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Assessment of residual effectiveness of applied phosphate by the ^{32}P exchange method

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Abstract

Effectiveness of residual phosphate was determined in 13 Pakistani soil series and an English soil, by the isotopic exchange method. Phosphate (^{31}P) was added to each soil to fulfill the maximum P sorption capacity. The soils after addition of phosphate were incubated at 10, 25 and 45 °C for 365 days to extend the observations equivalent to many years under field conditions. After one year of incubation, exchange with carrier free ^{32}P was measured. Results showed that the isotopically labile P (E values) decreased as temperature increased. A poor correlation was found between $CaCO_3$ and E values suggesting that high pH (Na), organic matter and reactivity of $CaCO_3$ control the ability of $CaCO_3$ in these soils to decrease labile P. The labile P in these soils decreased as the Olsen P decreased with time and this relationship was well described by the power equation. A linear relationship between solution P (intensity factor) and labile P (quantity factor) was found in these soils. It is concluded from this study that the residual effectiveness of phosphate varies from soil to soil, and increasing time of contact and temperature have a marked effect on its amount in a soil.

Key words: Intensity, quantity, isotopically labile P, calcium carbonate, sodium

Introduction

The effectiveness of freshly added phosphate decreases with prolonged contact between soil and phosphate and hence the labile pool of soil phosphate decreases. The decrease in the labile pool is also affected by increasing temperature. The contact time and temperature are important factors controlling the extent of adsorption and precipitation reactions (Barrow, 1974; Freeman and Rowell, 1981; Bramley and Barrow, 1992; Mendoza, 1992; Feng *et al.*, 1996; Panahi, 1997; Indiati *et al.*, 1999). Labile P is the fraction of the soil phosphate that is isotopically exchangeable with ^{32}P within a specified time (Olsen and Khasawneh, 1980) and represents the fraction of phosphate that is available to plants (Larsen, 1952; White, 1976; Holford, 1997). It is significantly correlated with the P uptake by plants, and is often used as a reference for evaluating the measurement of available P in the soil (Morel and Plenchette, 1994). Isotopically exchangeable P (E value) allows precise quantification of exchange of inorganic ions between the soil solution and the solid phase of the soil (Fardeau, 1993; Frossard *et al.*, 1995) and the value is an estimate of the amount of labile P, which is the sum of the P in the soil solution and exchangeable P at the soil surface (Russell *et al.*, 1954; Amer *et al.*, 1969). However, the solution P varied with soils (Rashid *et. al.*, 2007; Mehdi *et al.*, 2008). In the present study, the soils having variable amount of $CaCO_3$, clay and organic matter contents were incubated with phosphate (^{31}P) at three temperatures (10, 25 and 45 °C) for one year and then used for labile P estimation. The objectives of the study were to evaluate the effect of time and temperature on labile P and to determine the role of calcium carbonate, organic matter and pH on the isotopically exchangeable phosphate.

Material and Methods

Soils

Thirteen Pakistani benchmark soil series and an English calcareous soil (Usher series) having variable amounts of $CaCO_3$, clay and organic matter contents were used in the study. The basic properties of these soils are presented in Table 1.

Incubation of soils with phosphate

A known quantity of P as potassium dihydrogen phosphate solution was added to each soil on the basis of maximum P sorption capacities (the quantity added to each soil is given in Table 2) and the soils were incubated at 10, 25 and 45 °C for one year. During incubation, moisture content was maintained at 50 percent of maximum water holding capacities of the soils. Sub-samples were collected during incubation at different time intervals to monitor the changes of phosphate in the system. The effect of temperature equivalent time was calculated and was

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presented by Javid and Rowell (2002). After completion of incubation, soils were used for isotopic exchange and Olsen P was measured.

