E cat	Exchangea tions(cmol kg ⁻¹)	ble l(p+)	CEC (cmol(p ⁺) kg ⁻¹)	Clay (%)	OC (%)	CaCO ₃ (%)	Fe-ox (%)	Available P (mg kg ⁻¹)
				Na	Κ	Ca+ Mg						
Brown	0-30	8.1	0.16	0.33	0.18	74.8	80.1	43.7	0.54	11.2	4.3	11.7
	30-75	8.1	0.12	0.57	0.10	81.1	88.8	54.3	0.48	11.4	3.6	9.9
Black	0-28	8.3	0.15	0.15	0.22	57.1	67.0	54.8	0.31	13.9	1.5	14.4
	28-75	8.2	0.15	0.30	0.17	66.6	71.9	59.0	0.28	14.2	1.4	12.2
Red	0-20	8.1	0.12	0.07	0.18	11.0	11.3	21.7	0.27	12.4	0.3	11.5
	20-42	8.1	0.11	0.07	0.16	8.0	9.5	17.0	0.26	11.9	0.3	9.3

kg⁻¹ for brown; 57.1 and 66.6 cmol (p^+) kg⁻¹ for black and 11.0 and 8.0 cmol (p⁺) kg⁻¹ for red soils respectively. The exchangeable sodium and potassium contents of the soil solution of these calcareous soils were low. There was not much difference in the content of exchangeable sodium and potassium of these soils. The brown and black soils had high cation exchange capacity, but red soils were with very less CEC as compared to brown and black soils. There was a good amount of calcium carbonates for the soil P to react. The brown soil had 11.7 and 9.9 mg kg⁻¹ available P in surface and subsurface horizons respectively. The available P of surface and subsurface horizons was 14.4 and 12.2 mg kg⁻¹ for black; 11.5 and 9.3 mg kg⁻¹ for red soils respectively. These calcareous soils were low in available P. The red soils had less clay content as compared to brown and black soils.

Soil P fractions in surface and subsurface horizons of selected brown, black and red calcareous soils after incubation with KH_2PO_4 and DAP were presented in table 3 and table 4 respectively.

NaOH-P: Al - and Fe - bound P (Fraction-1)

The Al and Fe bound P increased in all the calcareous soils during first week of incubation. In the surface horizon of all the three calcareous soils, this fraction maintained its concentration (about 25 mg kg⁻¹) for about three weeks and then slightly decreased during the next three weeks. The value of Al-and Fe-bound P was varying from 5.6 to 48.9 mg kg⁻¹. Al- and Febound P was higher in sub- surface soils as compared to surface soils in both cases of fertilizers.

CB-P: Soluble Ca Phosphates (Fraction-2)

The soluble Ca - P was initially nil in all the soils, but rapidly increased after two days of fertilizer application and by the end of first week, it attained maximum. It was observed, soluble Ca Phosphate was the third highest P fraction formed on the addition of KH_2PO_4 and DAP fertilizers. CB-P ranged from 106.5 to 280.0 mg kg⁻¹. In black soils, this fraction intermediate between brown and red soils. Low amount of soluble Ca -P was in red soils as compared to brown and black soils. In red soils, this fraction

