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The Uptake by Crops of Fresh and Residual Phosphatic Fertilizers by Simultaneous Measurements with ^{32}P and ^{33}P

C. MOREL¹ and J. C. FARDEAU^{2*}

¹COFAZ, Service Agronomique, BP 133, 92202 Neuilly sur Seine, France and ²DB/SRA, CEN Cadarache, 13108 Saint-Paul-lez-Durance, France

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The effects of various residual P fertilizers, with or without fresh fertilizers cannot be measured directly by field or pot experiments. A radiotracer technique using $^{32}\text{PO}_4$ and $^{33}\text{PO}_4$ is described. Available soil phosphorus is ^{32}P -labelled and fresh P fertilizer is ^{33}P -labelled. Counting ^{33}P and ^{32}P in crops is carried out by measurements making use of the Cerenkov effect and using liquid scintillation procedures. From the results obtained in the example given, it can be concluded that the various kinds of residual P fertilizers can modify the uptake of the fresh P fertilizers applied.

Introduction

Only 1–20% of the phosphorus contained in P fertilizers is taken up by crops during the first year after their spreading (Engelstad and Terman, 1980; Fardeau, 1984). Therefore 80–99% remains in the soil and reacts with soil components, thus becoming “residual P”. Knowledge of the effect of this residual phosphorus, the so-called “residual effect”, is of a great interest for fertilization management (Barrow, 1980; Sanchez and Uehara, 1980). The percent of P utilization of a phosphatic fertilizer (PPU%) can easily be determined by isotopic labelling immediately after spreading (Dean *et al.*, 1947); but, due to the fact that the half-life of the two phosphorus isotopes of agronomical interest, ^{32}P and ^{33}P , is too short, the “residual effect” cannot be measured by the direct method of fertilizer labelling. A large amount of research has been conducted over the years on the agronomic evaluation of residual P but has been frustrated by the flagrant lack of significant yield response. The purpose of this report is to describe the measurements of the uptake of residual P with or without addition of new fresh P fertilizer, in terms of PPU%, and especially in terms of phosphorus taken up by crops and derived from one of two or more sources of nutrient. The experiments are conducted with ^{32}P and ^{33}P . The described method was applied to a neutral loamy soil which, over 15 years, had been annually treated with two kinds of phosphorus

fertilizers (superphosphate and soft rock phosphate), at three different rates (0, 21.8 and 43.6 kgP, $\text{ha}^{-1} \text{y}^{-1}$) and a fresh fertilization of ^{33}P -labelled triple superphosphate, at P contents of 0 and 33 ppm during the pot experiment.

Material and Methods

1. Methods

(A) P uptake from a fresh fertilizer

The measurement of the uptake of a phosphatic fertilizer by a crop is carried out with a ^{33}P labelled fertilizer using the method of Dean *et al.* (1947). Calculations are based on the assumption that during cropping, the two sources of phosphorus for crops, namely available soil P and fertilizer P, remain distinct. This system can be described as in Fig. 1.

Let R_{33} , as $^{33}\text{PO}_4$, and Q be the total quantities of radioactivity and phosphorus in the freshly added fertilizer. Let r_{33} and q be the cropped quantities of radioactivity and phosphorus. Using the measurements of R_{33} , r_{33} , Q and q , the following can be calculated:

—The percent of P utilization of the fresh fertilizer,

$$(\text{PPU}_{\text{f}} \%): \text{PPU}_{\text{f}} \% = 100. (r_{33}/R_{33}). \quad (1)$$

—The quantity q_{f} of fresh fertilizer taken up by the crop,

$$q_{\text{f}} = Q. (r_{33}/R_{33}).$$

*Author for correspondence.

Fig. 1. Model for P nutrition with available soil phosphorus and fresh P fertilizer.

—The phosphorus in the crop derived from fresh fertilizer

$$(\text{PDF}_{\text{ff}}\%): \text{PDF}_{\text{ff}}\% = (q_{\text{ff}}/Q)100,$$

which, according to Fardeau (1984), is equivalent to

$$\text{PDF}_{\text{ff}}\% = (\text{RAS}_q/\text{RAS}_Q)100 \quad (2)$$

where RAS is the specific radioactivity of phosphorus in the crop (RAS_q) and in fertilizer (RAS_Q).

