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FERTILIZER MANAGEMENT

Characterization and Agronomic Evaluation of Single Superphosphates Varying in Iron Phosphate Impurities

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ABSTRACT

An increase in the concentrations of water-insoluble iron phosphate (Fe-P) compounds in acidulated P fertilizers has raised the concern that the agronomic effectiveness of these P fertilizers will decrease. This study was conducted to evaluate the agronomic effectiveness of three sources of single superphosphate (SSP) varying in Fe-P impurities for upland and flooded rice (*Oryza sativa* L.) grown for 55 d. A modal chemical analysis and X-ray diffraction were used to characterize the SSP samples and their water-leached forms. A greenhouse study was conducted where rates of 0, 5, 15, 30, 50, and 100 mg P kg^{-1} as total available P (water plus citrate-soluble P) were applied from each SSP source and monocalcium phosphate (MCP) to a Hiwassee clay loam (thermic Rhodic Kanhapludult). The water-soluble P contents of the SSP sources were 46, 80, and 86% of the total available P (water + citrate) corresponding to an increase of Fe content (2, 4, and 7%) in the phosphate rock sources used for SSP production. The main Fe-P impurities in the SSP samples were identified as $Fe_3NaH_8(PO_4)_6{\cdot}6H_2O$ and $Fe_3H_9(PO_4)_6{\cdot}6H_2O$. Single superphosphate with only 46% of water solubility was 91% as effective as MCP in increasing dry matter yield and 76% as effective for P uptake by upland rice. The other two SSP sources were as good as MCP in effectiveness for upland rice. All of the SSP sources were equally as effective as MCP in producing dry matter yield and P uptake by flooded rice.

A gradual depletion of high-grade phosphate rock (PR) sources through mining is taking place all over the world (Lehr, 1980), and levels of impurities will certainly increase in the final acidulated P fertilizers as the P industry is forced to use lower-grade PR ores (Cathcart, 1980; Lehr, 1984). The impurity P compounds present in the final acidulated P fertilizer are generally water insoluble, and their composition depends on the mineralogical constitution of the ore and the process used to produce the P fertilizer (Lehr, 1980). Sikora et al. (1989) identified $MgAl(NH_4)_2H(PO_4)_2F_2$, $AlNH_4HPO_4F_2$, and $FeNH_4(HPO_4)_2$ as water-insoluble P compounds in monoammonium phosphate produced from North Carolina, Florida, and Idaho PR. Gilkes and Lim-Nunez (1980) concluded that 20% of P content in the Australian SSP was in the form of residual apatite and two water-insoluble phosphates, $Ca(Fe_{0.12}Al_{0.88})H(HPO_4)_2F_2{\cdot}2H_2O$ and $(Fe_{1.88}\ Al_{1.12})(K_{0.28}Na_{0.72})H_8(PO_4)_6{\cdot}6H_2O$.

The increasing content of impurity P compounds has raised the concern that the agronomic effectiveness of the P fertilizers would decrease because these compounds are water insoluble (Sikora and Giordano, 1995). The European Economic Community, for example, set a minimum level of 93% of total available P (water + citrate) as water-soluble P in fully acidulated P fertilizers marketed in the European community (Anonymous, 1975). Several researchers have found that the water-insoluble fractions of acidulated P fertilizers after water leaching are lower in agronomic efficiency compared with the original fertilizers without leaching or MCP. The P availability of the isolated water-insoluble fraction depended on the types of P fertilizer produced from different sources of PR (Bartos et al., 1991; Mullins et al., 1990; Prochnow et al., 1998). Gilkes and Lim-Nunez (1980) postulated that raw materials and manufacturing procedures should be chosen to limit the development of impurities, mainly $Ca(Fe, Al)\ H(HPO_4)_2F_2{\cdot}2\ H_2O$ and $(Fe, Al)(K, Na)H_8(PO_4)_6{\cdot}6H_2O$, in SSP and to minimize the content of apatite without substantially increasing the cost of the fertilizer. Greenhouse and field studies, however, have shown that the level of impurities in P fertilizers produced in the United States would have to be increased above current levels before effectiveness of P fertilizers would be affected (Mullins and Sikora, 1992, 1995). In one study by Mullins and Sikora (1995) with soils at pH 5.4 and 6.4, triple superphosphate required only 37 and 64%, respectively, of available P as water soluble to reach maximum yield of wheat (*Triticum aestivum* L.).

Phosphate rock ores with low grades of apatite and high amounts of iron and aluminum oxides (R_2O_3) need to go through an expensive process to reduce R_2O_3 content for the production of acidulated P fertilizers (McClellan and Gremillion, 1980). Even so, the acidulated P fertilizers sometimes still contain a considerable amount of Fe–Al–P compounds. These types of fertilizers cannot be marketed because they do not meet the regulations of water-soluble P content in the final products. It will be important to determine whether these P fertilizers should not be used or whether there should be an attempt to find some agronomic conditions under which they could be effectively utilized.

One possibility to improve the P availability of fertilizers containing high concentrations of Fe-P compounds (water insoluble but citrate soluble) would be to apply these fertilizers to flooded soils. In most rice soils, an increase in soil pH and a decrease in E_H on flooding are associated with the reduction of Fe^{3+} to Fe^{2+} that can result in an increase of P bioavailability from soil

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Abbreviations: FCA, fine concentrate apatite; Fe-P, iron phosphate; GCA, gross concentrate apatite; MCP, monocalcium phosphate; Pi, iron oxide–impregnated filter paper; PR, phosphate rock; RAE, relative agronomic effectiveness; RCA, refloatable concentrate apatite; R_2O_3, iron and aluminum oxides; SSP, single superphosphate.

native Fe-P (Ponnamperuma, 1978; Willet, 1991). It has also been reported that P availability of calcined Fe–Al–P minerals is agronomically effective in flooded rice soils (Int. Fert. Dev. Cent., 1998). Little information, however, is available in literature dealing with improvement in P availability of acidulated P fertilizers containing Fe-P compounds in soils under flooded conditions.

The specific objective of this study was to obtain information on the effectiveness of SSP sources containing different concentrations of Fe-P impurities for upland and flooded rice. This information is limited in literature reports and is relevant to many countries, such as China, India, Vietnam, Egypt, Brazil, New Zealand, Australia, and Nigeria, where SSP is one of the major P fertilizers being used.

MATERIALS AND METHODS

Single Superphosphate Fertilizers

Three sources of apatite concentrate [gross concentrate apatite (GCA), fine concentrate apatite (FCA), and refloatable concentrate apatite (RCA)] obtained from beneficiation of Araxá PR ore were used to produce SSP fertilizers (SSP1, SSP2, and SSP3). Table 1 shows the elemental chemical analysis of apatite concentrates for P by the molybdovanadate method (TVA, 1979) and for Ca, Fe, Si, Ba, and Mg by inductively coupled plasma atomic emission spectrometer (ICP).