				Soil P	fractions ii	n brown, bla	ck and red	Table 3 calcareous s	soils after i	ncubation v	vith KH ₂ PO ₄	ہ mg kg ¹			
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	DAI			S	oil P fractio	su					Sc	oil P fraction	1S		
Brown soil, surface horizon Brown soil, surface horizon 0 157 0.0 776.1 0.0 114.2 39.1 112.5 14.7 0.0 39.3 0.0 13 1 172 0.0 516.4 37.0 65.6 32.1 13.2 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 0.0 39.3 20.1 39.3 20.1 39.3 20.1 39.3 20.1 39.3 20.1 39.3 20.1 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 39.3 20.0 3		Fr.1	Fr.2	Fr.3	Fr.4	Fr.5	Fr.6	Fr.7	Fr.1	Fr.2	Fr.3	Fr.4	F	r.5	r.5 Fr.6
				Brow	a soil, surfi	ace horizon					Browr	ı soil, subs	urface h	loriz	lorizon
	0	15.7	0.0	776.1	0.0	114.2	39.1	112.5	14.7	0.0	359.3	0.0	157.0		41.7
	1	17.2	0.0	517.4	37.0	85.6	52.1	121.4	17.2	0.0	273.1	28.3	90.4		57.3
	6	15.7	0.0	316.2	143.6	456.7	59.9	135.7	14.2	0.0	287.5	50.0	444.8		61.2
	4	11.7	0.0	258.7	0.0	613.7	59.9	227.3	18.2	210.6	258.7	0.0	506.7		65.2
12 19.3 2279 129.3 2070 100 566.8 347.3 28 9.1 0.0 156.4 0.0 47.3 11.0 0.0 445.8 28 7.1 0.0 1560.4 0.0 47.3 73.0 166.8 0.0 475.3 27 7.1 0.0 1560.4 0.0 423.4 78.2 112.5 10.0 1250.4 0.0 475.3 27 7.1 0.0 377.3 38.8 2007 0.0 132.4 33.2 0.0 140.5 25.5 0.0 296.4 60.4 116.0 98.1 94.1 7.4 25.6 111.5 215.6 0.0 47.4 37.7 36.7 17.4 25.6 111.5 215.6 0.0 346.3 90.0 185.4 450.1 25.6 111.5 215.6 0.0 47.4 47.7 77.3 17.4 25.6 111.4 125.	5	17.7	257.7	804.9	0.0	385.3	67.8	144.5	16.2	265.1	186.8	0.0	361.6		63.9
18 22.3 153.6 1178.5 0.0 359.2 91.1 0.0 158.0.0 0.0 268.8 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.3 0.0 268.4 69.4 116.0 9.8 13.0 14.1 50.1 20.2	12	19.3	227.9	1293.5	0.0	506.7	88.6	136.8	21.3	252.7	733.0	0.0	447.2		49.5
28 9.1 0.0 1250.4 0.0 423.4 78.2 112.5 11.1 0.0 646.8 0.0 435.3 7.1 0.0 1500.0 0.0 347.3 28.0 140.3 13.2 0.0 646.8 0.0 455.3 1 0.0 1500.0 0.0 347.3 28.0 140.3 13.2 0.0 131.7 0.0 340.2 1 25.6 111.5 215.6 0.0 437.1 72.3 147.5 72.3 127.4 2 25.6 111.5 215.6 0.0 431.4 19.6 121.3 0.0 148.5 74.5 2 25.6 111.5 215.6 0.0 316.7 36.7 317.4 19.6 0.1 18.5 426.0 7 25.5 11.4 12.2 10.5 21.4 13.2 0.0 118.5 426.0 7 29.0 24.4 45.5 11.2 10.5 21	18	22.3	153.6	1178.5	0.0	359.2	91.2	94.9	20.3	213.1	1500.0	0.0	268.8		80.8
42 7.1 0.0 15000 0.0 347.3 28.0 140.3 13.2 0.0 122.17 0.0 340.2 1 23.7 Black soil, surface horizon Black soil, surface horizon Black soil, subsurface horizon Black soil, subsurface horizon Black soil, subsurface horizon 3 7.3 3 8.8 2007 0.0 132.4 33.2 0.0 331.7 7.2.3 127.4 1 23.7 0.0 27.3 146.9 11.0 0.0 344.4 74.7 2 55.6 111.5 215.6 0.0 401.4 12.2 146.9 17.0 0.0 345.7 2 25.5 174.3 174	28	9.1	0.0	1250.4	0.0	423.4	78.2	112.5	11.1	0.0	646.8	0.0	435.3		71.7
