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EVALUATION OF AVAILABLE PHOSPHORUS AND CADMIUM ASSOCIATED WITH PHOSPHATE ROCK FOR DIRECT APPLICATION

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Abstract

Three greenhouse experiments were conducted to evaluate available P and Cd associated with the use of phosphate rock (PR) for direct application. These experiments were: (1) "Estimation of Phosphorus Availability to Maize and Cowpea From Phosphate Rock as Enhanced by Water-Soluble Phosphorus;" (2) "Modified Iron Oxide-Impregnated Paper Strip (Pi) Test for Soils Treated With Phosphate Fertilizers;" and (3) "Effect of Acidulation of High Cadmium Containing Phosphate Rocks on Cadmium Uptake by Upland Rice."

In the first experiment, a medium-reactive Central Florida phosphate rock (PR) was used. The effectiveness of P sources in terms of increasing dry-matter yield and P uptake followed the order of TSP $\geq$ (PR + TSP) > PR for maize and TSP = (TSP + PR) > PR for cowpea. P uptake from PR in the presence of TSP was higher than P uptake from PR applied alone. With respect to P uptake from PR applied alone, the corresponding relative increase in P uptake from PR due to TSP influence was 165% for maize and 72% for cowpea. In the second experiment, a highly reactive North Carolina PR was used. Both Bray I and the Pi test (with $CaCl_2$) underestimated available P from PR with respect to TSP. Available P estimated by the Pi test with KCl was more closely related to P uptake with both PR and TSP. More P was extracted from PR by the Pi test with KCl than with $CaCl_2$, whereas no effect was observed for TSP. In the third experiment, a low-reactive Togo PR and a highly reactive North Carolina PR were used. Both PRs were fully acidulated to SSP and Togo PR was also partially acidulated with H_2SO_4 at 50% level to PAPR. Cd uptake by rice grain followed the order of NC-SSP > NC-PR and Togo-SSP > Togo PAPR > Togo PR. The results also showed that most of the Cd uptake was retained in rice root and straw. Total uptake of Cd, Ca, and P by the rice plant was higher from NC-PR than from Togo-PR. Cd concentration in rice grain showed no significant difference between NC-PR and Togo-PR, whereas Cd concentrations in root and straw were higher with NC-PR than that with Togo-PR.

1. INTRODUCTION

In 1993, the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture launched a 5-year Co-ordinated Research Project (CRP) on "The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of Phosphate Fertilizers, in Particular, Rock Phosphate." IFDC was invited to participate in this CRP as a collaborative institution. During the 5-year period, IFDC conducted three major experiments to contribute to meet part of the objectives of this CRP. These experiments were: (1) "Estimation of Phosphorus Availability to maize and Cowpea From Phosphate Rock as Enhanced by Water-Soluble Phosphorus;" (2) "Modified Iron Oxide-Impregnated Paper Strip (Pi) Test for Soils Treated With Phosphate Fertilizers;" and (3) "Effect of Acidulation of High Cadmium Containing Phosphate Rocks on Cadmium Uptake by Upland Rice."

The purpose of this paper is to present a summarized report on the three experiments conducted by IFDC. More detailed information can be found in the three papers published in scientific journals [1-3].

2. EXPERIMENT 1: ESTIMATION OF PHOSPHORUS AVAILABILITY TO MAIZE AND COWPEA FROM PHOSPHATE ROCK AS ENHANCED BY WATER-SOLUBLE PHOSPHORUS

2.1. Literature review and objective

Although direct application of phosphate rock (PR) may be a cost-effective means to supply phosphorus (P), PRs with low and medium reactivity often do not perform as well as soluble P fertilizers in terms of yield response of food crops [4-7]. One practice that has been reported to increase the plant's utilization of low- and medium-reactivity PR is to supply the early P requirement of the crop with water-soluble P fertilizer. By doing so, the plant would have better root development and, in turn, would be able to utilize PR more effectively than could a plant treated with PR alone [8]. The additional P can be supplied by compacting water-soluble P fertilizers, such as TSP, with PR or by partially acidulating PR with H_2SO_4 or H_3PO_4 [9-12].

Quantitative estimation of P availability from PR in soil as enhanced by water-soluble P has not been reported. Because of possible interactions (priming effect) among water-soluble P, PR, and soil P, use of radioactive ^{32}P as a tracer is essential to distinguish P availability from soil P, PR, or water-soluble P. The objective of this study was to use ^{32}P as a tracer to estimate quantitatively the enhancement effect of water-soluble P (TSP) on P availability applied from a medium-reactivity PR to maize and cowpea grown on an acid soil.

