

# Effect of Applying Soluble and Coated Phosphate Fertilizers on Phosphate Availability in Calcareous Soils and on P Absorption by a Rye-Grass Crop

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The effect of using several phosphoric fertilizers on phosphate availability in calcareous soils with a high phosphorus fixation capacity was studied. Tests were run with commercial fertilizers, differing in the ionic species provided (urea phosphate, triple superphosphate, simple superphosphate, and diammonium phosphate), and experimental controlled-release fertilizers (lignin-coated triple superphosphate and rosin-coated diammonium phosphate), each providing phosphate to the soil at a different rate. Simultaneous experiments were run (in calcareous soils) with a plant (glasshouse test) and with no plant (incubation test). Phosphate availability and, therefore, plant phosphorus absorption increased in such soils when fertilizing with urea phosphate (UP) or with lignin-coated triple superphosphate (TSPL-11). Other fertilizers such as uncoated superphosphates or diammonium phosphate (DAP) did not significantly increase P availability compared to the unfertilized soil. The electroultrafiltration (EUF) technique was also used for predicting the P absorbed by a crop in calcareous soils after applying a phosphate fertilizer.

**Keywords:** Phosphate fertilizers; calcareous soils; available P; uptake P

## INTRODUCTION

The shortage of available P in calcareous soils is due to its fixation by the formation of Ca phosphates insoluble at high pHs (Sample et al., 1980). This problem affects arid and semiarid agricultural soils and is difficult to solve since the response to phosphoric fertilization is scarce (Chand and Tomar, 1993; Taha et al., 1980). The amount of phosphorus a crop can use efficiently depends on an adequate concentration of phosphate ions being maintained in the soil solution in competition with fixation processes. The soil's physical-chemical properties play a major role on phosphate fixation in calcareous soils (Chand and Tomar, 1993) where acid fertilizers, such as triple calcium superphosphate, have been traditionally applied. Nevertheless, Díez et al. (1992) demonstrated the low efficiency obtained by using that fertilizer due to its rapid fixation in this type of soil.

In recent years, interest in researching controlled release fertilizers which include phosphate rocks and partially acidulated phosphate rocks in acid soils has been renewed (Hagin and Harrison, 1993; Rajan and Marwaha, 1993; Kumar et al., 1993). Despite the fact that coated fertilizers have been traditionally used only as controlled-release nitrogen fertilizers, Díez et al. (1992) demonstrated that the use of coated phosphate fertilizers had clear advantages for controlling phosphorus fixation in calcareous soils.

The overall effectiveness of controlled-release phosphate fertilizers depends on their chemical and physical features, the soil's characteristics, and the nature of the plant species (Bolan et al., 1993).

The purpose of this paper is to study and compare the effect various kinds of phosphate fertilizers have on P absorption by a crop and P contents in calcareous, high phosphate fixation power soils. Likewise, the relations existing between the soil's EUF obtained P fractions after fertilizer application and P absorbed by

**Table 1. Fertilizer Characteristics**

fertilizer <sup>a</sup>	composition		ionic composition		pH (1:2)	
	% N	% P	% coating	N		P
TSP		19.6			H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.6
TSPL-4		18.8	4		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.6
TSPL-11		17.4	11		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.7
DAP	18.0	20.1		NH <sub>4</sub> <sup>+</sup>	HPO <sub>4</sub> <sup>2-</sup>	7.5
DAP-22	14.0	15.7	22	NH <sub>4</sub> <sup>+</sup>	HPO <sub>4</sub> <sup>2-</sup>	7.8
SSP		7.9			H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.3
UP	17.7	19.5		urea	H <sub>3</sub> PO <sub>4</sub>	2.0

<sup>a</sup> TSP, triple superphosphate; DAP, diammonium phosphate; SSP, single superphosphate; UP, urea phosphate.

the plant is analyzed in order to assess the EUF's ability to predict a fertilizer's response to a crop's P absorption in calcareous soil.

## MATERIALS AND METHODS

An incubation test was run at the same time as a rye-grass crop was being grown in a glasshouse with two calcareous soils. Eight treatments were used for the two tests: one without phosphate fertilizer (control), four with soluble phosphate fertilizers, and three with experimental coated controlled-release fertilizers. All the fertilizers used are given in Table 1. TSP (triple superphosphate), DAP (diammonium phosphate), and UP (urea phosphate) are commercial, water soluble phosphate fertilizers. The latter is traditionally used in fertigation. TSPL-4, TSPL-11, and DAP-22 are experimental coated fertilizers with 4, 11, and 22% of coating, respectively. They were prepared under laboratory conditions using the method as described in Spanish patent no. 536.567 (Jiménez et al., 1984).