These various data can also be determined by an indirect method using labelling of the available P in soil (Fardeau *et al.*, 1983).

(B) P uptake from residual fertilizers

If, over many years, P inputs due to fertilization are higher than P uptake by crops, as very frequently occurs in the intensive agriculture of North-Western European (Larsen, 1973) an increase, ΔP , in the total P in the plough soil layer arises. This increase, ΔP , sometimes induces an increase in the available soil P. The estimation of the increase in the available soil P is always made either by chemical extractants or by crop analysis. But as available soil phosphorus was chemically identified (Larsen, 1967; Fardeau and Jappe, 1976) as isotopically exchangeable PO_4 ions, L, determined according to the LARSEN method (Larsen, 1952), the increase, ΔL , of the available soil phosphorus, $L + \Delta L$, of the soil with phosphate residues can be determined and compared to ΔP , as well as the uptake of P from ΔL and ΔP . But, as without the isotopic method, estimation of the residual effect is possible if, and only if, soil samples with and without residual P fertilizers are available. These should be taken, for example, in long term trials using P fertilization.

1. *Measurement without fresh fertilizer.* The model used for calculations is shown in Fig. 2.

Let

L be the quantity of available soil P determined according to the Larsen method in soil without residual P (System A).

r_{32} and q be the quantities of radioactivity and phosphorus of the crop on soil without residual P.

$L + \Delta L$ be the quantity of available P in soil with residual P (System B).

r'_{32} and q' be the quantities of radioactivity and phosphorus of the crop in soil with residual P.

Fig. 2. Model for P nutrition with native available soil phosphorus and residual P fertilizer.

R_{32} be the radioactivity quantity in systems A and B for the labelling of available P, L and $L + \Delta L$, respectively,

ΔP be the increase of total P in soil, due to residual P, between systems A and B.

In crop B, $r'_{32} = r_L + r_{\Delta L}$, where r_L is the radioactivity taken up from L and $r_{\Delta L}$ is the radioactivity taken up from ΔL . A similar relation, $q' = q_L + q_{\Delta L}$, is useful for P uptake.

From Larsen's assumption, it can be deduced that:

$$\text{From crop A: } (r_{32}/q) = (R_{32}/L) \quad (3)$$

$$\text{From crop B: } (r'_{32}/q') = (R_{32}/L + \Delta L) \quad (4)$$

and from the Fried assumption (Fried and Dean, 1952), it can be deduced for crop B:

$$\begin{aligned} (q_L/L) &= (q_{\Delta L}/\Delta L) \\ &= (q_L + q_{\Delta L})/(L + \Delta L) = q'/(L + \Delta L). \end{aligned} \quad (5)$$

Therefore using the measurements of R_{32} , r_{32} , r'_{32} , q and q' , ΔP and the various relations, the following can be calculated:

—The $\text{PDF}_{\text{ff}}\%$, i.e. the phosphorus taken up by the crop and derived from residual phosphorus:

$$\begin{aligned} \text{PDF}_{\text{ff}}\% &= 100(q_{\Delta L}/q') \\ &= 100[(q'/r'_{32}) - (q/r_{32})]/(q'/r'_{32}) \end{aligned}$$

or

$$\text{PDF}_{\text{ff}}\% = 100[1 - (\text{RAS}'_q/\text{RAS}_q)]$$

—The $\text{PPU}_{\text{ff}}\%$ of ΔP which equals $(q_{\Delta L}/\Delta P)100$

$$\text{PPU}_{\text{ff}}\% = (q'/\Delta P) \cdot [1 - \text{RAS}'_q/\text{RAS}_q]100. \quad (6)$$

It appears that the PDF_{ff} can be estimated, as in many applications of the isotopic dilution method, only by determinations of RAS on aliquots of the crops.

2. *Measure of residual effect in the presence of a fresh fertilizer.* The P nutrition of a crop can be described as in Fig. 3. Available soil phosphorus is $^{32}\text{PO}_4$ labelled and the fresh fertilizer is $^{33}\text{PO}_4$ labelled.