Black soil, surface horizon Black soil, surface horizon 0 204 0.0 37/3 38.8 200.7 0.0 132.4 33.2 0.0 33.17 72.3 127.4 1 23.7 0.0 296.4 69.4 116.0 9.8 139.6 35.5 0.0 39.8 14.1 501.1 2 25.6 111.5 156.0 0.0 40.3 32.2 139.6 35.5 0.0 34.4 74.7 2 25.6 111.5 156.0 0.0 40.4 55.7 31.3 14.6 50.1 2 25.5 10.0 244.8 99.0 0.0 256.4 260.3 2 11.2 131.4 15.2 131.4 15.2 131.6 135.0 0.0 256.3 260.3 256.3 260.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3 266.3	42	7.1	0.0	1500.0	0.0	347.3	28.0	140.3	13.2	0.0	1221.7	0.0	340.2		63.9
				Black	soil, surfa	ce horizon					Black	soil, subsu	rface horizo	ų	
	0	20.4	0.0	377.3	38.8	200.7	0.0	132.4	33.2	0.0	331.7	72.3	127.4		0.0
2 25.6 0.0 269.5 55.1 441.5 7.3 146.9 21.0 0.0 39.8 14.1 501.1 7 275 210.7 1500.0 0.0 401.4 12.2 131.4 196.0 0.0 118.5 426.0 7 275 220.7 1570.0 0.0 401.4 12.2 107.5 0.0 0.0 0.0 457.5 426.0 8 14.2 0.0 498.5 0.0 244.4 452.5 21.0 0.0 0.0 0.0 276.3 226.7 11.0 79.0 0.0 0.0 276.3 276.0 276.7 286.7 276.7 0.0 0.0 0.0 0.0 276.3 276.3 276.7 286.7 276.3 276.7 286.7 276.7 286.7 276.7 286.7 276.7 286.7 276.7 286.7 276.7 286.7 276.7	1	23.7	0.0	296.4	69.4	116.0	9.8	139.6	35.5	0.0	398.0	84.4	74.7		24.1
4 25.6 111.5 215.6 0.0 425.9 12.2 131.4 19.6 121.3 0.0 118.5 426.0 7 27.5 220.7 1500.0 0.0 401.4 12.2 105.5 21.0 260.8 0.0 0.0 452.7 18 31.3 174.3 175.2 0.0 316.7 36.7 99.3 24.3 24.48 199.0 0.0 452.7 28 14.2 0.0 0.0 294.4 45.2 87.9 21.5 135.0 0.0 0.0 298.5 29 0.0 0.0 294.4 45.2 87.9 21.5 0.0 20.0 20.0 20.3 29 0.0 0.0 295.5 11.0 70.0 7.0 70.0 27.4 436.7 20 0.0 0.0 17.4 25.6 0.0 10.0 10.5 57.1 210.9 0.0 0.0 130.4 93.1 7.0 <th>6</th> <td>25.6</td> <td>0.0</td> <td>269.5</td> <td>55.1</td> <td>441.5</td> <td>7.3</td> <td>146.9</td> <td>21.0</td> <td>0.0</td> <td>39.8</td> <td>14.1</td> <td>501.1</td> <td></td> <td>9.6</td>	6	25.6	0.0	269.5	55.1	441.5	7.3	146.9	21.0	0.0	39.8	14.1	501.1		9.6
7 27.5 220.7 1500.0 00 401.4 12.2 105.5 21.0 260.8 0.0 452.7 18 31.3 174.3 175.2 0.0 316.7 36.7 99.3 $24.4.8$ 199.0 0.0 257.1 28 14.2 0.0 498.5 0.0 450.5 33.0 74.5 11.2 0.0 0.0 270.3 29 0.0 498.5 0.0 498.5 0.0 476.6 0.0 270.3 28 142 0.0 498.5 0.0 450.5 33.0 74.5 11.2 249.6 0.0 270.3 270.3 28 100.9 0.0 476.6 0.0 300.6 200 270.3 278.6 436.7 10 285.6 0.0 212.8 0.0 217.4 133.0 236.6 0.0 237.8 436.7 10 <th>4</th> <td>25.6</td> <td>111.5</td> <td>215.6</td> <td>0.0</td> <td>425.9</td> <td>12.2</td> <td>131.4</td> <td>19.6</td> <td>121.3</td> <td>0.0</td> <td>118.5</td> <td>426.0</td> <td></td> <td>7.2</td>	4	25.6	111.5	215.6	0.0	425.9	12.2	131.4	19.6	121.3	0.0	118.5	426.0		7.2