TSPL-4 and TSPL-11 were obtained by coating TSP pellets with Kraft pine lignin, marketed by Westvaco under the name of *Indulin At*. DAP-22 was obtained by coating DAP with a mixture of the same proportion of three types of rosin: polymerized, esterified, and natural (nonvolatile fraction of pine resin). These products were supplied by Union Resinera Española.

The treatment differed depending on the phosphate fertilizer used. Apart from their varying nutrient content, single (SSP) and triple (TSP) superphosphates come in different particle sizes (powder and pelleted, respectively). The ionic phosphorus

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**Table 2. Physical–Chemical Characteristics of Experimental Soils**

	soil 1 <sup>a</sup>	soil 2 <sup>a</sup>
pH H <sub>2</sub> O	7.9	7.9
texture	loam	sand-loam
clay (%)	23.0	10.0
types of clays	montmorillonite	illite
	beidellite	beidellite
CaCO <sub>3</sub> (%)	50.6	42.7
Ca exchange (mg/kg)	4400	3550
Ca active (%)	9.37	12.0
organic matter (%)	1.2	0.9
Al (ppm)		0.1
Fe (ppm)	0.1	
EUf–KI (mg of K/kg)	90	51
EUf–KII (mg of K/kg)	100	56
EUf–PI (mg of P/kg)	1.5	1.0
EUf–PII (mg of P/kg)	1.3	0.7
EUf–CaI (mg of Ca/kg)	410	540
EUf–CaII (mg of Ca/kg)	420	572
EUf–P/EUf–Ca	0.004	0.0027
EUf–NO <sub>3</sub> I (mg of N/kg)	8.1	2.7
EUf–NO <sub>3</sub> II (mg of N/kg)	1.8	0.7
EUf–Norg I (mg of N/kg)	21	15
EUf–Norg II (mg of N/kg)	8	8

<sup>a</sup> Pertains to an Ap horizon of a *Calcixerollic xerochrepts* (USDA). EUf–I: EUf at 200 V and 20 °C. EUf–II: EUf at 400 V and 80 °C.

species is the H<sub>2</sub>PO<sub>4</sub><sup>−</sup> ion. Urea phosphate (UP) is a crystalline mixture of H<sub>3</sub>PO<sub>4</sub> and urea, highly soluble and with a low pH solution value. Diammonium phosphate (DAP) is pelleted, and its ionic species is HPO<sub>4</sub><sup>2−</sup>.

The surface horizon (0–15 cm) of two *Calcixerollic xerochrepts* was chosen for both experiments. One came from Balsicas (Murcia) and was chosen as representative of a calcareous Mediterranean area with a seric climate (soil 1). The other came from Cifuentes (Guadalajara) and was representative of the Central area (soil 2). Their characteristics are given in Table 2. The nutrient dynamics of the soils were evaluated by the electroultrafiltration (EUf) technique (Nemeth, 1979; Diez et al., 1985), since this procedure has proved more suitable for characterizing nutrient dynamics than single chemical extraction (Nemeth and Makdum, 1981).

Ca exchange was determined by displacement with an ammonium acetate solution at pH 7. Soil pH was measured in distilled water with a soil solution ratio of 1:2. The soil's organic matter content was determined using the Walkley–Black oxidation method (Walkley and Black, 1934) and total N by the Kjeldhal method (MAPA, 1994). Carbonates were determined using gasometry with the CO<sub>2</sub> released from the soils being treated with HCl (1:1). The Drouineau method was used to determine active calcium carbonate (Drouineau, 1942) by means of extraction with pH 8 ammonium oxalate while the excess was evaluated with potassium dichromate. P, N, and K proportioning was calculated on the basis of the method as proposed by Wicklicky and Nemeth (1981), considering the Ca contents and P reserves of the soils obtained by EUf. Using this technique, 349 kg·ha<sup>−1</sup> of P for soil 1 and 201 kg·ha<sup>−1</sup> for soil 2 were estimated. These doses were applied from the different experimental fertilizers to each pot. Furthermore, N doses applied to each soil were 250 and 300 kg·ha<sup>−1</sup>, respectively, and a dose of 360 kg·ha<sup>−1</sup> of K was also applied to soil 2.