Measurement of isotopically exchangeable P

From incubated soils, triplicate 1.5 g soil samples were weighed into 100 mL glass centrifuge tubes. To each glass tube 29 mL 30 mM KCl containing 0.05% formaldehyde was added. The suspension was shaken end-over-end (1 rpm) for 22 h at room temperature and then 1 mL of solution containing 1 μCi of carrier free $H_3{}^{32}PO_4$ was added to each glass tube. The glass tubes were again shaken for a further 22 h. The suspension was centrifuged for 5 min at 2500 rpm. The supernatant liquid was decanted and filtered through a Whatman No 1 filter paper. Phosphate was measured in the liquid by the method of Murphy and Riley (1962). Phosphorus (^{32}P) was measured as counts per minute by Cerenkov radiation counting in a liquid scintillation counter (Warren and Sahrawat, 1993).

Table 1: Some properties of soils used

Soil Series	pH	Olsen P	P Maxima*	CaCO$_3$**	L O I ***	Clay
		μg g^{-1}			%	
Pindorian	7.71	31.2	153	*	1.0	15
Gujrianwala	8.04	2.5	270	*	1.3	22
Guliana	7.83	2.2	454	*	1.6	27
Kotli	7.27	5.6	667	*	2.7	58
Hafizabad	8.93	8.8	222	3.0	1.0	15
Bhawal	8.28	6.7	238	3.2	1.2	18
Matli	8.05	13.0	416	3.7	2.0	40
Rajar	8.66	0.9	223	8.9	1.1	22
Jhatpat	8.45	4.3	500	18.7	1.9	68
Shahdra	8.06	7.0	303	1.9	0.7	12
Rustam	8.45	3.9	400	2.9	0.6	40
Sultanpur	8.56	2.4	263	3.8	1.2	17
Lyallpur	8.40	3.8	256	2.9	1.1	20
Usher	7.80	16.5	588	20.5	10.7	48

*Langmuir P maxima **Traces ***Loss on ignition

pH, 1:2.5 in deionized water; Olsen P, Rowell (1994), P maxima, Le Mare (1982); CaCO$_3$, Collin Calcimeter; LOI, Rowell (1994); Caly, Sheldrich and Wang (1993)

Calculation of E values

Phosphate exchange takes place between the solution and the solid phase and can be represented by the following equation:

$$^{32}P_l \text{ (solution)} + {}^{31}P_s \text{ (solid)} = {}^{32}P_s \text{ (solid)} + {}^{31}P_l \text{ (solution)}$$

At equilibrium, the E value can be calculated as below:

$$\text{Isotopically exchangeable P } (\boldsymbol{E} \text{ value}) = {}^{31}P / f$$

(Warren and Sahrawat, 1993)

where $f = {}^{32}P_a / {}^{32}P_l$

Thus the ***E*** value was determined by measuring at equilibrium the P concentration in solution (^{31}P) and the amount of ^{32}P left in the solution ($^{32}P_l$). Since the amount of $^{32}P_a$ (added) is known, the value of ***f*** was calculated.

Results and Discussion

The ***E*** values of the soils decreased as the temperature of incubation increased (Table 2). In all soils, the maximum ***E*** value was observed at 10 °C and this value decreased further as temperature was raised to 25 and to 45 °C. Among the Pakistani soils at 10 °C the maximum ***E*** value (69.4 μg P g^{-1}) was observed in Rustam while the minimum (0.19 μg P g^{-1}) was in the Jhatpat soil. At 25 °C the maximum ***E*** value (9.67 μg P g^{-1}) was in Hafizabad and the minimum (0.01 μg P g^{-1}) in Jhatpat soil. Similarly at 45 °C the maximum ***E*** value (1.9 μg P g^{-1}) was in Shahdra and the minimum (0.001 μg P g^{-1}) was again in the Jhatpat soil series.

In Table 3 the temperature effect was viewed as a time factor (equivalent days at 25 °C) using the Arranius principle. The method of conversion of the temperature data is described by Javid and Rowell (2002). As the contact time between soil and phosphate increases, the capacity of the soils to exchange sorbed phosphate decreases. The decrease in exchangeable phosphate with time is due to the movement of the phosphate into the adsorbing material by diffusion or the adsorbed phosphate becoming bound more tightly (Barrow, 1974; Bramley *et al.*, 1992; Mendoza, 1992). In calcareous soils where precipitation is probably the main mechanism of phosphate loss from solution, as time passes, the precipitated phosphate is converted into the sparingly soluble compounds i.e. octacalcium phosphate and apatite (Freeman and Rowell, 1981; Feng *et al*., 1996; Panahi, 1997) and thus the exchangeable fraction of the phosphate is reduced.

