



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; Indiaty *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 $\text{H}_3^{32}\text{PO}_4$ 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).

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 ($^{32}\text{P}_i$). Since the amount of $^{32}\text{P}_a$ (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 ($69.4 \mu\text{g P g}^{-1}$) was observed in Rustam while the minimum ($0.19 \mu\text{g P g}^{-1}$) was in the Jhatpat soil. At 25 °C the maximum E value ($9.67 \mu\text{g P g}^{-1}$) was in Hafizabad and the minimum ($0.01 \mu\text{g P g}^{-1}$) in Jhatpat soil. Similarly at 45 °C the maximum E value ($1.9 \mu\text{g P g}^{-1}$) was in Shahdra and the minimum ($0.001 \mu\text{g P g}^{-1}$) was again in the Jhatpat soil series.

Table 1: Some properties of soils used

Soil Series	pH	Olsen P	P Maxima*	CaCO_3^{**}	LOI***	Clay
		$\mu\text{g g}^{-1}$			%	
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:

$$^{32}\text{P}_i (\text{solution}) + ^{31}\text{P}_s (\text{solid}) = ^{32}\text{P}_s (\text{solid}) + ^{31}\text{P}_i (\text{solution})$$

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

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

(Warren and Sahrawat, 1993)

where $f = ^{32}\text{P}_a / ^{32}\text{P}_i$

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.

This decrease was greater for Jhatpat with 18.7% calcium carbonate than in Rajar with 8.9%. However, Usher with 20.5% CaCO₃ 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).

Table 2: Effect of temperature on labile P (*E* values) 365 days after ³¹P 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).

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).

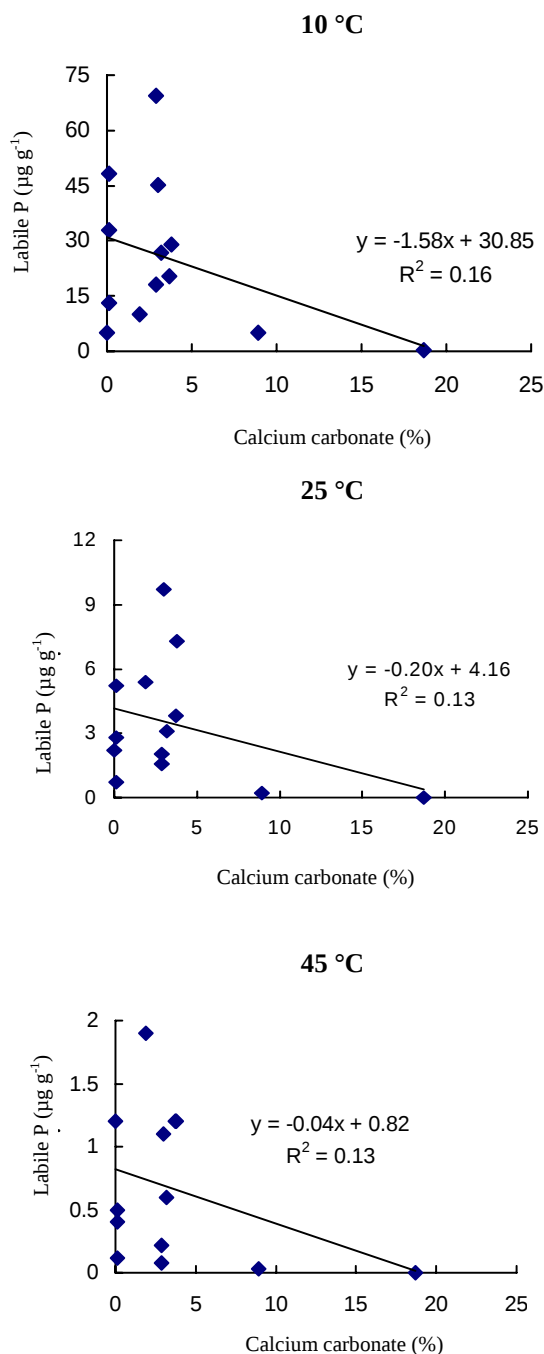


Figure1: Relationship between labile P (E values) and calcium carbonate at various temperatures

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 $Y = aX^b$ 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 $Y = \text{P concentration in 30 mM KCl}$ and $X = E \text{ value}$)

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

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