The experimental design involved random blocks with each treatment tested in triplicate. Pots with no leaching device were used, and 2 kg of soil was placed in each. During the experiment, the pots were watered to field capacity once a week.

The incubation test was carried out in an incubation chamber at a controlled temperature. The soils' P content was assessed with the EUf technique (Diez et al., 1985). Such technique predicts the long- and short-term availability of P from both soils (Nemeth, 1979; Sen Tran et al., 1992). It essentially consists of an electrodialysis process providing information on a considerable number of parameters regarding soil fertility by using a program of potentials, time, and temperatures applied to soil suspended in water.

In order to evaluate the evolution of available P throughout the experiment, 5 g soil samples were taken before and after fertilization over 4 months. They were passed through a 1 mm sieve and subjected to a EUf process in a VOGEL 724 unit using the following program:

Fraction I	30 min, 20 °C, 200 V, 15 mA
Fraction II	5 min, 80 °C, 400 V, 150 mA

Phosphate was colorimetrically determined in the extracts using the ammonium molybdate method (AOAC, 1990) and an AAI Technicon Analyzer.

The rye-grass crop experiment took place in a glasshouse at a controlled temperature. In all cases, 4 g of English rye-grass seed (*Lolium perenne*) were sowed in each pot. Four successive cuts were taken from the rye grass at 25 day intervals. The dry matter yield and P uptake was determined in the plant material in each of the pots. The digestion method used was the sulfonitric method. The plant P uptake was determined by the spectrophotometric ammonium molybdate method (AOAC, 1990).

The EUf–P fractions were related to the total plant P uptake by simple correlation analysis.