Table 2: Effect of temperature on labile P (*E* values) 365 days after ^{31}P application

Soil series	Amount of ^{31}P added, μg g^{-1} before incubation	Incubation temperature 10 °C	25 °C	45 °C
		Isotopically labile P μg g^{-1}		
Pindorian	200	48.19	5.17	0.47
Gujrianwala	200	13.11	0.73	0.12
Guliana	400	32.97	2.79	0.40
Kotli	400	4.92	2.19	1.20
Hafizabad	200	45.33	9.67	1.07
Bhalwal	200	26.71	3.13	0.62
Matli	400	20.37	3.80	1.15
Rajar	200	4.90	0.23	0.03
Jhatpat	400	0.19	0.01	0.01
Shahdra	400	10.09	5.43	1.90
Rustam	400	69.40	2.03	0.08
Sultanpur	200	28.85	7.25	1.20
Lyallpur	200	12.43	1.57	0.22
Usher	400	16.86	5.57	2.30

Table 3: Effect of incubation for 365 days to 10 and 45 °C compared to 25 °C. Data expressed for each temperature as an equivalent number of days at 25 °C to reach the measured E value

Soil Series	Incubation temperature 10 °C	45 °C
	Equivalent days at 25 °C	
Pindorian	87	2810
Gujrianwala	50	1968
Guliana	62	1936
Kotli	51	2012
Hafizabad	45	3084
Bhawal	54	2254
Matli	42	2530
Rajar	62	2234
Jhatpat	98	2540
Shahdra	41	2524
Rustam	75	3533
Sultanpur	32	3153
Lyallpur	46	1737
Usher	28	2778

Effect of calcium carbonate on labile P

In two of the highly calcareous soil series (Rajar and Jhatpat), labile P values fell to very low values (Table 2). This decrease was greater for Jhatpat with 18.7% calcium carbonate than in Rajar with 8.9%. However, Usher with 20.5% $CaCO_3$ had the least fall in E value. It was also noticed that in some soils (Pindorian, Gujrianwala and Guliana) with traces of calcium carbonate, there were larger decreases in the ***E*** value than in the moderately calcareous soils (Hafizabad, Bhalwal, Matli, Shahdra, Sultanpur). Thus, there is not a simple relationship between calcium carbonate and adsorption. Low ***E*** values suggest that a considerable amount of sorbed phosphate was precipitated and converted into compounds which were sparingly soluble and had reduced exchangeability. The higher ***E*** values in the Usher soil may be due to less precipitation of the applied phosphate due to the presence of a large amount of organic matter which inhibits the precipitation of phosphate (LeMare *et al.,* 1987; Inskeep and Silvertooth, 1988; Grossl and Inskeep, 1991; Kastelan-Macan *et al.*, 1996). The higher ***E*** values in Hafizabad and Sultanpur soils compared to soils (having traces of calcium carbonate Pindorian, Gujrianwala and Guliana) may be due to the higher pH values in these soils. The presence of Na may inhibit the precipitation (Furedi-Milhofer *et al.*, 1975; Zhang *et al.*, 1992). The results of Talibudeen and Arambarri (1964) suggested that, for a group of soils containing carbonates of similar geological origin, the isotopic exchange index and the recovery of added phosphate were both inversely proportional to the carbonate content. In the present set of soils, except Usher, the geological origin of the soils is similar. However, a negative but poor correlation was observed between calcium carbonate and the ***E*** values (Figure 1). The r^2 values were 0.16 (10 °C), 0.13 (25 °C) and 0.13 (45 °C). These results suggested that although calcium carbonate was present in these soils in varying amounts, its ability to decrease labile P was dependent not on the total amount, but on the organic matter content, pH of the soil and probably the calcium carbonate reactivity (specific surface area).