1229.0 267.2 175.2 0.0 316.7 36.7 99.3 24.4 199.0 0.0 285.4 18 31.3 174.3 175.2 0.0 294.4 45.2 87.9 21.5 135.0 0.00.0 270.3 28 14.2 0.0 498.5 0.0 294.4 45.2 87.9 21.5 135.0 0.00.0 270.3 28 14.2 0.0 498.5 0.0 2297.1 11.0 79.0 70.0 477.6 0.0 270.3 29 10.9 0.0 0.0 2297.1 11.0 79.0 70.0 477.6 0.0 270.3 260.0 0.0 478.8 103.2 2297.1 11.0 79.0 0.0 347.1 85.4 100.5 0 275 0.0 432.8 103.2 232.8 0.0 17.4 25.6 0.0 347.1 85.4 100.5 1 282 0.0 0.0 347.1 85.4 100.5 $33.3.9$ 37.8 436.7 1 282 0.0 0.0 275.2 0.0 272.4 48.9 0.0 97.6 0.0 499.3 2 32.8 216.4 584.3 0.0 274.4 133.0 $33.3.9$ 2 31.3 173.5 389.5 0.0 270.4 3.9 $23.3.9$ 2494.9 0.0 271.3 2 1277.4 32.6 0.0 191.1 33.6	5	27.5	220.7	1500.0	0.0	401.4	12.2	105.5	21.0	260.8	0.0	0.0	452.7		7.2
18 31.3 175.2 0.0 294.4 45.2 87.9 21.5 135.0 0.0 0.0 270.3 28 14.2 0.0 498.5 0.0 450.5 33.0 74.5 11.2 0.0 477.6 0.0 293.6 42 10.9 0.0 0.0 200 229.7 11.0 79.0 7.0 0.0 477.6 0.0 293.6 42 10.9 0.0 0.0 229.7 11.0 79.0 7.0 0.0 477.6 0.0 257.1 40 0.0 0.0 232.8 0.0 17.4 25.6 0.0 34.4 93.1 2.0 34.4 93.1 2.0 34.4 133.0 34.3.6 100.5 333.9 1 28.2 0.0 0.0 303.0 34.4 93.1 2.0 34.4 133.0 33.9 1 28.8 0.0 329.5 0.0 34.4 145.9 1247.4	12	29.0	267.2	175.2	0.0	316.7	36.7	99.3	24.3	244.8	199.0	0.0	285.4		9.6
28 14.2 0.0 496.5 0.0 450.5 33.0 74.5 11.2 0.0 477.6 0.0 298.6 42 10.9 0.0 0.0 0.0 229.7 11.0 79.0 7.0 0.0 199.0 0.0 257.1 42 10.9 0.0 0.0 229.7 11.0 79.0 7.0 0.0 199.0 0.0 257.1 7 Red soil, surface horizon Red soil, surface horizon Red soil, subsurface horizon Red soil, subsurface horizon 1 282 0.0 47.4 93.1 2.0 17.4 25.6 0.0 34.6.7 100.5 1 282 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 97.6 0.0 409.3 37.0 0.0 0.0 307.4 39.2 295.6 0.0 97.6 0.0 97.6 0.0 79.3 2 32.8 0.0 28.2 <	18	31.3	174.3	175.2	0.0	294.4	45.2	87.9	21.5	135.0	0.0	0.0	270.3		22.9
42 109 00 00 00 229.7 11.0 79.0 7.0 00 199.0 0.0 257.1 0 27.5 0.0 432.8 103.2 232.8 0.0 17.4 25.6 0.0 336.3 37.8 436.7 1 28.2 0.0 432.8 103.2 232.8 0.0 17.4 25.6 0.0 347.1 85.4 100.5 2 38.5 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 347.1 85.4 100.5 2 38.5 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 97.6 0.0 409.3 37.0 0.0 0.0 329.5 0.0 327.4 48.9 0.0 97.6 0.0 409.3 37.1 37.3 389.5 0.0 329.4 40.9 0.0 97.6 0.0 409.3 31.3 <t< td=""><th>28</th><td>14.2</td><td>0.0</td><td>498.5</td><td>0.0</td><td>450.5</td><td>33.0</td><td>74.5</td><td>11.2</td><td>0.0</td><td>477.6</td><td>0.0</td><td>298.6</td><td></td><td>20.5</td></t<>	28	14.2	0.0	498.5	0.0	450.5	33.0	74.5	11.2	0.0	477.6	0.0	298.6		20.5
