General Impact Factor (GIF): 0.875

e- ISSN: 2394-5532
p- ISSN: 2394-823X

International Journal of Applied And Pure Science and Agriculture
www.ijapsa.com

Reaction products of Phosphorous fertilizers in calcareous soils with different parent materials

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Abstract

The transformation of added phosphorus into distinct fractions during incubation of three calcareous soils of different parent materials was studied. Applied phosphate transformed mostly into Pedogenic Ca-P followed by reductant-soluble P in all the three soils. 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. The mild reductant-soluble P decreased rapidly and vanished after first few days of incubation. None of the fertilizers used did contribute to this fraction of P. The reductant-soluble P increased to about 5 times (up to 500 mg kg^{-1}) by the end of first week of incubation and remained so during remaining period of incubation.The lithogenic apatite did not show much variation either from the start or during incubation.

Key words: P- fertilizers, reaction products, calcareous soil

I. Introduction

Phosphorus 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 proportions 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 percent 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%) indicating transformation into very sparingly soluble forms. The 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 solubilities of these compounds. In the present study, an attempt has been made to know the transformation of added Phosphorus in selected soils.

II. Material and Methods

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. 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 KH_2PO_4. The fertilizers, 124 mg of DAP or 42.75 mg of KH_2PO_4 were finally powdered and thoroughly mixed with 500 g soil samples. The amount of fertilizers added was equivalent to100 kg P_2O_5 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 thus at 0, 1, 2, 4, 7, 12, 18, 28 and 42 days of incubation. Each subsample was also analyzed for pH and EC. The soil phosphorus was sequentially fractionated using the fractionation technique modified and developed by J. M. Ruiz, A. Delgado and J. Torrent (Ruiz *et al*., 1997) *viz.* 0.1 M NaOH + 1M NaCl extracable P (Al and Fe phosphates), 0.27 M Na- citrate + 0.11 $NaHCO_3$ extracable P (Soluble Ca phosphates), 0.25M Na citrate extracable P (Pedogenic Ca phosphate), 0.2M Na citrate+0.05M ascorbate extracable P (mild reductant soluble P), 0.27M Na citrate–0.11M $NaHCO_3$–0.12M Na dithionite (CBD) extracable P (Reductant soluble P), 1M NaOAc extracable P (Residual Pedogenic Ca phosphates) and1M HCl extracable P (Lithogenic apatite).

III. Result and Discussion

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.1 and table.2 respectively.

Fraction- 1: Al - and Fe - bound P

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. Al- and Fe-bound P was higher in sub- surface soils as compared to surface soils in both cases of fertilizers. 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. Therefore this fraction appears to be more bound to Al in these soils. This suggests that portion of added phosphate was transformed into Al-P because of increase in the concentration of P in soil solution (Srivastava *et al*., 1969).

Fraction- 2: Soluble Ca Phosphates

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. 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 was higher in surface soils than sub- surface soil when these soils were applied with KH_2PO_4. But, when these soils were applied with DAP, this fraction was higher in sub- surface soil. 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.

Fraction- 3: Pedogenic Ca- P

Pedogenic Ca - 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. All the three calcareous soils were similar with respect to this content. The nature of variation remained similar for different soils at different horizons were same irrespective of the fertilizers added.

Fraction 4: Mild reductant soluble P (Occluded P)

This fraction was present in these calcareous soils only initially about 50 mg kg^{-1} and 100 mg kg^{-1} of KH_2PO_4 and DAP respectively up to about three days. After which it vanished irrespective of the soils and fertilizers added. As the days of incubation increased, there was a decrease in the occluded P, with respect to all the sources. This is due to the presence of coatings of iron oxide, which are in a highly oxidized state (Hesse, 1994).

Fraction- 5: Reductant soluble P

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. 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 as.

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.

Fraction- 6: Residual Ca-P

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. 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. 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.

Fraction- 7: Lithogenic apatite

The lithogenic apatite P fraction was higher in sub- surface 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. 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. Similar result such as lithogenic apatite content remained unchanged after fertilizer P was reported by (Jun Wang, 2010).

IV. Conclusion

From the present study, it is 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.

ACKNOWLEDGEMENT

The financial support provided by University of Agricltural Sciences, Raichur is gratefully acknowledged.

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DAI	*Soil P fractions*							*Soil P fractions*						
	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
	Brown soil, surface horizon							**Brown soil, subsurface 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
2	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 soil, surface horizon							**Black soil, subsurface 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
7	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 soil, surface horizon							**Red soil, subsurface 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
2	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

DAI	*Soil P fractions*							*Soil P fractions*						
	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
	Brown soil, surface horizon							Brown soil, subsurface horizon						
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	185.7
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	235.4
2	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	248.2
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	160.2
7	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	150.3
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	134.8
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	134.8
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	126.7
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	113.9
	Black soil, surface horizon							**Black soil, subsurface horizon**						
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	88.6
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	93.7
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	9.6	89.6
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	101.8
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	7.2	103.9
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	102.9
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	102.9
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	95.7
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	86.0
	Red soil, surface horizon							**Red soil, subsurface horizon**						
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	0.0	24.1
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	25.0
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	1.0	26.6
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	32.5
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	1.0	31.6
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	9.8	17.5
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	19.2
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	14.0
42	22.1	0.0	1374.1	0.0	349.2	26.5	16.9	22.2	0.0	672.5	0.0	294.4	31.5	23.0

Table.1 Soil P fractions in brown, black and red calcareous soils after incubation with KH_2PO_4, mg kg^{-1}
Table.2. Soil P fractions in brown, black and red calcareous soils after incubation with DAP, mg kg^{-1}