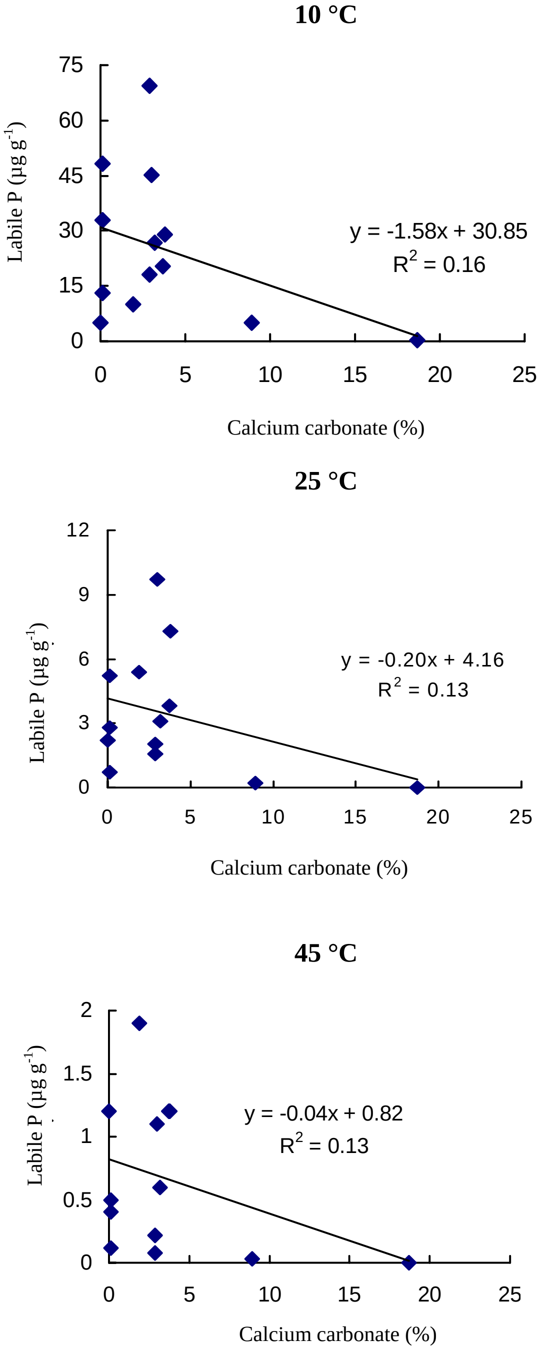

Figure1: Relationship between labile P (*E* values) and calcium carbonate at various temperatures

Relationship between Olsen P and labile P

The relationship between Olsen P and labile P (***E*** values) was examined regression between labile P (Y) and Olsen P (X) by using the power equation Y = a X^b based on three values (the three temperatures) for each soil. The parameters of the power equation presented in Table 4 show that all soils had a highly significant power relationship between Olsen P and labile P and the r^2 values ranged from 0.90 to 0.99.

Table 4: Relationship between *E* values (Y) and Olsen P (X) (parameters of the of the power equation Y = aX^b)

Soil series	a	b	r^2
Pindorian	0.001	2.449	0.99
Gujrianwala	0.0003	2.368	0.99
Guliana	0.000006	3.119	0.97
Kotli	0.000009	2.589	0.99
Hafizabad	0.000002	3.424	0.99
Bhalwal	0.00001	3.158	0.99
Matli	0.0009	1.874	0.98
Rajar	0.0001	2.391	0.98
Jhatpat	0.000002	2.272	0.90
Shahdra	0.0004	1.980	0.97
Rustam	0.000008	2.890	0.99
Sultanpur	0.00003	2.864	0.99
Lyallpur	0.0005	2.325	0.99
Usher	0.0004	1.985	0.98

Quantity (labile P) / intensity (solution P in 30 mM KCl at equilibrium) relationships

The plots of the intensity (solution P in 30 mM KCl) against the quantity (labile P) factor were well described by a linear relationship. The parameters of the equations are presented in Table 5. The slope of the line (parameter b of the equation) varied with the soils. Its value ranged from 0.077 (Hafizabad) to 0.962 (Jhatpat). In all the soils, the r^2 values were highly significant with a range from 0.95 to 0.99. Linear relationships between isotopically exchangeable and solution P in calcareous soils have been reported previously by Talibudeen and Arambarri (1964).