2.2. Materials and methods

The soil used was a Hartsells silt loam classified as a Typic Hapludult (Table I). The soil was air-dried and screened to less than 2 mm. The PR used was a finely ground (<0.15 mm or 100 mesh) Central Florida PR (CFPR). Its total P and citrate-soluble P were 14.2% and 1.4%, respectively. Radioactive ^{32}P-tagged TSP was prepared by adding ^{32}P-labeled H_2PO_4 to CFPR. After curing, the TSP aggregates were crushed and ground to powder (<0.15 mm), which had a total P content of 18.8%. The specific activity of the ^{32}P-tagged TSP was 43.6 MBq g^{-1} P at the time of planting the crops in the greenhouse.

One mL of ^{32}P solution with radioactivity of 1,850 MBq was diluted to 5 L in a KH_2PO_4 solution containing 20 mg P L^{-1}. The specific activity of the diluted solution was 0.37 MBq ^{32}P mL^{-1}. Four kg of soil was mixed thoroughly with 80 mL of the diluted ^{32}P solution and 720 mL of water. The soil was then equilibrated for 1 week and mixed with CFPR at 0, 12.5, 25, 50, 100, and 200 mg P kg^{-1}. A second set of 4-kg soil samples was mixed separately with CFPR and ^{32}P-tagged TSP at total P rates of 12.5, 25, 50, 100, 200, and 400 mg P kg^{-1}. The P ratio of CFPR:TSP was fixed at 50:50. A third set of soil samples was mixed with ^{32}P-tagged TSP at P rates of 12.5, 25, 50, 100, and 200 mg P kg^{-1}. Phosphorus added at 400 mg P kg^{-1} contained 200 mg P kg^{-1} as CFPR and 200 mg P kg^{-1} as ^{32}P-tagged TSP. This treatment was used to compare with the application of 200 mg P kg^{-1} as CFPR alone or 200 g P kg^{-1} as ^{32}P-tagged TSP alone.

Additional nutrients were added to each pot at constant rates as follows: 200 mg N kg^{-1} as urea for maize (*Zea mays* L.) and 20 mg N kg^{-1} as urea for cowpea (*Vigna unguiculata* L.), 150 mg K kg^{-1} as K_2SO_4. Other nutrients were added at adequate levels. The pots were placed in a randomized block design with three replicates for each treatment.

TABLE I. SELECTED SOIL PROPERTIES OF THE HARTSELLS AND HIWASSEE SOILS

Soil Properties	Hartsells	Hiwassee
pH (1:1 soil/water)	5.0	5.6
Organic Matter (g kg^{-1})	37	19
Clay content (g kg^{-1})	200	340
Extractable P (mg kg^{-1})		
Bray I	2.0	0.9
Pi-test	3.9	2.9
Effective cation exchange Capacity ($cmol_c$ kg^{-1})	4.7	3.9

Six seeds of maize were planted in each pot, and water was added on a daily basis to bring the soil to approximately 80% of field capacity. After germination, the maize plants were thinned to three plants per pot. Six weeks after planting, the aboveground portions of the maize plants were harvested. For cowpea, three seeds inoculated with a commercial inoculant (Nitragin) were planted in each pot and thinned to one plant after germination. The aboveground portions of the cowpea plants were harvested at the flowering stage (approximately 45 days after planting).

The plant materials were ground using a Wiley mill, and samples were digested with a mixture of HNO_3 and $HClO_4$. Phosphorus concentration in the plant digests was determined using the ammonium molybdate-ascorbic acid method. The activity of ^{32}P in the plant digests was measured by a liquid scintillation counter. Radioactivity counts were corrected for background and for decay to the days of planting when the ^{32}P was applied to the soil.

Based on the isotopic dilution method, the amount of P uptake by the plants from soil, CFPR, and ^{32}P-tagged TSP were calculated as described by Chien et al. [1].

Various response functions were used to describe the relationship between crop yield or P uptake and rate of P applied from three different P sources. Because the experimental data of all three P sources could not be fitted with the same response function containing only a one-term coefficient for the independent variable (i.e., rate), the ratio of the two fitted coefficients could not be used to calculate the relative agronomic effectiveness (RAE) as suggested by Chien et al. [3]. Instead, the method of averaging values across all P rates was used.

The index RAE was defined as:

$$RAE(\%) = (Y_1 - Y_0) / (Y_2 - Y_0) \times 100$$

where
Y_1 = Yield or P uptake obtained with CFPR or (CFPR + TSP),
Y_2 = Yield or P uptake obtained with TSP, and
Y_0 = Yield or P uptake obtained with check (no P added).

To compare treatment effects among various P sources, values of LSD were calculated ($P = 0.05$) and used to detect the significant differences in average values of P uptake across all P rates.