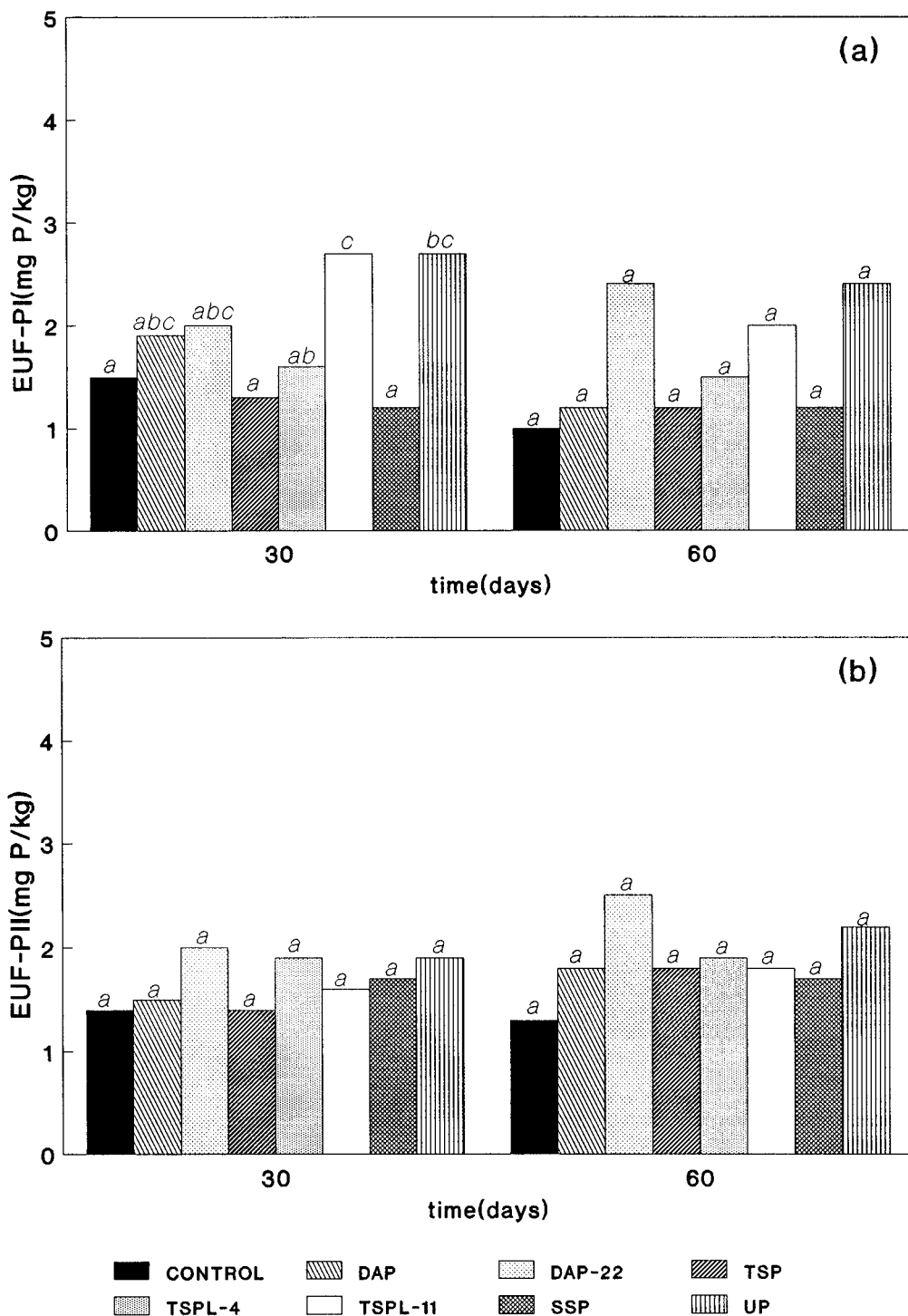
## RESULTS AND DISCUSSION

Table 2 shows the physical–chemical properties of the soils. They are both high calcium carbonate content (active and total) calcareous soils. As a result, the EUf–Ca fractions are also very high, particularly EUf–CaII which is associated with insoluble Ca forms. A major difference between them both is that these Ca fractions are considerably greater in soil 2 than in soil 1. Another feature differentiating both soils is their total clay content (23% for soil 1 and 10% for soil 2). Both soils have a high phosphate fixing capacity since they have a high pH, high Ca content, and scarce organic matter and, in addition, display clays with a pyrophosphate fixing capacity (beidellites). This is why the EUf–PI content is very low: 1.5 and 1.0 mg·kg<sup>−1</sup> for soils 1 and 2, respectively. Bearing in mind that P reserves (EUf–PII) are also very low in both soils (1.3 and 0.7 mg·kg<sup>−1</sup>), the conclusion to be drawn is that P availability is very low, so there is a marked lack of this nutrient. In addition, the values of the EUf–PI/EUf–CaI ratio are 10-fold lower than the optimum 0.4 established by Diez (1980) for the plant's adequate phosphorus nutrition. This thus corroborates the problem of this type of soil in relation to phosphorus availability. A very high dose of fertilizers would thus be required for the plant to uptake a normal amount of phosphorus under these conditions.

In the incubation test, Figures 1 and 2 show the evolution of EUf–PI and EUf–PII for each of the fertilizers tested and the control, over 30 and 60 days incubation for each soil. Fraction EUf–PI provides information on easily available P at the time of the analysis (Nemeth, 1979). The values of this index, after 30 and 60 days obtained after applying the different fertilizers, in no case exceeded 5 mg of P/kg of soil (45 kg of P·ha<sup>−1</sup>) despite the P doses added. However, a large increase of easily available P is observed in the TSPL-11 and UP treatments in both soils compared to their initial EUf–PI values.

The ANOVA for this index (EUf–PI) (Table 3) shows there is an effect from the fertilizer, but there is none with respect to the soil or incubation time.

Applying uncoated, conventional phosphoric fertilizers (TSP, SSP, and DAP) did not significantly alter the EUf–PI values with respect to the unfertilized soil. That is to say, P available did not increase in these soils by applying these fertilizers, not even with TSP, despite being one of the fertilizers traditionally used in calcare-



**Figure 1.** Values of EUF-PI (a) and EUF-PII (b) for each of the fertilizers tested and the control, in relation to incubation time for the soil 1. Bars with the same letter are not significantly different by LSD (0.05).