Conclusions

The phosphate sorbed (not extracted with the Olsen method) in one year of incubation was investigated for its exchangeability with carrier free ^{32}P for calcareous soils. The results showed that labile P decreased with time and increasing temperature. The temperature effect can be considered in terms of an equivalent time at 25 °C. The E values followed a power equation for each soil and a unified equation described the approximate behavior of all the soils. A negative but poor correlation was observed between the E values and $CaCO_3$ content. It was noted that organic matter (Usher) and pH (Hafizabad and Sultanpur) may have affected the correlation and resulted in poor r^2 values. The ***E*** values increased in the soils as the Olsen P increased. For each soil, the relationship was well described by a power equation. A linear relationship was observed for each soil between P present in the 30 mM KCl solution and the E values. The relationships were sufficiently similar for a unified line to be obtained for all the soils. The residual effectiveness of phosphate varies from soil to soil and increasing temperature has marked effect on its amount in a soil.

Table 5: Quantity / intensity relationship of phosphate (parameters of the linear equation Y = a + bx, where Y= P concentration in 30 mM KCl and X= E value)

Soil series	a	b	r^2
Pindorian	0.250	0.101	0.99
Gujrianwala	0.140	0.176	0.99
Guliana	0.398	0.130	0.99
Kotli	0.383	0.304	0.99
Hafizabad	0.378	0.077	0.99
Bhalwal	0.243	0.104	0.99
Matli	0.355	0.157	0.99
Rajar	0.090	0.097	0.99
Jhatpat	0.003	0.962	0.99
Shahdra	0.179	0.186	0.95
Rustam	0.380	0.095	0.99
Sultanpur	0.336	0.086	0.96
Lyallpur	0.144	0.112	0.99
Usher	0.584	0.154	0.98

References

Amer, F., S. Mahdi, and A. Alradi. 1969. Limitations in isotopic measurements of labile phosphate in soils. *Journal of Soil Science* 20: 91-100.

Barrow, N.J. 1974. The slow reactions between soil and anions. I. Effects of time, temperature and water contents of a soil on the decrease in the effectiveness of phosphate for plant growth. *Soil Science* 118: 380-386.

Bramley, R.G.V. and N.J. Barrow. 1992. The reaction between phosphate and dry soil. II. The effect of time, temperature and moisture status during incubation on the amount of plant available P. *Journal of Soil Science* 43: 759-766.

Bramley, R.G.V., N.J. Barrow and T.C. Shaw. 1992. The reaction between phosphate and dry soil. I. The effect of time, temperature and dryness. *Journal of Soil Science* 43: 749-758.

Fardeu, J.C. 1993. Le phosphore assimilable des sols: Sa representation par un modile fonctionnel a' plusierurs compartiments. *Agronomie* 13 : 317-331.

Feng, G.U., Yang-MaoQiu., Bai-DengSha., Huang-JinSheng., G. Feng, M.Q. Yang, D.S. Bai and J.S. Huang. 1996. Study on changes of morphology and availability of phosphorus in calcareous soil by labelled ^{32}P method. *Acta Pedologica Sinica* 33: 301-307.

Freeman, J.S. and D.L. Rowell. 1981. The adsorption and precipitation of phosphate onto calcite. *Journal of Soil Science* 32: 75-84.

Frossard, E., M. Brossard, M.J. Hedley, and A. Metherell. 1995. Reactions controlling the cycling of P in soils. p. 107-137. *In*: Phosphorus in Globol Environment, H. Tiessen, ed. John Wiley & Sons Ltd., New York, USA.

Furedi-Milhofer, H., E. Oljica-Zabcic, and B. Purgaric. 1975. Precipitation of calcium phosphate from electrolyte solution. IV. Precipitation diagrams of system calcium chloride-sodium phosphate 0.15 M sodium chloride. *Inorganic Nuclear Chemistry* 37: 2047-2051.

Grossl, P.R. and P.W. Inskeep. 1991. Precipitation of dicalcium phosphate dihydrate in the presence of organic acids. *Soil Science Society of America Journal* 55: 670-675.

Holford, I.C.R. 1997. Soil phosphorus: its measurement, and its uptake by plants. *Australian Journal of Soil Research* 35: 227-239.