An AOAC (1999) procedure modified by Bartos et al. (1991) was used to remove the water-soluble P from the original fertilizers. Subsamples of SSP weighing 25 g were agitated with 250 mL of deionized water for 1 h. The water was then removed under suction in a Buchner-type funnel, and the residue remaining in the filter paper was washed with two 80-mL portions of deionized water and rinsed with acetone to promote rapid drying of water-leached SSP.

Finely ground (−0.15 mm) samples of SSP, in the original form and water leached, were analyzed for total contents of P, Si, Fe, Al, Ca, Mg, K, Na, Ti, Ba, Sr, and Zn using a sequential dissolution procedure (TVA, 1979; Myshlyaeva and Krasnoshchekov, 1974). The concentrations of Fe, Al, Ca, Mg, Ti, Ba, Sr, and Zn were determined by ICP spectrometer and K and Na by an atomic absorption spectrophotometer. Total F was analyzed by the specific ion electrode method (Assoc. of Florida Phosphate Chemists, 1980), and SO_4^{2-}–S was analyzed following the gravimetric procedure with $BaSO_4$ (AOAC, 1999). The original SSP fertilizers were also analyzed for citrate- and water-soluble P following the procedure described in AOAC (1999), and the percentage of water-soluble P in the *available P* (sum of water-soluble and citrate-soluble P) was calculated. Determination of free water was conducted using the vacuum desiccation method (AOAC, 1999). After removing the free water, the water of hydration was determined by distillation with the n-amyl alcohol method (Duncan and Brabson, 1969). Total water was obtained by the summation of free water and water of hydration.

Table 1. Chemical analysis of apatite concentrates used to produce single superphosphate (SSP1, SSP2, and SSP3).

Analysis	Apatite concentrate† GCA	FCA	RCA
	g kg^{-1}		
P	157	152	139
Ca	346	334	290
Fe	21	40	71
Si	4	4	13
Ba	14	13	9
Mg	2	1	1

† GCA, gross concentrate apatite for SSP1; FCA, fine concentrate apatite for SSP2; RCA, refloatable concentrate apatite for SSP3.

Twenty-gram samples of the original and the water-leached residue of each SSP were weighed and ground with 10 mL of freon for 7 min in a shaker box. The samples were scanned using a Siemens D-500 X-ray powder diffractometer at a starting point of 5.0 2-Theta(°), endpoint of 65.0 2-Theta(°), step-size of 0.02 2-Theta(°), dwell time of 3 s, and energy = Cu (40 kV, 30 mA). The data were then analyzed by the software Jade 5.0 (XRD pattern processing) to which X-ray patterns of Fe–Al–P compounds contained in the publication of Frazier et al. (1991) were added. The compounds present in the samples were then identified based on the XRD spectral lines of pure compounds listed in the standard powder diffraction files (PDF).

A modal analysis was applied to estimate the mineralogical composition of SSP. The modal analysis was based on qualitative information on the type of compounds provided by X-ray, quantitative information on total elemental content and water of hydration, solubility index of the compounds, and the chemical composition of the compounds or minerals.

Greenhouse Evaluation

A greenhouse study was conducted with a Hiwassee clay loam (thermic Rhodic Kanhapludults) (Soil Survey Staff, 1960). The soil had 3 mg kg^{-1} resin-extractable P (Van Raij and Quaggio, 1983), 1.7 mg kg^{-1} extractable P by the iron oxide–impregnated filter paper (Pi) (Menon et al., 1989b), 10.4 cmol$_c$ kg^{-1} cation exchange capacity, 18 g kg^{-1} organic matter, and pH of 5.3 (1:1 soil/water ratio).

The three powdered SSP sources and MCP were mixed with the soil at rates to supply 0, 5, 15, 30, 50, and 100 mg P kg^{-1} as available P (water + citrate) (AOAC, 1999). The rates of P applied were based on available P, instead of total P, for the following reasons: (i) The citrate-insoluble P is considered by AOAC standards to be plant unavailable; (ii) acidulated P fertilizers in USA, Brazil, China, and some other countries are sold and applied on the basis of their AOAC available P content; (iii) studies that have evaluated the effect of water-soluble P on fertilizer effectiveness have been based on available P rates applied (Mullins and Sikora, 1995); and (iv) to check the legislation that required minimum water-soluble P in available P content of acidulated P fertilizers. Other nutrients were added at rates of 200 mg kg^{-1} N as urea and 200 mg kg^{-1} K as KCl and at adequate levels of secondary and micronutrients for plant growth. Sources and rates of P were arranged employing a randomized complete block design with three replications.

Eight seeds of upland rice (cultivar IR-47686) were planted in 4-kg soil pot at a depth of about 1 cm and subsequently thinned to two plants per pot 10 d after germination. The pots were watered using deionized water to maintain 75% field moisture capacity during the entire experiment. Flooded rice seedlings of cultivar IR-36 were grown in 7-kg soil pot for 4 wk and then transplanted to four plants per pot. The soil was flooded under 0.5 cm of water for 2 wk before transplanting. After transplanting, the floodwater was kept at 2 cm above the soil surface until the plants were harvested.

Plants were harvested by cutting the stalk 55 d after germination for upland rice and after transplanting flooded rice seedlings, followed by drying at 60°C for 2 wk and weighing. The concentration of P in the harvested plants was determined after digestion of subsamples with H_2SO_4–H_2O_2 by ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962).

After upland rice was harvested, 50-g soil samples were collected, dried, and ground to 2-mm size, and available P was determined by the Pi test (Menon et al., 1989b). For the flooded rice, a new procedure was used to determine P availability of the flooded soil in situ. Following the procedure described by Menon et al. (1989a), Pi strips were prepared with paraffin wax on both ends. A spatula was used to insert four Pi strips in each pot, with only one of the waxed ends above the soil surface. After 24 h, the four Pi strips from each pot were carefully pulled out from the soil and rinsed with deionized water. The Pi strips were then combined for extraction by shaking for 1 h with 40 mL of 0.1 *M* H_2SO_4 and filtering, followed by P determination (Murphy and Riley, 1962). Available P as measured by the Pi test was expressed in milligrams of P per kilogram for upland rice and micrograms of P per strip for flooded rice.

Data Analysis

The relationships between dry matter yield or P uptake and rate of P applied, Pi-extractable P and rate of P applied, and dry matter yield or P uptake and Pi-extractable P were evaluated using regression procedures (SAS Inst., 1985).

Except for the relationships between dry matter yield or P uptake and Pi-extractable P, a combined multiple-regression analysis using a dummy variable as described by Chien et al. (1988) was performed for all P sources. This resulted in a common intercept and a single value of Sy^ (standard deviation of yield response) and R^2 for the four regression equations (one for each P source). Three response functions (linear, semilog, and square root) were tested to describe the relationship between the parameters studied, and the one presenting the greatest R^2 with the lowest root mean square error was chosen. The models tested were as follows:

$$Yi = \beta o + \beta i X + \varepsilon_i,\ X \geq 0, \qquad [1]$$

$$Yi = \beta o + \beta i \ln X + \varepsilon_i,\ X \geq 1,\ \text{or} \qquad [2]$$

$$Yi = \beta o + \beta i X^{1/2} + \varepsilon_i,\ X \geq 0 \qquad [3]$$

where Y*i* is the dry matter yield, P uptake, or Pi-extractable P obtained with material *i*, *X* is the rate of P applied, β*i* is the slope of the response function for material *i*, β*o* is the common intercept, and ε_i is the error term of the fitted model.