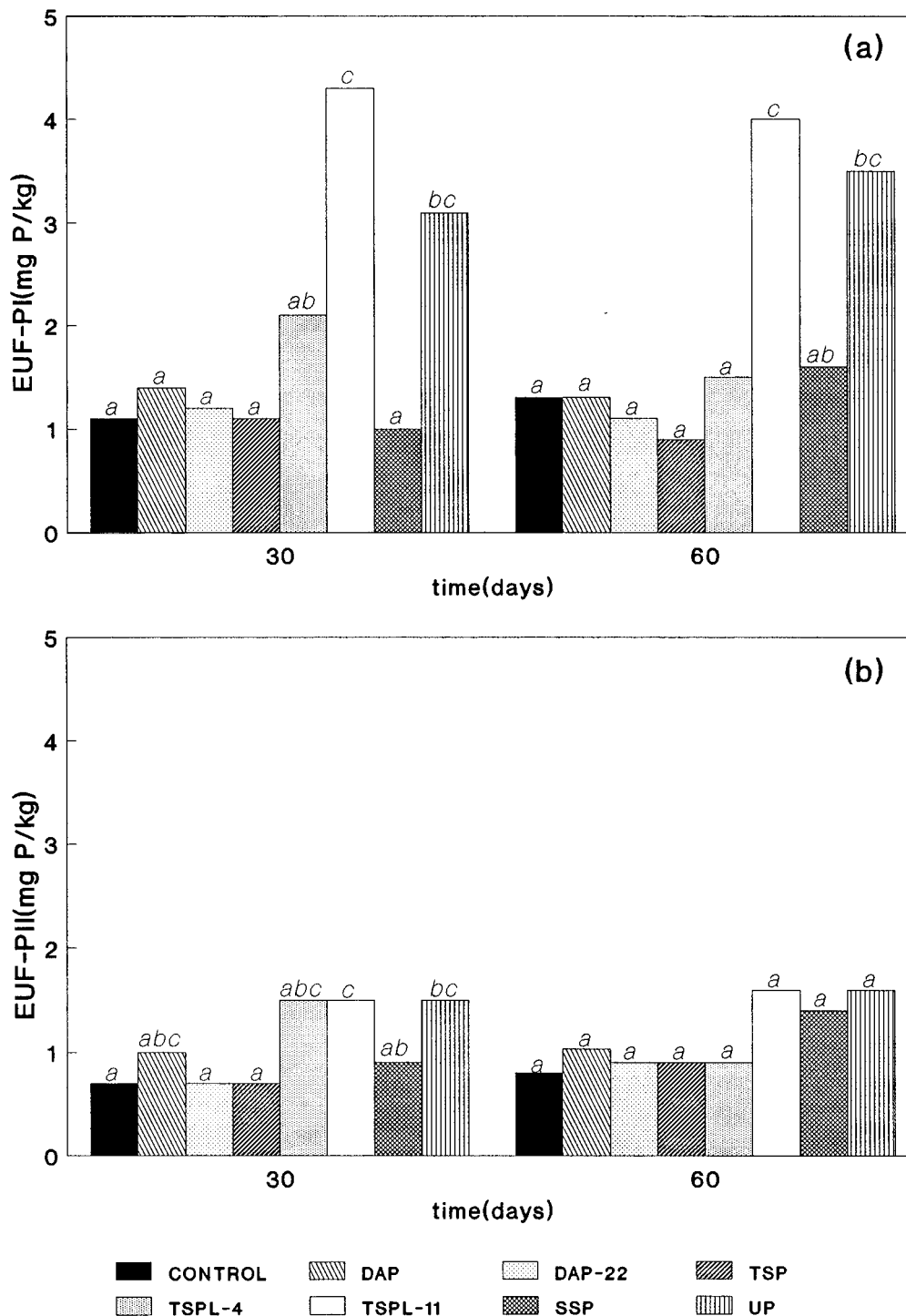
ous soils. However, when TSP was applied coated with lignin (TSPL-4 and TSPL-11), the EUF-PI values increased in both soils after 30 days experimentation. This increase was proportional to the product coating percentage, being significantly higher in the case of TSPL-11 (11% coating).

The use of DAP and DAP-22 did not lead to significant increases in the EUF-PI index ( $P < 0.05$ ) in either of the soils, although average values in soil 1 are slightly higher than in the control.

The EUF-PII index represents reserve P (Nemeth, 1979). The type of soil clearly influences this index (Table 3), which is greater in soil 1 than in soil 2 (Figures 1 and 2). This is due to soil 1 clay fixed phosphate content being greater. The incubation time

and type of fertilizer applied (treatment) also influences the index. Figures 1 and 2 show how some treatments increase the reserve's phosphorus content compared to the control's. These differences are significant ( $P < 0.05$ ) for TSPL-11 and UP treatments after 30 days of incubation in soil 1.