Red soil, surface horizonRed soil, surface horizon0 27.5 0.0 432.8 103.2 232.8 0.0 17.4 25.6 0.0 336.3 37.8 436.7 1 282 0.0 303.0 34.4 93.1 2.0 17.4 25.6 0.0 347.1 85.4 100.5 2 38.5 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 97.6 0.0 490.3 4 37.0 0.00.0 304.4 0.0 28.2 34.4 145.9 1247.4 0.0 490.3 7 32.8 216.4 584.3 0.0 304.4 0.0 282.2 34.4 145.9 1247.4 0.0 490.3 7 32.8 216.4 584.3 0.0 270.4 3.9 23.3 34.8 170.2 158.3 0.0 251.3 12 31.3 173.5 389.5 0.0 270.4 3.9 23.3 34.8 170.2 1583.8 0.0 251.3 18 25.9 194.1 1500.0 0.0 497.8 0.0 16.6 30.6 0.0 694.2 0.0 244.1 8 226.6 0.0 594.9 0.0 264.2 20.0 251.3 18 225.0 0.0 197.6 0.0 197.6 0.0 244.1 18 226.6 0.0 197.2 2494.9 0.0 244.1 <th>42</th> <td>10.9</td> <td>0.0</td> <td>0.0</td> <td>0.0</td> <td>229.7</td> <td>11.0</td> <td>79.0</td> <td>7.0</td> <td>0.0</td> <td>199.0</td> <td>0.0</td> <td>257.1</td> <td></td> <td>40.9</td>	42	10.9	0.0	0.0	0.0	229.7	11.0	79.0	7.0	0.0	199.0	0.0	257.1		40.9
0 27.5 0.0 432.8 103.2 232.8 0.0 17.4 25.6 0.0 336.3 37.8 436.7 1 28.2 0.0 303.0 34.4 93.1 2.0 15.8 40.9 0.0 347.1 85.4 100.5 2 38.5 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 347.1 85.4 100.5 4 37.0 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 347.4 85.4 100.5 37.0 0.0 0.0 0.0 329.5 0.0 38.2 35.6 0.0 97.6 0.0 499.3 7 32.8 216.4 584.3 0.0 382.2 34.4 145.9 1247.4 0.0 499.3 7 32.8 236.5 0.0 270.4 3.9 23.3 2494.9 0.0 244.1 8 170.2				Red s	oil, surface	horizon					Red so	oil, subsurt	ace horizon		
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2 38.5 0.0 75.7 26.2 295.5 0.0 27.4 48.9 0.0 184.4 133.0 333.9 4 37.0 0.0 0.0 0.0 329.5 0.0 38.2 35.6 0.0 97.6 0.0 409.3 7 32.8 216.4 584.3 0.0 304.4 0.0 28.2 34.4 145.9 1247.4 0.0 490.3 12 31.3 173.5 389.5 0.0 270.4 3.9 23.3 34.8 170.2 1583.8 0.0 251.3 18 25.9 194.1 1500.0 0.0 191.6 0.0 16.6 30.6 0.0 694.2 0.0 244.1 28 23.6 0.0 595.0 0.0 497.8 0.0 16.6 30.6 0.0 694.2 0.0 244.1	1	28.2	0.0	303.0	34.4	93.1	2.0	15.8	40.9	0.0	347.1	85.4	100.5		0.0
4 37.0 0.0 0.0 329.5 0.0 38.2 35.6 0.0 97.6 0.0 409.3 7 32.8 216.4 584.3 0.0 304.4 0.0 28.2 34.4 145.9 1247.4 0.0 490.3 12 31.3 173.5 389.5 0.0 270.4 3.9 23.3 34.8 170.2 1583.8 0.0 251.3 18 25.9 194.1 1500.0 0.0 191.6 0.0 19.1 33.6 155.3 2494.9 0.0 244.1 28 23.6 0.0 595.0 0.0 497.8 0.0 16.6 30.6 0.0 694.2 0.0 391.4	0	38.5	0.0	75.7	26.2	295.5	0.0	27.4	48.9	0.0	184.4	133.0	333.9		1.0
7 32.8 216.4 584.3 0.0 304.4 0.0 28.2 34.4 145.9 1247.4 0.0 430.8 12 31.3 173.5 389.5 0.0 270.4 3.9 23.3 34.8 170.2 1583.8 0.0 251.3 18 25.9 194.1 1500.0 0.0 191.6 0.0 19.1 33.6 155.3 2494.9 0.0 244.1 28 23.6 0.0 497.8 0.0 16.6 30.6 0.0 694.2 0.0 391.4	4	37.0	0.0	0.0	0.0	329.5	0.0	38.2	35.6	0.0	97.6	0.0	409.3		0.0
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28 23.6 0.0 595.0 0.0 497.8 0.0 16.6 30.6 0.0 694.2 0.0 391.4	18	25.9	194.1	1500.0	0.0	191.6	0.0	19.1	33.6	155.3	2494.9	0.0	244.1		5.9
	28	23.6	0.0	595.0	0.0	497.8	0.0	16.6	30.6	0.0	694.2	0.0	391.4		4.9