The relative agronomic effectiveness (RAE) was calculated for each SSP. Relative agronomic effectiveness was defined as the ratio of the two slopes:

$$\text{RAE}i = \beta i/\beta\text{MCP} \times 100 \qquad [4]$$

where β*i* is the slope of the response function of the SSP tested and βMCP is the slope of the response function of the standard source of P as MCP. This expression ranks the SSP with respect to MCP according to their agronomic potential to produce a yield response (Chien et al., 1990). Use of RAE made it possible to compare the effectiveness of the P materials between upland and flooded rice, even when utilizing different pot sizes, rice cultivars, and planting methods.

To determine if there was a statistically significant difference between two P sources in the range of P rates applied, the *F* value (= t^2) was calculated according to the formula:

$$t = \frac{(\beta ia - \beta ib)}{\sqrt{[\text{SE}(\beta ia)]^2 + [\text{SE}(\beta ib)]^2}} \qquad [5]$$

where β*ia* is the slope of the response function for the first P material tested, β*ib* is the slope for the second P material tested, SE(β*ia*) is the standard error for β*ia*, and SE(β*ib*) is the standard error for β*ib*.

RESULTS AND DISCUSSION

Characterization of Single Superphosphate

The Fe content in the apatite concentrate followed the order GCA < FCA < RCA (Table 1). Iron in the final SSP was expected to follow the same trend and was confirmed by data showing SSP1 < SSP2 < SSP3 (Table 2). There was a similar trend between the amounts of Fe impurities in SSP and the water solubility or percentage of water-soluble P in the available P fraction (fi parameter, Table 2), with SSP1 having the greatest water solubility and the least Fe content. Several studies have reported the effect of Fe impurities on water solubility of acidulated P fertilizers using different P sources (Gilkes and Lim-Nunez, 1980; Gilkes and Mangano, 1983; Hammond et al., 1989; Slack, 1968; Prochnow et al., 1998). They attributed the decrease in water solubility to the formation of Fe–Al–P compounds, which are water insoluble but generally citrate soluble.

X-ray powder diffraction of the original and water-leached SSP was used to identify the primary components of the P fertilizers. Figure 1 summarizes the results found for SSP3. The following criteria were used to identify P compounds: (i) suggestions made by Jade 5.0–XRD pattern processing, (ii) the existence of at least one spectral line standing alone for that particular compound, and (iii) matching the results obtained for the original and water-leached form of each SSP.

Analysis by X-ray powder diffraction indicated that MCP was present in the three SSP sources but not in the water-insoluble fraction. Figure 2 illustrates this situ-

Table 2. Chemical analysis of monocalcium phosphate (MCP) and single superphosphate (SSP) in the original form and water leached.

		P§																
P† source	PC‡	T	A	H_2O	Si	Fe	Al	Ca	Mg	K	Na	Ti	Ba	Sr	Zn	F	SO_4^{2-}–S	fi¶
									g kg^{-1}									%
SSP1	Original	94.7	85.6	73.4	0.0	12.7	1.5	214.0	0.7	0.2	2.1	2.3	12.1	7.3	0.3	13.0	378.7	86
SSP1	Leached	25.8	NA#	NA	2.5	16.7	1.7	239.3	0.1	0.3	2.4	3.3	18.4	9.9	0.2	19.0	513.9	NA
SSP2	Original	82.7	70.3	55.9	0.0	22.1	2.2	193.5	0.8	0.2	2.0	3.5	8.4	6.3	0.4	11.8	388.1	80
SSP2	Leached	32.8	NA	NA	1.2	23.7	1.9	210.8	0.1	0.3	1.6	4.2	10.5	6.7	0.2	14.2	459.3	NA
SSP3	Original	79.3	71.6	32.8	5.0	42.9	2.7	175.3	0.9	0.3	2.7	4.7	8.6	5.6	0.6	11.9	373.3	46
SSP3	Leached	57.5	NA	NA	5.3	48.8	2.0	180.1	0.1	0.3	2.5	9.2	9.7	4.8	0.2	12.3	384.4	NA
MCP	Original	241.9	241.5	238.4	0.0	0.0	0.0	170.0	0.1	0.0	0.1	0.0	0.0	0.1	0.0	0.2	2.7	99

† SSP1, SSP2, and SSP3 produced from gross, fine, and refloatable Araxá concentrate apatite, respectively.
‡ PC, phosphate condition: original = not water leached; leached = water leached.
§ P analysis: T = total P; A = available P (water + citrate); H_2O = water-soluble P.
¶ Percentage of available P as water-soluble P: fi = (water-soluble P/available P) × 100.
# NA, not available.