These soils' EUF-P indices showed no generally spectacular increase from applying the different phosphate fertilizers. This is due to their being calcareous soils with a high pH and high Ca content. Under these conditions, phosphoric retrogradation processes were so marked that, despite adding different forms of P through fertilizers, the soils' P content did not noticeably increase.



**Figure 2.** Values of EUF-PI (a) and EUF-P II (b) for each of the fertilizers tested and the control, in relation to incubation time for the soil 2. Bars with the same letter are not significantly different by LSD (0.05).

**Table 3. Probabilities of Larger *F* Values from the Analysis of Variance for EUF-PI, EUF-P II, and P Uptake**

	EUF-PI	EUF-P II	P uptake
soils	0.377	<0.001	<0.001
incubation times	0.492	0.0272	
treatments	<0.001	<0.001	0.006

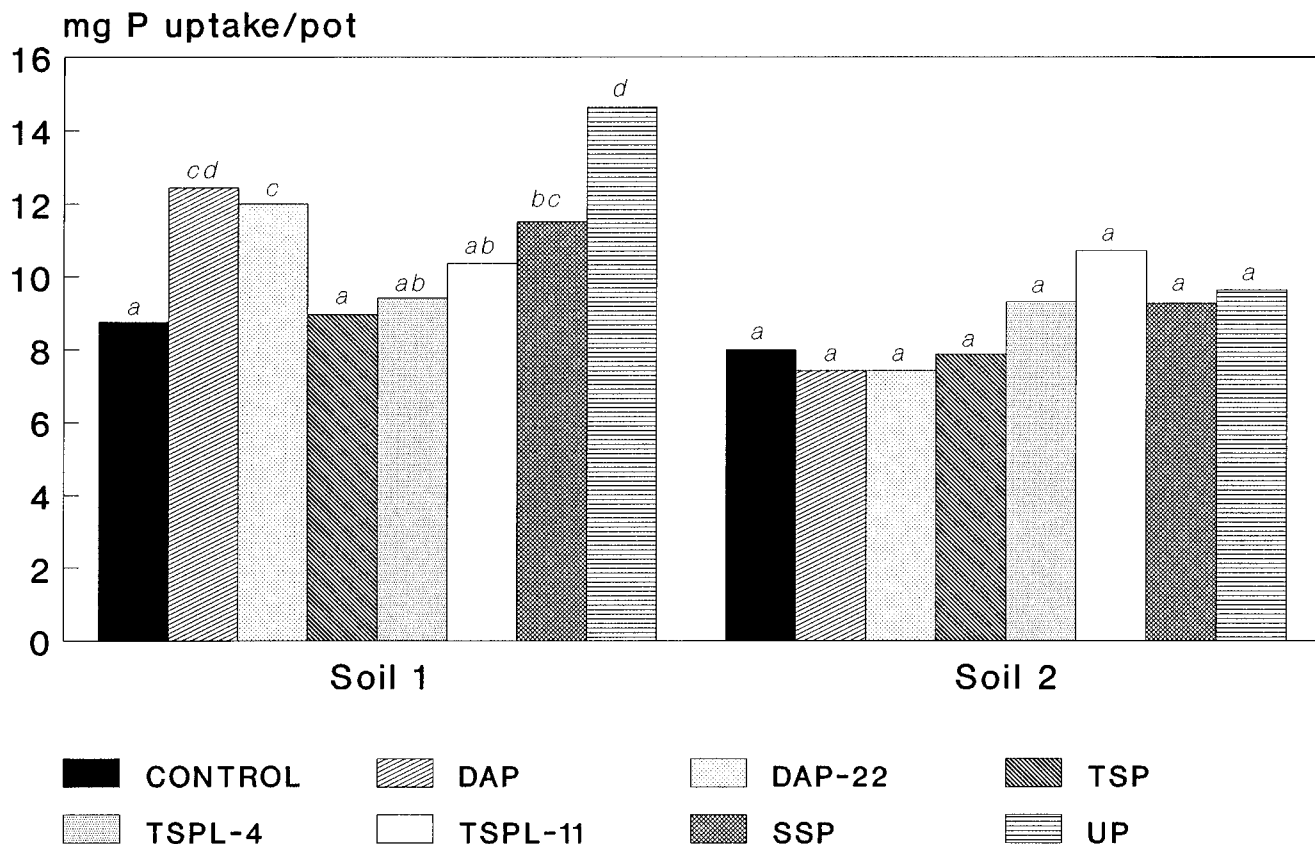
With respect to P by rye-grass uptake P in the glasshouse experiment, Figure 3 shows the P absorbed by the plant during four cuts for the different treatments. Table 3 shows that the P uptake is determined by the type of soil and fertilizer. These values are higher in soil 1 than in soil 2, since the P rates applied were different (349 kg·ha<sup>-1</sup> in soil 1 and 201 kg·ha<sup>-1</sup> in