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			Soil 1	P fractions	in brown, bl	ack and rec	Table 4 l calcareous	soils after	incubation	with DAP, 1	ng kg ¹			
DAI			S	oil P fraction	S1					Sc	il P fraction	s		
	Fr.1	Fr.2	Fr.3	Fr.4	Fr.5	Fr.6	Fr.7	Fr.1	Fr.2	Fr.3	Fr.4	Fr.5	Fr.6	Fr.7
			Вгоwп	soil, surface	horizon					Вгочн	soil, subsurj	face horizon		
0	24.3	0.0	776.1	0.0	128.4	9.8	88.3	24.8	0.0	316.2	0.0	123.7	49.5	227.3
1	18.2	0.0	589.3	145.8	104.7	12.0	164.4	24.3	0.0	344.9	152.3	66.6	62.6	156.7
7	18.7	0.0	431.2	87.0	1079.9	11.3	176.5	28.4	0.0	301.8	67.4	497.1	65.2	221.8
4	16.2	146.2	115.0	0.0	463.8	12.8	195.3	27.4	106.5	244.3	0.0	437.7	65.2	173.2
7	14.2	272.5	675.5	0.0	409.1	17.3	175.4	29.9	280.0	28.7	0.0	366.3	70.4	144.5
12	15.7	230.4	359.3	0.0	456.7	29.3	132.4	40.0	220.5	459.9	0.0	516.2	58.7	142.3
18	19.8	242.8	1135.4	0.0	337.8	31.9	119.2	14.7	225.4	1394.1	0.0	318.7	76.9	122.5
28	9.6	0.0	1500.0	0.0	440.0	25.2	121.4	14.2	0.0	517.4	0.0	428.2	67.8	137.7
42	5.6	0.0	1451.6	0.0	316.4	17.7	141.7	22.3	0.0	1437.3	0.0	366.3	77.6	121.4
			Black 5	soil, surface I	iorizon					Black s	oil, subsurfa	ce horizon		
0	21.8	0.0	606.3	57.1	116.0	0.0	121.0	36.9	0.0	278.6	0.0	259.1	0.0	87.6
1	25.2	0.0	336.9	30.6	71.4	7.3	145.8	39.7	0.0	384.7	58.2	105.4	28.9	94.7
2	25.2	0.0	0.0	67.3	441.5	2.4	142.7	41.1	0.0	106.1	90.4	469.9	12.0	115.1
4	26.6	162.7	40.4	97.9	425.9	4.9	135.5	33.2	235.7	26.5	0.0	410.6	16.9	108.0
4	27.5	241.7	0.0	0.0	401.4	17.1	130.3	28.5	254.0	0.0	0.0	469.9	12.0	98.8
12	28.5	232.4	302.4	0.0	316.7	39.1	112.7	30.4	114.4	663.3	0.0	318.4	12.0	91.7
18	30.4	16.3	606.3	0.0	294.4	30.6	98.3	27.6	0.0	1500.0	0.0	329.4	20.5	86.6
28	14.7	0.0	148.2	0.0	450.5	20.8	92.1	13.1	0.0	106.1	0.0	335.9	22.9	81.5
42	15.2	0.0	309.9	0.0	229.7	12.2	86.9	6.5	0.0	1500.2	0.0	245.9	25.3	89.6
			Red sc	il, surface h	orizon					Red so	l, subsurface	e horizon		
0	29.7	0.0	389.5	81.9	93.1	0.0	16.6	32.5	0.0	325.4	100.2	53.9	0.0	0.0
1	29.0	0.0	270.5	113.0	82.4	2.0	23.3	42.1	0.0	282.0	42.7	104.1	0.0	23.3
7	30.9	0.0	97.4	3.3	304.4	0.0	32.4	46.3	0.0	216.9	39.4	393.1	0.0	24.1
4	29.4	0.0	0.0	0.0	408.3	0.0	17.4	32.9	0.0	0.0	0.0	418.3	0.0	29.1
7	30.1	246.3	681.7	0.0	351.0	0.0	24.1	30.2	258.1	1225.7	0.0	339.3	3.0	30.0
12	27.1	216.4	1500.0	0.0	291.9	0.0	36.5	31.0	224.5	271.2	0.0	256.7	8.9	29.1
18	27.5	169.8	422.0	0.0	232.8	0.0	28.2	32.1	147.8	1500.0	0.0	188.5	8.9	24.1
28	26.3	0.0	898.1	0.0	379.6	2.9	15.9	28.7	0.0	1421.0	0.0	452.4	0.0	29.0
42	24.0	0.0	1125.3	0.0	311.6	28.5	17.3	20.6	0.0	564.1	0.0	235.2	29.5	20.3