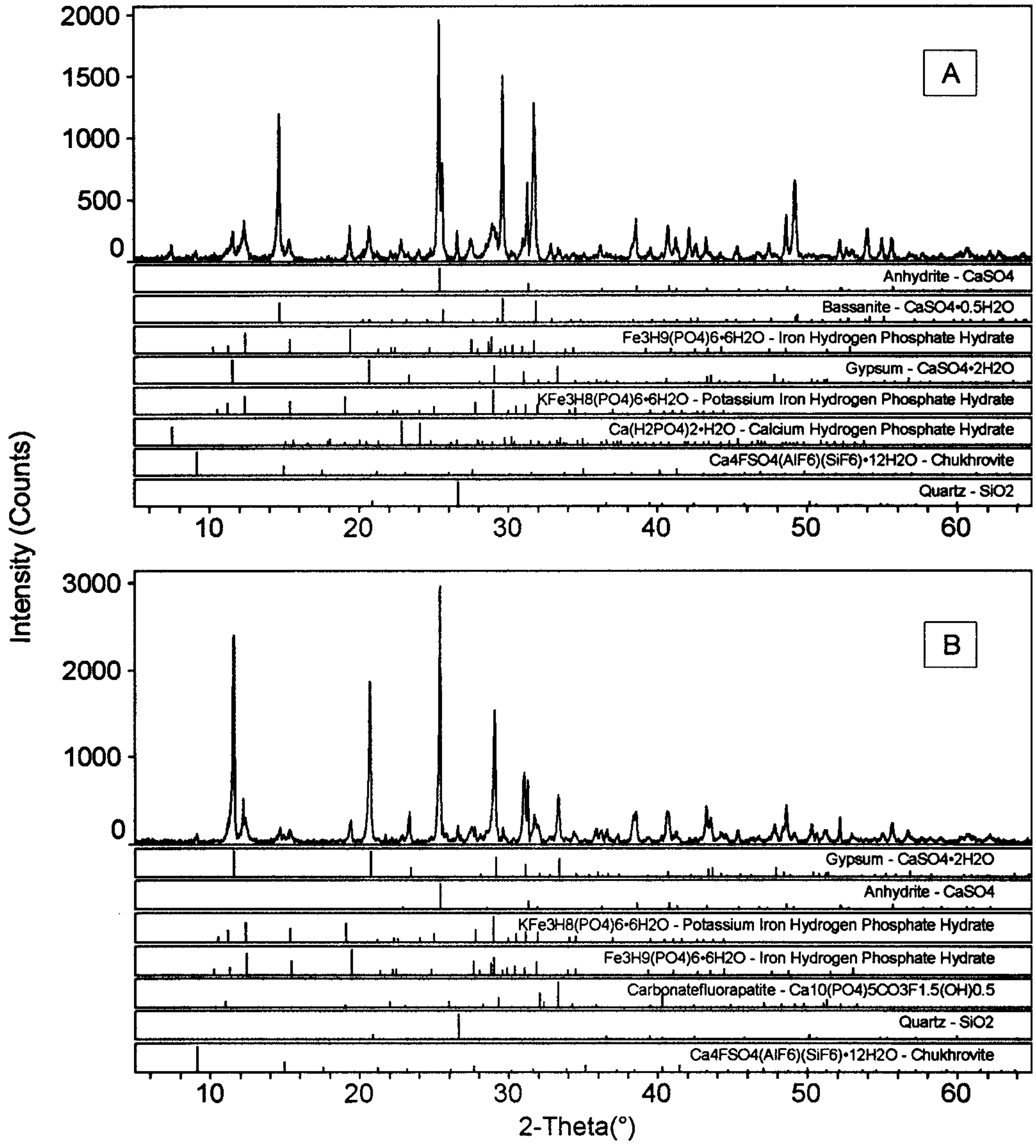

Fig. 1. X-ray diffractograms including the 2-Theta(°) spectral lines of compounds detected by software Jade 5.0 (XRD pattern processing) in samples of (A) original single superphosphate (SSP) produced from refloatable concentrate apatite (SSP3) and (B) its water-insoluble fraction.

ation for SSP2, which denotes that the three strongest peaks (dotted lines) for MCP are present for the original SSP but not for the leached SSP. X-ray diffraction analysis of the water-insoluble fraction of SSP3 (Fig. 1) confirmed that most Fe was in the Fe-P form. The main Fe-P compound identified in SSP3 (highest amount of Fe) was $Fe_3H_9(PO_4)_6{\cdot}6H_2O$. Figure 3 compares the X-ray patterns of the water-insoluble fraction of SSP1, SSP2, and SSP3. The strongest line for $Fe_3H_9(PO_4)_6{\cdot}6H_2O$ [2-Theta(°) = 19.45, d(A) = 4.56] is present in SSP3, whereas the line is almost absent for SSP1 and SSP2. The presence of this compound is in accordance with the work of other authors who identified or described a similar compound, $Fe_3KH_8(PO_4)_6{\cdot}6H_2O$, in acidulated P fertilizers (Frazier and Lehr, 1967; Lehr et al., 1967; Gilkes and Lim-Nunez,1980). The difference between the two compounds is the absence of K for the one identified by software Jade 5.0–XRD pattern used in the present study. The low amounts of K in the three SSP sources (Table 2) led to low contents of $Fe_3KH_8(PO_4)_6{\cdot}6H_2O$. It is known that the generic Fe-P compound (Fe, Al)(K, Na)$H_8(PO_4)_6{\cdot}6H_2O$ will preferably form with K, but in the absence of K, the compound will still form including Na [$Fe_3NaH_8(PO_4)_6.6H_2O$], followed by the formation of the analog H_9 member (Frazier et al., 1989). The results show that the H_9 member [$Fe_3H_9(PO_4)_6{\cdot}6H_2O$] present in the three SSP sources could be associated with the lesser water solubility of the SSP.

The modal analysis was used to estimate the mineralogical composition of the three SSP sources. The percentage of $Fe_3H_9(PO_4)_6$ in SSP is in the order of SSP1 < SSP2 < SSP3; the percentage of MCP is in the order of SSP1 > SSP2 > SSP3 (Table 3). Thus, the X-ray patterns of the P sources are in accordance with the mineralogical composition estimated by the modal analysis and provide direct evidence for the presence of apatite and the compounds $Fe_3KH_8(PO_4)_6{\cdot}6H_2O$, $Fe_3H_9(PO_4)_6{\cdot}6H_2O$, $Ca_4SiAlSO_4F_{13}{\cdot}12H_2O$, $CaSO_4$, and MCP.