**Table 4. Linear Coefficients of Correlation (*r*) of the Relationships between the Uptake P by Rye Grass and the EUF-P Indices**

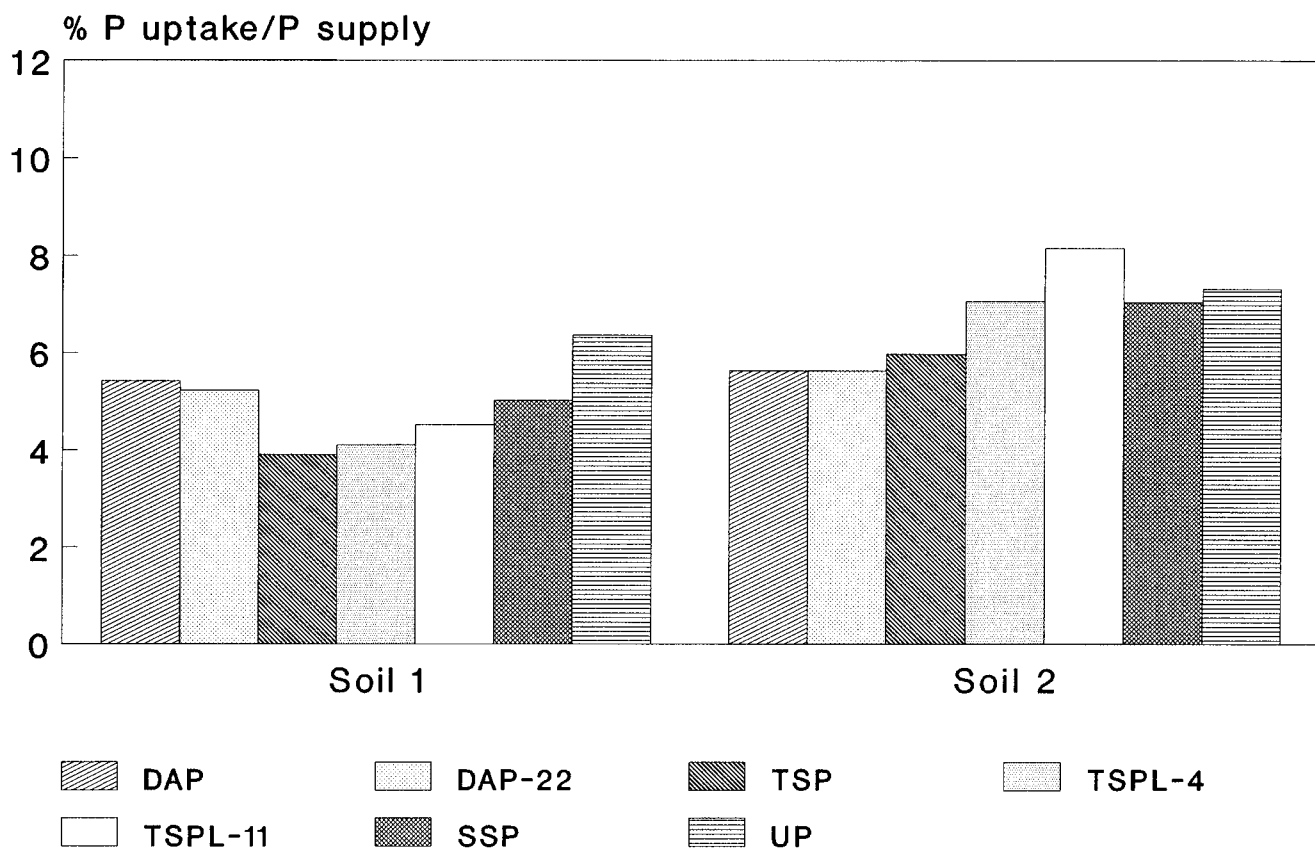
soil	time (days)	EUF-P	<i>r</i>
1	30	I	0.57
		II	0.86**
2	60	I	0.61
		II	0.61
	30	I	0.82**
		II	0.80*
60	I	0.84**	
	II	0.80*	

\*\*\* Significant at *P* < 0.01 and 0.05 levels, respectively.

soil 2). In addition, the reserve phosphate fraction (EUF-P II) in soil 1 was also significantly greater than



**Figure 3.** Phosphorus absorbed by the plant throughout the growing period with the different fertilizers and the control. Bars with the same letter are not significantly different by LSD (0.05).