The purpose is to measure the $\text{PPU}\%$ and the $\text{PDF}\%$ of the fresh and the residual phosphorus. The calculations of the $\text{PPU}_{\text{ff}}\%$ and $\text{PDF}_{\text{ff}}\%$ are conducted as in model I. The calculations of the $\text{PPU}_{\text{ff}}\%$ and $\text{PDF}_{\text{ff}}\%$ are performed based on the values of q_{ff} and q'_{ff} , and the quantities of P are derived from the

Fig. 3. Model for P nutrition with native available soil phosphorus, residual P fertilizer and fresh P fertilizer.

fresh fertilizer without and with residual P respectively. When these values are known, q_L and $q_{L+\Delta L}$, i.e. the quantities of phosphorus taken up from available soil P without and with residual phosphorus, can be calculated.

It can be deduced, as previously described in model II, that the $\text{PDF}_{\text{rf}}\%$ of ΔP equals:

$$\text{PDF}_{\text{rf}}\% = 100[(q''/r'_{32}) - (q_L/r_{32})]/(q''/r'_{32}) \quad (7)$$

where

$$q_L = q - (Q \cdot r_{33})/R_{33}$$

and

$$q'' = q' - (r'_{33}/R_{33}),$$

and, as in model II,

$$\text{PPU}_{\text{rf}}\% = q'_{\Delta L}/\Delta\text{P} = (q' \cdot \text{PDF}_{\text{rf}}\%)/\Delta\text{P}. \quad (8)$$

(C) Experimental procedure

Two treatments must be carried out for each soil sample with different types and contents of residual phosphorus fertilizers:

(i) In the first treatment, available soil phosphate is $^{32}\text{PO}_4$ -labelled. This labelling is realized by isotopic exchange according to Larsen (Fardeau and Triboi, 1974), by manual or automatic mixing of soil, sieved at 2 mm, with a $^{32}\text{PO}_4\text{H}_3$ carrier-free solution. The solution containing 0.06 MBq mL^{-1} was added using 50 mL kg^{-1} of dry soil. Five kilograms of soil were prepared at the same time. This treatment corresponds to systems A and B in model II.

(ii) In the second treatment, for which available soil phosphate has been $^{32}\text{PO}_4$ -labelled as previously, $^{33}\text{PO}_4$ -labelled triple superphosphate in solid form was added to give a P content of 33 ppm. Any other P fertilizers can be used to provide fresh fertilizer. This treatment corresponds to systems C and D in model III.

After mixing, 1 kg of dry soil is put into pots. Each treatment was carried out on five samples. Soils were wetted at field capacity and sown with 1 g *Lolium perenne*. Five cuts were carried out at three weekly

intervals. After each cutting, 60 ppm of nitrogen and potassium were supplied using ammonium nitrate and potassium sulfate.

After each cutting, samples were dried and weighed. Total phosphorus uptakes and total radioactivity were determined after mineralization of each sample. ^{32}P and ^{33}P were measured by using the Cerenkov effect and scintillation procedures respectively.

II. Soil Samples

These were collected in a long term field experiment conducted by the Institut National de la Recherche Agronomique and located in the Department of Aisne. Their main characteristics are given in Table 1. This experimental design was 15 years old. Various phosphatic fertilizers were compared, especially superphosphate and rock phosphate at annual rates of 0, 50 and $100 \text{ kgP}_2\text{O}_5 \text{ ha}^{-1}$.

Results

(A) Dry matter yield and phosphorus uptake

They were summed for the five successive cuts and are reported in Table 2.

The variations in dry matter yields were too low to authorize conclusions about the effect of residual phosphorus with or without fresh P fertilizers. This result is similar to that obtained in numerous field experiments. It can be concluded that in this soil and with this crop, phosphorus did not appear as the first limiting factor for dry matter crop production.

Phosphorus uptake differed with different treatments. Fresh P fertilization increased P uptakes and, without the fresh P-fertilization, P uptake by crop was greatly increased with P residues of superphosphate spread at $100 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$.