Indiati, R., A. Coppola and A. Buondonno. 1999. Changes of soil phosphorus availability in Italian Alfisols as estimated by short-term soil + phosphorus equilibration procedures using Olsen, Mehlich 3, and paper-strip methods. *Communications in Soil Science and Plant Analysis* 30: 983-997.

Inskeep, W.P. and J.C. Silvertooth. 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. *Soil Science Society of America Journal* 52: 941-946.

Javid, S. and D.L. Rowell. 2002. A laboratory study of the effect of time and temperature on the decline in Olsen P following phosphate addition to calcareous soils. *Soil Use and Management* 18: 127-134.

Kastelan-Macan, M., M. Petrovic and D. Ballay. 1996. The role of fulvic acids in phosphorus sorption and release from mineral particles. *Water Science and Technology* 34: 259-265.

Larsen, S. 1952. The use of ^{32}P in studies on the uptake of phosphorus by plants. *Plant and Soil* 4: 1-10.

Le Mare, P.H. 1982. Sorption of isotopically exchangeable and non exchangeable phosphate by some soils of Colombia and Brazil and comparison with soil of Southern Nigeria. *Journal of Soil Science* 33: 691-707.

Le Mare, P.H., J. Pereira and W.J. Goedert. 1987. Effect of green manure on isotopically exchangeable phosphate in a dark-red latosol in Brazil. *Journal of Soil Science* 38: 199-209.

Mendoza, R.E. 1992. Phosphorus effectiveness in fertilized soils evaluated by chemical solutions and residual value for wheat growth. *Fertilizer Research* 32: 185-194.

Mehdi, S.M., O. Rehman, A.M. Ranjha and J. Akhtar. 2008. Phosphorus recommendations for fodder based cereal crops. *Soil and Environment* 27: 155-165.

Morel, C. and C. Plenchette. 1994. Is the isotopically exchangeable phosphate of a loamy soil the plant available-P. *Plant and Soil* 158: 287-297.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31-36.

Olsen, S.R. and F.E. Khasawneh. 1980. Use and limitation of physical-chemical criteria for assessing the status of phosphorus in soils. p. 361-410. *In*: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.). ASA, CSSA, SSSA, Madison, Wisconsin, USA.

Panahi, M.K.P.K. 1997. The effects of gypsum on the sorption reactions of phosphate in some calcareous soils. PhD Thesis, The University of Reading, England.

Rashid, M., A.M. Ranjha, M. Waqas, A. Hannan, A. Bilal, A. Saeed and M. Zafar. 2007. Effect of P fertilization on yield and quality of oat (*Avena sativa* L.) fodder on two different textured calcareous soils. *Soil and Environment* 26: 33-41, 2007.

Rowell, D.L. 1994. Soil Science. Methods and Applications. Longman scientific & Technical, UK.

Russell, R.S., J.B. Rickson and S.N. Adams. 1954. Isotopic equilibria between phosphates in soil and their significance in the assessment of fertility by tracer methods. *Journal of Soil Science* 5: 85-105.

Sheldrich, B.H. and C. Wang. 1993. Particle size distribution. p. 499-511. *In:* Soil Sampling and Method of Analysis. M.R. Carter (ed.). Canadian Society of Soil Science. Lewis Publishers, Boca Raton, Florida, USA.

Talibudeen, O. and P. Arambarri. 1964. The influence of the amount and the origin of calcium carbonates on the isotopically exchangeable phosphate in calcareous soils. *Journal of Agriculture Science* 62: 93-97.

Warren, G.P. and K.L. Sahrawat. 1993. Assessment of fertilizer P residues in a calcareous Vertisol. *Fertilizer Research* 34: 45-53.

White, R.E. 1976. Concepts and methods in the measurement of isotopically exchangeable phosphate in soil. *Phosphorus in Agriculture* 67: 9-16.

Zhang, J., A. Ebrahimpour and G.H. Nancollas. 1992. Dual constant composition studies of phase transformation of dicalcium phosphate dihydrate into octacalcium phosphate. *Journal of Colloid and Interface Science* 152: 132-140.