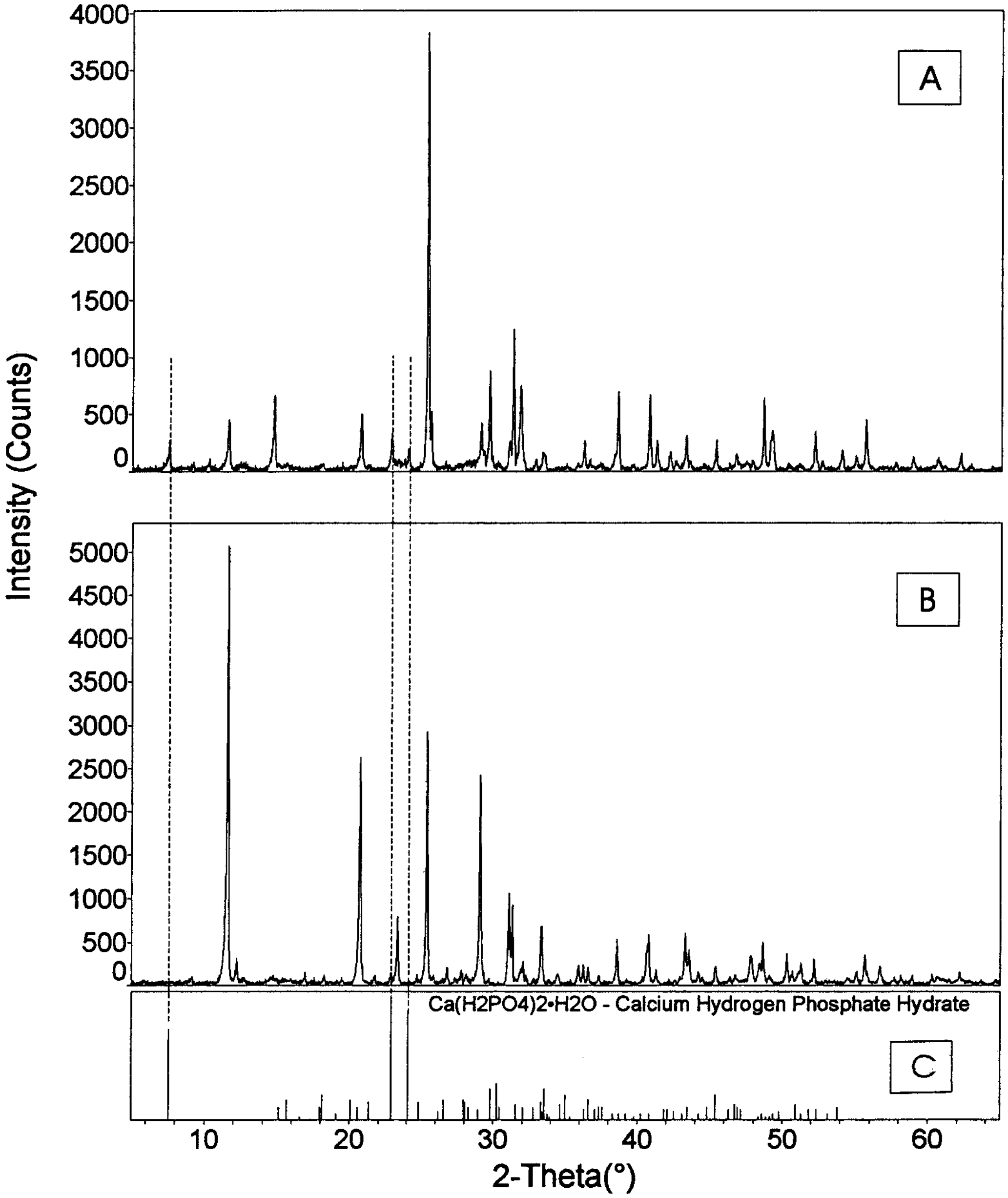

Fig. 2. X-ray diffratograms of (A) the original single superphosphate (SSP) produced from fine concentrate apatite (SSP2) and (B) its water-insoluble fraction, and (C) the 2-Theta(°) spectral lines for the pure compound $Ca(H_2PO_4)_2{\cdot}H_2O$ [monocalcium phosphate (MCP)].

Greenhouse Evaluation of Single Superphosphate

The square-root model best described the relationship between dry matter yield or P uptake by upland rice and the rate of P applied (Fig. 4 and Table 4). Single superphosphate 1 and SSP2 were statistically the same as MCP in increasing dry matter yield of upland rice, whereas SSP3 was the least effective P source. Calculated RAE values were SSP1 = 98%, SSP2 = 96%, and SSP3 = 91% (Table 5). For P uptake by upland rice, SSP1, SSP2, and MCP were equally effective, whereas SSP3 was the least efficient P source (Table 4). Calculated RAE values for P uptake by upland rice were SSP1 = 88%, SSP2 = 93%, and SSP3 = 76% (Table 5).

Linear model ($R^2 = 0.93$) best explained the relationship between Pi-extractable P and rate of P applied (Fig. 5). Available P as measured by Pi test showed that SSP1 and SSP2 were not statistically different from MCP, whereas SSP3 was the least effective P source in providing available P for upland rice. The relatively poor performance of SSP3 for upland rice was attributed to its lowest percentage of water-soluble P in total available P fraction (Table 2), corresponding to its highest amounts of the water-insoluble forms of $Fe(K, Na)H_8(PO_4)_6{\cdot}6H_2O$ (Table 3). The Pi-extractable P of the soil samples collected after harvest of upland rice significantly correlated with dry matter yield (semilog model, $R^2 = 0.73$) or with P uptake (square-root model, $R^2 = 0.85$) (Fig. 6).

For flooded rice, the linear model best described the relationship between dry matter yield or P uptake and P rate (Fig. 7). All of the P sources were equally effective in increasing dry matter yield (Table 6). The RAE val-

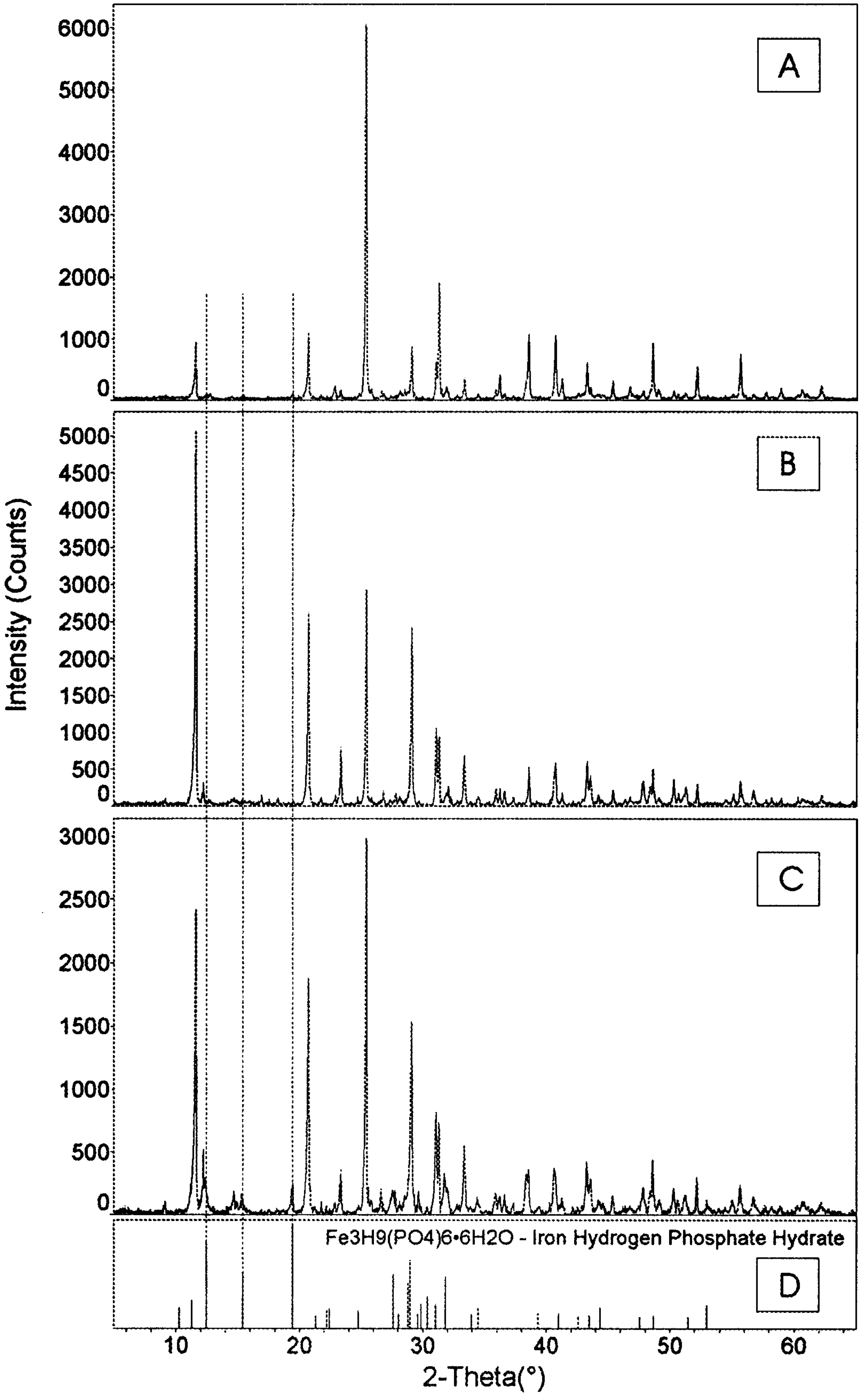

Fig. 3. X-ray diffractograms of the leached (A) single superphosphate 1 (SSP1), (B) SSP2, and (C) SSP3, and (D) the 2-Theta(°) spectral lines for the pure compound $Fe_3H_9(PO_4)_6{\cdot}6H_2O$.