(B) Specific radioactivity of P in crops

As the values of the $\text{PPU}\%$ and $\text{PDF}_{\text{rf}}\%$ or $\text{PDF}_{\text{rf}}\%$ can be calculated from values of the specific radioactivity of phosphorus (RAS), these data are

Table 1. Main soil characteristics (Level 1: 50 kg P₂O₅ ha⁻¹; level 2: 100 kg P₂O₅ ha⁻¹)

Residual P	0	Superphosphate		Rock phosphate	
		Level 1	Level 2	Level 1	Level 2
Clay (<2 µm)	11.7	14.4	14.8	11.6	12.6
Silt (2–20 µm)	32.6	32.2	32.9	32.4	32.8
Silt (20–50 µm)	50.0	49.1	47.0	47.0	47.6
Sand (>50 µm)	5.7	4.3	5.3	9.0	7.0
Organic matter (P.100)	1.29	1.35	1.39	1.37	1.39
N Kjeldahl (P.1000)	0.75	0.80	0.81	0.84	0.84
C/N	10.0	9.9	10.0	9.5	9.6
CaCO ₃ (P.100)	0.0	0.0	0.0	0.3	0.7
Total-P (ppm P205)	1005	939	1126	1110	1253
NaHCO ₃ -P (ppm P205)	44	42	66	40	33
Exchange capacity (m-equiv (100 g) ⁻¹)	6.9	7.2	7.2	7.1	6.9
Exchangeable calcium (m-equiv (100 g) ⁻¹)	15.7	11.3	10.5	13.2	20.4
Exchangeable magnesium (m-equiv (100 g) ⁻¹)	0.26	0.26	0.26	0.28	0.32
Exchangeable potassium (m-equiv (100 g) ⁻¹)	0.26	0.28	0.28	0.25	0.35

Table 2. Dry matter yield and P uptake (5 cuts summed up). (Data followed by different letters are significantly different: $P = 0.05$)

Residual P	0	SSP residues		RP residues	
		Level 1	Level 2	Level 1	Level 2
Dry matter (g) yield	3.81 c +	4.21 bc	4.25 bc	4.35 ab	4.01 bc
+ TSP	4.17 bc	4.27 bc	4.41 ab	4.44 ab	4.76 a
P uptake (mg)	15.3 e	16.4 de	22.2 b	17.8 cd	13.5 f
+ TSP	19.2 c	19.4 c	25.4 a	22.8 b	21.8 b

given in Tables 3 and 4. For an easier comparison of the various results, the RAS values are calculated as follows; $(100 \cdot r/R)/p$, where r and p are the quantities of radioactivity and phosphorus, and where R is the quantity of radioactivity in the labelled source of nutrient.

According to this assumption, RAS of the ³³P-labelled fertilizer was $(100 \cdot 100/100)/33 = 3.33 \text{ mg}^{-1}\text{P}$.

³³P-RAS in crop. The calculated values are shown in Table 3. They were given for the five cuts and for the total phosphorus uptake. Only rock phosphate, as residual fertilizer at 100 kg P₂O₅ ha⁻¹ induced a significantly different result.

³²P-RAS. Two ³²P-RAS can be calculated. The first is related to the total P in the crop and the second is related to the phosphorus taken from the available soil phosphorus which was ³²P-labelled. This last RAS is known from the total P in the crop decreased by the phosphorus taken up from the fresh ³³P-fertilizer. Since only the RAS of the phosphorus taken up from the available soil P is useful in calculating the PPU_{rf}% and PDF_{rf}%, these data are given directly in Table 4. These data are the mean values of the 10 similar samples, five with and five without fresh fertilizer. This data was modified only by the use of residual P from superphosphate at 100 kg P₂O₅ ha⁻¹.

Table 3. Specific activity of phosphorus in crop with ³³P-labelled fresh fertilizer. (Data followed by the same letter: homogen group at $P = 0.05$)

Cut no.	0	Superphosphate		Rock phosphate	
		Level 1	Level 2	Level 1	Level 2
1	0.37	0.45	0.39	0.48	0.64
2	0.48	0.55	0.49	0.68	0.82
3	0.50	0.57	0.54	0.71	0.84
4	0.41	0.47	0.49	0.63	0.69
5	0.42	0.43	0.47	0.57	0.62
Mean	0.43B	0.50B	0.47B	0.60AB	0.73A

Table 4. Specific activity of phosphorus in crop derived from available soil phosphorus without or with fresh fertilizer. (Data followed by the same letter: homogen group at $P = 0.05$)

Cut no.	0	Superphosphate		Rock phosphate	
		Level 1	Level 2	Level 1	Level 2
1	1.26	1.13	0.83	1.07	1.12
2	1.51	1.34	0.98	1.40	1.52
3	1.42	1.25	0.88	1.27	1.40
4	1.24	1.10	0.78	1.09	1.19
5	1.21	1.10	0.78	1.03	1.10
Mean	1.32A	1.19A	0.87B	1.16A	1.26A

Fig. 4. P in crop derived from native available soil phosphorus, residual P fertilizer and fresh P fertilizer.