**Figure 4.** Percentage of phosphorus absorbed by the rye grass in comparison with the phosphorus provided in the different fertilizer treatments.

in soil 2. It must have been partly used to feed the plant. The highest P-absorbed values were obtained with UP in soil 1 (67% compared to the control treatment). TSPL-11 was the treatment absorbing most P

in soil 2 (34% compared with control). As far as TSPs are concerned, P absorption is clearly affected by the coating. These products' efficiency increased with the coating percentage. SSP and TSP provide the same ion

species ( $\text{H}_2\text{PO}_4^-$ ) but P absorption in SSP treatments was greater in both soils. This was probably due to this fertilizer's particle size leading to better distribution in the soil. This factor has a positive influence on P absorption by the plant's roots due to this element's low mobility in soil.

DAPs did not improve P absorption in soil 2 compared to the control while they did, significantly ( $P < 0.05$ ), in soil 1. The  $\text{HPO}_4^{2-}$  from DAPs' solution joins the soil at a high pH also. When Ca content is very high (soil 2), rapid, intense insoluble phosphate retrogradation probably occurs. Phosphate fertilizer efficiency is consequently very low.

With the aim of evaluating the fertilizer efficiency, the percentage of P uptake in comparison to P supply, i.e., the percentage of plant uptaken P, is shown in Figure 4. P uptake in both soils increases with the coating percentage in lignin-coated TSP fertilizers. This corroborates the foregoing observations. The highest percentage of P uptake was obtained with the TSPL-11 treatment in soil 2.

The efficiency as shown by UP in both the incubation and rye-grass crop test may be explained by this compound's very low pH counteracting the phosphoric retrogradation processes occurring at high pHs and the ionic forms provided with urea phosphate favoring the formation of more soluble compounds.

TSP increases its efficiency both in the incubation and crop test when embodying a lignin coating since, under these conditions, the nutrient joins the soil more slowly and retrogradation processes are attenuated.

A linear correlation was established between rye grass absorbed P after the four cuts made during the course of the experiment and fractions EUF-PI and EUF-P II of the different treatments in each soil after 30 and 60 days of the incubation test (Table 4).

The most significant correlation in soil 1 was obtained with the EUF-P II fraction after 30 days of the incubation test. This can be explained because this type of soil has a high carbonate and exchange Ca content, as a result of a higher clay content (Table 2). The plant-absorbed P must therefore depend to a greater extent on the reserve P related to fraction EUF-P II. The correlation obtained in this soil with fraction EUF-PI is not significant. This fraction, which represents easily available P, would seem to be insufficient to meet the plant's requirements despite having been increased with one of the fertilizer treatments.

A significant correlation was also obtained in soil 2 with EUF-P II after 30 and 60 days but the highest level of significance was obtained for the correlation with EUF-PI in the same time periods. Available P is generally higher than reserve P and therefore has more influence on the plant's P absorption.

This means that, in calcareous soils with a very low P/Ca ratio, there is a significant correlation between the P absorbed by the crop and P contents in the soil, obtained by EUF when applying various types of phosphoric fertilizers. On the basis of this good correlation, the efficiency of a phosphoric fertilizer applied to a crop in this type of soil using the laboratory EUF technique can be predicted.

Extrapolating glasshouse-obtained results to agricultural areas with high phosphate fixing power calcareous soils is undoubtedly of great importance. Firstly, because the efficiency of traditional fertilizers is proven to be very low, even that of SSP and SST, which are those normally recommended. Most of the phosphate is swiftly lost through retrogradation. Secondly, it was seen that the use of fertilizers with a highly acidic

solution pH, such as UP, or with FLC containing triple superphosphate, may increase the time P is available in some of these soils. A promising door is thus opened for the recovery of high phosphorus fixing power calcareous soils.

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