Table 3. Modal analysis of the mineralogical composition of three single superphosphate (SSP) sources.

Compound†	P source‡		
	SSP1	SSP2	SSP3
	g kg^{-1}		
$Fe_3KH_8(PO_4)_6$	4	4	6
$Fe_3NaH_8(PO_4)_6$	5	34	64
$Fe_3H_9(PO_4)_6$	4	62	123
Na_2SiF_6	3	4	3
$Ca_{10}(PO_4)_6OH_{0.97}F_{1.03}$	28	26	31
$Ca_4SiAlSO_4F_{13}$	22	4	21
SiO_2	0	0	7
CaF_2	3	14	0
$MgSO_4$	4	4	5
$SrSO_4$	15	13	12
$ZnSO_4$	1	1	2
$Ti_2(SO_4)_3$	9	14	19
$BaSO_4$	19	11	13
$Al_2(SO_4)_3$	3	13	11
$Ba(H_2PO_4)_2$	2	4	3
$CaSO_4$	492	497	469
$Ca(H_2PO_4)_2$	342	191	128
Free water	14	39	18
Water of hydration	49	53	74
Total water	63	92	92
Total	1064	988	1009

† Chemical formula of the possible compounds present in SSP1, SSP2, and SSP3 without considering the water of hydration.
‡ SSP1, SSP2, and SSP3 produced from gross, fine, and refloatable Araxá concentrate apatite, respectively.

ues for dry matter yield of flooded rice are SSP1 = 97%, SSP2 = 111%, and SSP3 = 102% (Table 5). Thus, unlike upland rice, SSP3 was as effective as SSP1 and SSP2 in dry matter yield of flooded rice. However, similar to upland rice, SSP3 was still less effective than SSP2 in P uptake by flooded rice (Fig. 7), probably due to its lower water solubility. The RAE values for P uptake by flooded rice are SSP1 = 94%, SSP2 = 110%, and SSP3 = 85% (Table 5).

The Pi-extractable P was measured by the new procedure of inserting Pi strips directly into the flooded soil after the rice was harvested. A linear model ($R^2 = 0.93$) was found to be the best to explain the relationship between Pi-extractable P and rate of P applied (Fig. 8). All SSP sources were statistically the same in providing Pi-extractable P to flooded rice. Single superphosphate 2 and SSP3 were also equally effective as MCP, whereas SSP1 was more effective than MCP, probably due to its lower water solubility compared with MCP, which resulted in a lower P fixation by the soil. The results showed a highly significant correlation between Pi-extractable P and dry matter yield (semilog model, $R^2 = 0.92$) or P uptake (square-root model, $R^2 = 0.88$) (Fig. 9). The Pi test thus is a potential in situ method to monitor available P in flooded soil.

Table 4. Regression estimates for the square-root model describing the relationship between dry matter yield or P uptake by upland rice and applied P rate.

P source	Estimate	Dry matter yield	P uptake
Intercept	β_0	0.50	0.25
MCP	β_1	2.912** A†	3.698** A
		(0.101)‡	(0.162)
SSP1	β_2	2.847** A	3.280** A
		(0.101)	(0.162)
SSP2	β_3	2.791** AB	3.456** A
		(0.101)	(0.162)
SSP3	β_4	2.653** B	2.814** B
		(0.101)	(0.162)
No. of observations		63	63
$Sy^{\wedge}$§		2.48	3.96

** Significant at the 0.01 level.
† Values followed by the same letter are statistically not different from each other ($p = 0.05$).
‡ Values in parentheses are standard errors of estimates.
§ $Sy^{\wedge}$ = standard deviation of yield response.

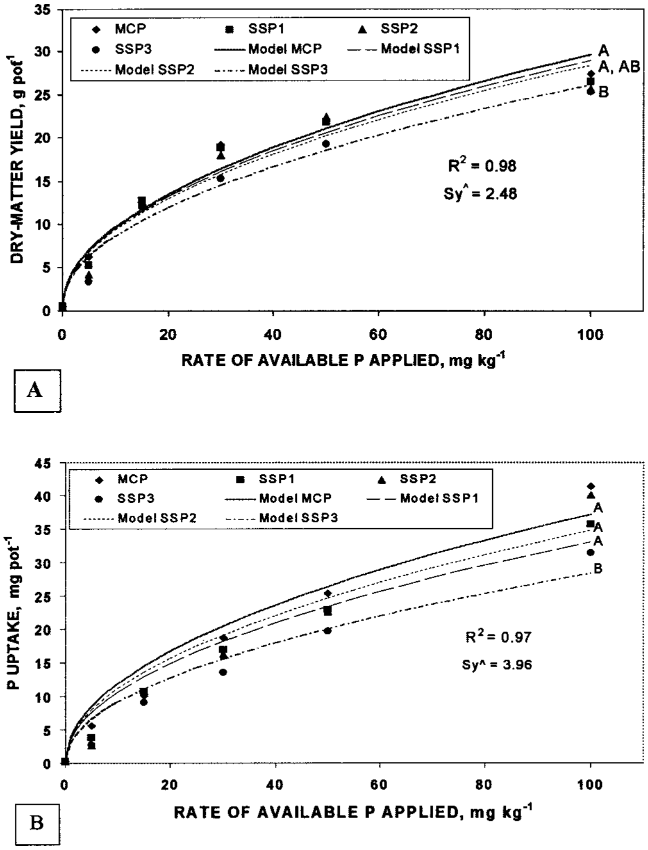

Fig. 4. (A) Dry matter yield and (B) P uptake by upland rice obtained with different P sources. Models followed by the same letter are statistically not different from each other in the slope ($p \leq 0.05$). MCP, monocalcium phosphate; SSP, single superphosphate.

The results of upland rice showed that higher agronomic performance would be expected for P fertilizers with high water solubility. However, it also should be pointed out that SSP3, with only 46% of total available P as water soluble, was 91% as effective as MCP (100%

Table 5. Calculated values of relative agronomic effectiveness of single superphosphate (SSP) with respect to monocalcium phosphate (MCP) for upland and flooded rice.