Discussion

(A) Phosphorus in crops is derived from available soil P, and fresh and residual fertilizer applied as superphosphate at $100 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$

Phosphorus derived from available soil P and residual and fresh fertilizer are shown in Fig. 4. Without fresh fertilizer, PDF_{fr}, % of the residual P reached 34%. With the application of a fresh fertilizer, with a P content of 33 ppm, the cropped phosphorus taken up from fresh P was 15%, from residual P 29% and from the native soil phosphorus 56%. The PPU_{fr} of the fresh fertilizer was, in this last case, 11.8% and the PPU_{fr} was only 3.5%. These low values can be explained by the phosphorus fixing capacity of the soil.

(B) Effect of residual P on available soil phosphorus

This effect can be estimated from the kinetics of the ^{32}P -RAS which give the isotopic composition of the phosphorus derived from the available soil phosphorus with or without residual P-fertilizers. These kinetics are shown in Fig. 5. All these kinetics are similar. The lower values obtained during the first cut are due to the phosphorus derived from *Lolium* seeds (Binh Truong and Pichot, 1976) which significantly decreases the RAS of the phosphorus derived from the available soil P. The decrease of the P-RAS at the second cut is due partly to the continuation of the isotopic exchange (Fardeau *et al.*, 1985) and partly to a desorption of phosphate ions from soil (Roche, 1983).

As annual input of rock phosphate at 50 and $100 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ and superphosphate at $50 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ did not significantly modify the ^{32}P -RAS in crops, it can be concluded that available soil P was not increased in these treatments. For this reason, the

Fig. 5. Kinetics of the RAS of P in crop derived from available soil phosphorus.

PDF_{fr}% and the PPU_{fr}% are not significantly different from zero. This clear result is similar and can explain numerous field experiments. Moreover, as the P-RAS of P cropped on soil without P fertilization did not significantly differ from P-RAS of P cropped on soil with rock phosphate, it also can be concluded that there was no specific dissolution of rock phosphate in the *Lolium perenne* rhizosphere (Heck and Saive, 1983).

In this soil, only superphosphate at an annual rate of $100 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$ increased the available soil P. In this treatment the PDF_{fr}% was 38% and the PPU_{fr}% was 3.9%, a very low value.

(C) Influence of the various residual P fertilizers on the uptake of the fresh fertilizer applied as superphosphate

Input of fresh fertilizer, as superphosphate i.e. a water soluble form, increased total P uptake by crops but decreased the gaps between the various treatments. These results are in accordance with those published based on field experimental data (Bolland and Bowden, 1984; Boniface and Trocme, 1988). A part of the increase in P uptake was due to the utilization of the fresh fertilizer, and part was due to the available soil P and could be explained by greater soil exploration (Morel *et al.*, 1987). The kinds of residual P had modified the uptake of the fresh fertilizer. The increase of P uptake with the fresh P added at a P content of 33 ppm rate was higher for soil samples which have received annual applications of rock phosphates. This result could be explained not only by the greater utilization of the fresh

fertilizer but also by a greater uptake from the soil compared to soil without P residues. In comparison, with P superphosphate residues the increase of P uptake came only from the fresh fertilizer. These data show the interaction between fresh P and kinds of residual P on P nutrition. In field experiments, effects of residual P are usually tested using a fresh fertilizer (Bolland and Bowden, 1984; Bolland *et al.*, 1984; Sharpley, 1987). But, as shown by numerous isotopic labelling, only isotopic determination can accurately identify the origin of phosphorus in crops which can depend on the kinds of residual P fertilizers. So field experiments cannot give precise information about the various source of phosphorus for crops.

Conclusion

In order to understand the P-nutrition in crops, the double labelling technique was used with ^{32}P and ^{33}P . The results obtained made it clear that crop P nutrition in the field with old and fresh P fertilizers cannot be explained without knowledge of the effects of the various sources of P for crop nutrition.

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