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was higher in surface soils than sub-surface soil when these soils were applied with KH₂PO₄. But, when these soils were applied with DAP, this fraction was higher in sub- surface soil.

C1-C2-P: Pedogenic Ca- P (Fraction-3)

Pedogenic Ca - P (C-P) was the quantitatively highest fraction among all other fractions. Even though this fraction was found to decrease during first few days, it increased later and remained high during the period of incubation. C-P ranged from 0 to 1500 mg kg⁻¹. All the three calcareous soils were similar with respect to this content.

CAs-P: Mild reductant soluble P (Occluded P) (Fraction-4)

This fraction was present in these calcareous soils only initially about 50 mg kg⁻¹ and 100 mg kg⁻¹ of KH₂PO₄ and DAP respectively up to about three days. After which it vanished irrespective of the soils and fertilizers added. CAs-P ranged from 14.1 to 152.3 mg kg⁻¹. As the days of incubation increased, there was a decrease in the occluded P, with respect to all the sources.

CBD- P: Reductant soluble P (Fraction-5)

Reductant soluble P started to increase about 5 times (about 500 mg kg⁻¹) with in the first week of incubation and remained so during next period of incubation. CBD-P ranged from 53.9 to 1079.9 mg kg⁻¹. In brown soils, reductant soluble P was higher in surface horizon on the addition of KH_2PO_4 and DAP. Both horizons showed a similar trend during the course of incubation.