P source	Dry matter yield	P uptake
	%	
	Upland rice	
MCP	100	100
SSP1	98	88
SSP2	96	93
SSP3	91	76
	Flooded rice	
MCP	100	100
SSP1	97	94
SSP2	111	110
SSP3	102	85

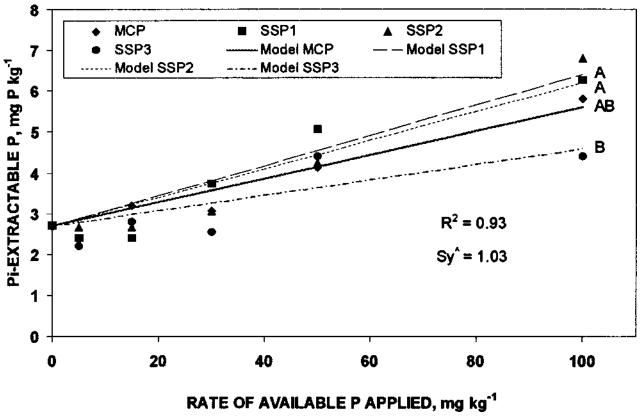

Fig. 5. Phosphate extracted by iron oxide–impregnated filter paper (Pi-extractable P) of soil samples collected after upland rice was harvested as related to P rate applied. Models followed by the same letter are statistically not different from each other in the slope ($p \leq 0.05$). MCP, monocalcium phosphate; SSP, single superphosphate.

water soluble) for dry matter yield and 76% as effective as MCP for P uptake (Table 5). The results agree with those of Mullins and Sikora (1995), who concluded that triple superphosphate fertilizers required only 37% water-soluble P to reach maximum yields of wheat at soil pH 5.4, whereas the fertilizers required 63% water-soluble P at pH 6.3. They suggested that products with low water solubility are not necessarily very poor sources of P for upland crops.

The idea that the acidulated P fertilizers with low water solubility but high citrate solubility can be efficient in providing available P to plants is further supported by the data on flooded rice. Although SSP3 was less effective than MCP in terms of P uptake, there was no significant difference between the two P sources for dry matter yield (Fig. 7). Also, Pi-extractable P in the flooded soil from SSP3 was not statistically lower than other P sources with higher water solubility (Fig. 8). The RAE values of the three SSP sources were also generally higher for flooded rice than upland rice (Table 5). For example, RAE of SSP3 increased from 91% for upland rice to 102% for flooded rice in increasing dry matter yield and from 76% for upland rice to 85% for flooded rice in terms of P uptake. These results suggest that P fertilizers containing Fe-P compounds similar to those found in this study can produce a higher agronomic efficiency for flooded rice than upland crops.

The higher agronomic effectiveness of SSP, especially SSP3, in flooded soil suggests that, similar to native soil Fe-P minerals, a reductive dissolution of fertilizer Fe-P compounds can increase P availability to flooded rice. In this study, $Fe_3H_9(PO_4)_6{\cdot}6H_2O$ was identified as the

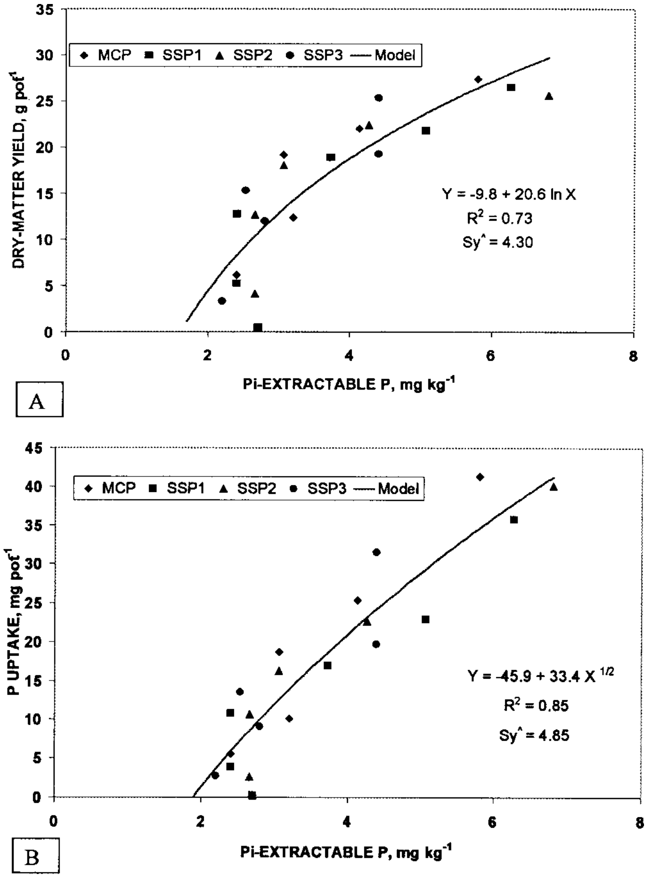

Fig. 6. Relationship between (A) dry matter yield or (B) P uptake by upland rice and P extracted by iron oxide–impregnated filter paper (Pi-extractable P) of soil samples collected after the plant was harvested. MCP, monocalcium phosphate; SSP, single superphosphate.

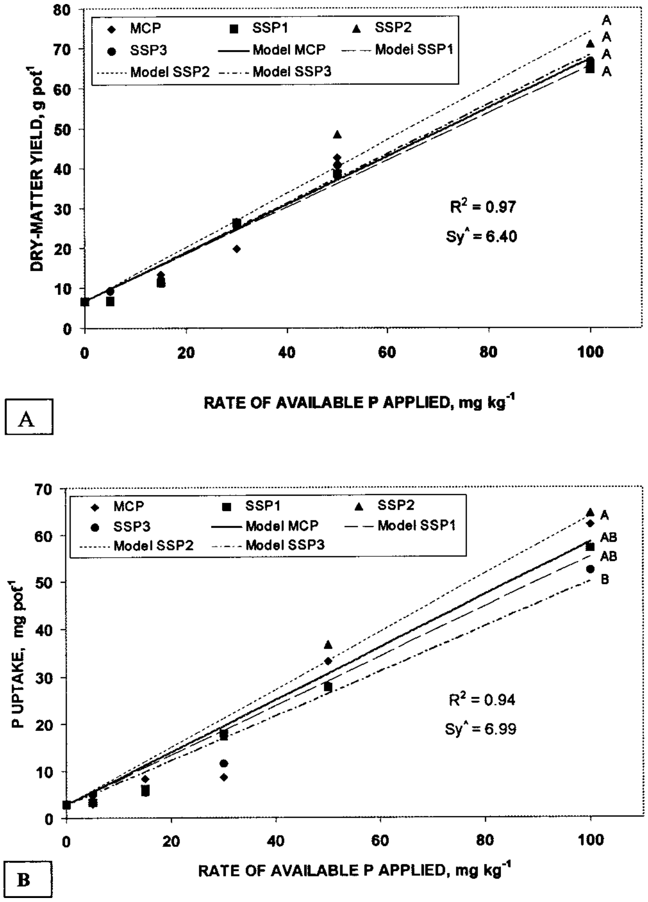

Fig. 7. (A) Dry matter yield and (B) P uptake by flooded rice obtained with different P sources. Models followed by the same letter are statistically not different from each other in the slope ($p \leq 0.05$). MCP, monocalcium phosphate; SSP, single superphosphate.