NaOAc-P: Residual Ca-P (Ca-P excluding lithogenic apatite) (Fraction-6)

When brown soils of both horizons were applied with KH_2PO_4 , residual Ca-P increased during initial days of incubation in both surface and sub-surface brown soils. NaOAc -P ranged from 0.0 to 91.2 mg kg⁻¹. On the addition of KH_2PO_4 , this fraction was high in sub-surface soils as compared to surface brown soil. In black soils, more content of residual Ca - P was observed when it was treated with KH_2PO_4 than DAP. This fraction was higher in surface soils than sub-surface black soil on the addition of KH_2PO_4 . On the addition of DAP, this fraction was more in sub-surface red soil than KH_2PO_4 addition.

HCl-P: Lithogenic Ca-P (Fraction-7)

The lithogenic apatite P fraction was higher in subsurface horizon when brown soils were applied with both KH_2PO_4 and DAP. This fraction increased during initial one week and attained maximum on 7 DAI and then gradually decreased during the course of incubation. The black soil was intermediate between brown and red soils of this fraction.

DISCUSSION

NaOH-P: Al - and Fe - bound P

Al- and Fe- bound P fraction was higher in red soil than in brown or black soil, despite having least amount of free Fe-oxide content. This fraction constitutes a small fraction of calcareous soil. Since the increase of soil pH is generally associated with increase of Ca-content and decrease of Al-and Feoxides, the amount of this fraction is very low compared to all other fractions (Fig. 1a). The low Aland Fe-P content might be due to low Al activity as a consequence of its precipitation at higher pH (Adhami *et al.*, 2007).







Soluble and Pedogenic Ca Phosphates

Ruiz *et al.*, (1997) reported that soluble Ca - P values exceeded the Al- and Fe- bound P values in calcareous soils, probably because citrate complexes Ca, thus partly dissolving Ca- rich phosphates (Fig.2a). It is likely that metastable phase (dicalcium, octacalcium and tricalcium phospahate) and possibly a small fraction of stable phase (hydroxyapatite) were dissolved in citrate bicarbonate (Delgado and Torrent, 2000).

The nature of variation of pedogenic Ca phosphate remained similar for different soils at different horizons were same irrespective of the fertilizers added (Fig. 3a). It is partly available to plants (Samadi, 2006). Citrate is common reagent to evaluate P availability of fertilizers. The high content of pedogenic Ca-P in these soils indicated that the high risk of adverse effects of P on both agricultural production and environmental quality (Adhami *et al.*, 2007). Delgado *et al.* (2002), explained that citrate releases P related to Ca-phosphate as a consequence of Ca-complexation by citrate.

Mild Reductant and Reductant Soluble P

Citrate ascorbate extractable P is assumed to be associated with poorly crystalline Fe oxides (Ruiz *et al.*, 1997). The high content of this fraction indicates that most of the reductant soluble P could be easily reduced and solubilised when subjected to reducing condition. P occluded in poorly and highly crystalline Fe oxides (mild reductant soluble P and reductant soluble P, respectively) is not related to the degree of enrichment of P in to the soil. It is a consequence of pedogenic process of the soil. The reductant soluble P (CAs-P and CBD-P) provides an index of P that can

be potentially released when soils are subjected to reducing condition (Fig. 4a & 5a).



Residual and Lithogenic Ca-P

High amounts of $CaCO_3$ and its large surface area lead to more rapid precipitation of P (Tisdale *et al.* 2002); consequently, less formation of residual Ca-P (Fig.6a).

During initial days of incubation, this fraction was higher in surface soils in case of both fertilizers and maintained same concentration during remaining days of the incubation (Fig. 7a). Similar result such as





lithogenic apatite content remained unchanged after fertilizer P was reported by Wang *et al.*, (2010). The phosphorous extracted with a dilute acidic solution is primary P minerals such as hydroxylflourapatite (Adhami *et al.*, 2007).

CONCLUSION

From the present study, it was seen that each phosphorus fractions responded distinctly with addition of different fertilizers. In this study, in brown soil and black soil, the order of occurrence of inorganic fractions was: lithogenic apatite> reductant-soluble P> residual P> Al- and Fe- bound P. In case of red soil, however, the lithogenic apatite fraction was lesser than the residual P fraction. This may be attributed to the calcareous nature of these soils.

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