Table 6. Regression estimates for the linear model describing the relationship between dry matter yield or P uptake by flooded rice and applied P rate.

P source	Estimate	Dry matter yield	P uptake
Intercept	β_0	6.70	2.87
MCP	β_1	0.605** A†	0.555** AB
		(0.036)‡	(0.040)
SSP1	β_2	0.589** A	0.524** AB
		(0.032)	(0.035)
SSP2	β_3	0.674** A	0.6100** A
		(0.032)	(0.035)
SSP3	β_4	0.617** A	0.472** B
		(0.036)	(0.040)
No. of observations		61	61
Sy^§		6.40	6.99

** Significant at the 0.01 level.

† Values followed by the same letter are statistically not different from each other (p = 0.05).

‡ Values in parentheses are standard errors of estimates.

§ Sy^ = standard deviation of yield response.

main form of Fe-P compound in the water-insoluble fraction of SSP3 (Fig. 1 and 3; Table 3). This compound would be expected to provide more available P when applied to the reduced flooded soil than to the oxidized upland soil. Further research is needed to investigate other Fe–Al–P compounds that are also possibly present in commercial acidulated P fertilizers.

The legislation imposed by some European countries and Brazil that requires high water solubility of P in the total available P fraction of acidulated P fertilizers is not supported by the results of this greenhouse study. This is in agreement with the data presented by Sikora and Giordano (1995) and Johnston (1999). They also concluded that the requirement of high water solubility for all acidulated P fertilizers is not necessary. However, the information obtained under greenhouse conditions suggests that more research on the issue of P water solubility in fully acidulated P fertilizers is necessary, especially under field conditions. In addition, evaluation of the agronomic performance of acidulated P fertilizers should also characterize the P compounds present in the water-insoluble fraction.

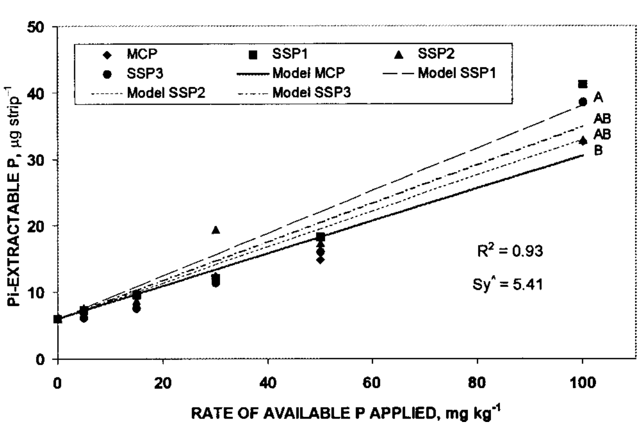

Fig. 8. Phosphate extracted by iron oxide–impregnated filter paper (Pi-extractable P) of soil samples collected after flooded rice was harvested as related to P rate applied. Models followed by the same letter are statistically not different from each other in the slope ($p \leq 0.05$). MCP, monocalcium phosphate; SSP, single superphosphate.

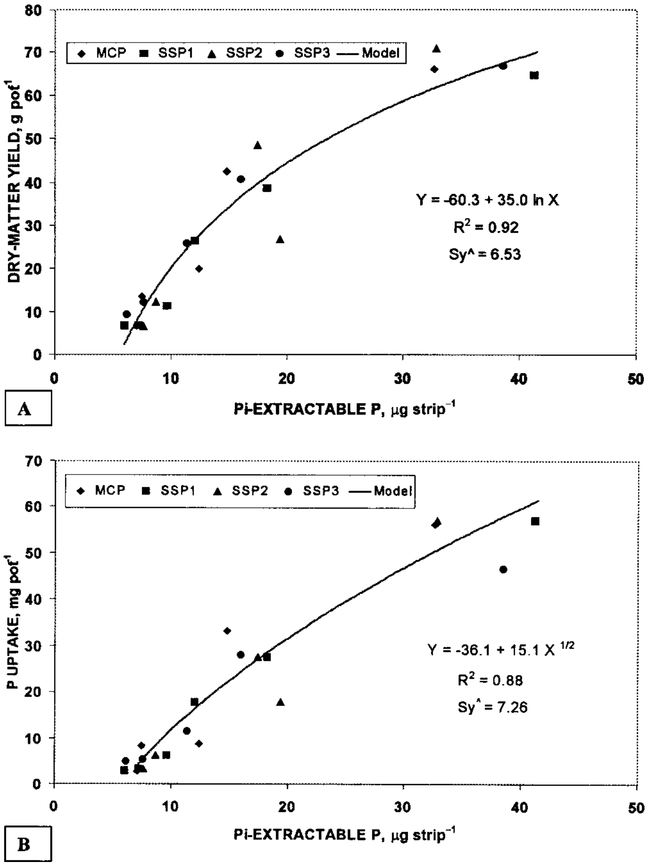

Fig. 9. Relationship between (a) dry matter yield or (b) P uptake by flooded rice and P extracted by iron oxide–impregnated filter paper (Pi-extractable P) of soil samples collected after the plant was harvested. MCP, monocalcium phosphate; SSP, single superphosphate.

The results of this study show that $Fe_3H_9(PO_4)_6{\cdot}6H_2O$ present in superphosphates should not be seen as totally undesirable. Furthermore, the need to limit the presence of water-insoluble compounds in the final superphosphate, as suggested by Gilkes and Lim-Nunez (1980), may not be necessary. In their study, the water-insoluble Fe–Al–P compounds were isolated and compared with water-soluble P for agronomic effectiveness. Such comparison could underestimate the effectiveness of water-insoluble P because there is a possible enhancement effect of water-soluble P on the agronomic effectiveness of water-insoluble P when the two P sources are present together (Chien et al., 1996).

In summary, the information that water-insoluble but citrate-soluble Fe-P compounds should not be considered completely undesirable can be very important to fertilizer industries and farmers. Legislation may need to be modified based on further agronomic research.

CONCLUSIONS

The results of this study show that acidulated P fertilizers with total available P content as low as 46% that of water-soluble P was as effective as water-soluble MCP in increasing dry matter yield of upland and flooded rice. This suggests that these types of acidulated P fertilizer should not be discarded solely based on the criteria of low water solubility as stipulated by legislation that requires 90 to 93% water solubility. The results also suggest that acidulated P fertilizers with low water-soluble P content containing Fe-P compounds can be agronomically more effective for flooded rice than upland crops, probably due to reduced soil conditions on flooding that promote dissolution of Fe-P.

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