2.3. Results and discussions

The average values of dry-matter yield and P uptake across P rates for maize and cowpea are shown in Tables II and III. For maize, the effectiveness of P sources in terms of increasing dry-matter yield and P uptake followed the order of TSP > (CFPR + TSP) > CFPR. The lower effectiveness of CFPR than that of TSP was due to its lower solubility. Chien and Friesen using the same PR reported a similar result [7]. Mixing CFPR and TSP at a P ratio of 50:50, however, significantly increased dry-matter yield and P uptake. The RAE increased from 31% with CFPR to 83% with (CFPR + TSP) in dry-matter yield and from 37% with CFPR to 86% with (CFPR + TSP) in P uptake. For cowpea, the effectiveness of P sources followed the order of TSP = (CFPR + TSP) > CFPR (Tables II and III). The RAE increased from 55% with CFPR to 98% with (CFPR + TSP) for dry-matter yield and from 50% with CFPR to 92% with (CFPR + TSP) for P uptake.

The calculated values of P uptake by maize or cowpea from CFPR applied alone or as (CFPR + TSP) are shown in Figs 1 and 2.

It can be seen that P uptake from CFPR in the presence of TSP was significantly higher than that from CFPR applied alone. In other words, water-soluble P from the applied TSP enhanced P uptake from CFPR when CFPR was mixed with TSP. For example, at 100 mg P kg^{-1} of CFPR applied, P uptake by maize from CFPR applied alone was 2.30 mg P pot^{-1}, whereas the P uptake from CFPR applied in the presence of TSP was 7.49 mg P pot^{-1} (Fig. 1). The same comparison for P uptake by cowpea was 3.04 mg P pot^{-1} with CFPR alone versus 5.06 mg P pot^{-1} with (CFPR + TSP) (Fig. 2).

TABLE II. DRY-MATTER YIELD AND RELATIVE AGRONOMIC EFFECTIVENESS (RAE) OBTAINED WITH VARIOS P SOURCES FOR MAIZE AND COWPEA

P Source	Maize		Cowpea	
	Dry-Matter Yield[2] g pot^{-1}	RAE %	Dry-Matter Yield[2] g pot^{-1}	RAE %
Check	1.07	0	0.60	0
CFPR[1]	4.10	31	3.85	55
CFPR + TSP	9.13	83	6.45	98
TSP	10.78	100	6.55	100
LSD 0.05	1.32	-	1.22	-

[1] CFPR = Central Florida phosphate rock.

[2] Averaged across P rates.

TABLE III. PHOSPHORUS UPTAKE AND RELATIVE AGRONOMIC EFFECTIVENESS (RAE) OBTAINED WITH VARIOUS P SOURCES FOR MAIZE AND COWPEA

P Source	Maize		Cowpea	
	P Uptake[2] mg P pot^{-1}	RAE %	P Uptake[2] mg P pot^{-1}	RAE %
Check	1.15	0	0.79	0
CFPR[1]	9.12	37	8.72	50
CFPR + TSP	19.93	86	15.38	92
TSP	23.00	100	16.70	100
LSD 0.05	3.97	-	3.65	-

[1] CFPR = Central Florida phosphate rock.

[2] Averaged across P rates.

At a given rate of PR applied, the difference between P uptake from PR applied alone and P uptake from PR applied with TSP represents the quantitative estimation of the enhancement effect of water-soluble P (TSP) on the effectiveness of PR. The average increase in P uptake from CFPR due to TSP influence, across all the PR rates applied, was 3.48 mg P pot^{-1} for maize and 1.38 mg P pot^{-1} for cowpea (Table IV). With respect to CFPR applied alone without TSP, the relative increase in P uptake from CFPR due to TSP influence was 165% for maize and 72% for cowpea (Table IV). The result thus shows a significant beneficial effect of adding water-soluble P to increase the effectiveness of PR utilization by crops.

The CFPR and TSP were applied separately to the soil in the present study, because of their physical separation, the chemical interaction between CFPR and TSP as reported by Mokwunye and Chien [14] was probably negligible. Instead, the enhancement effect was most likely due to an increased early plant-root development, as induced by water-soluble P, which enabled the plant to use PR more effectively than could a plant treated with PR alone [8].

TABLE IV. THE AVERAGE INCREASE IN P UPTAKE BY MAIZE AND COWPEA FROM CFPR AS ENHANCED BY TSP

P Source	P Uptake From CFPR	
	Maize	Cowpea
	mg P pot^{-1}	
CFPR[1] alone (A)	2.11	1.93
CFPR + TSP (B)	5.59	3.31
(B-A)	3.48	1.38
(B-A)/(A), %	165	72

[1] CFPR = Central Florida phosphate rock.

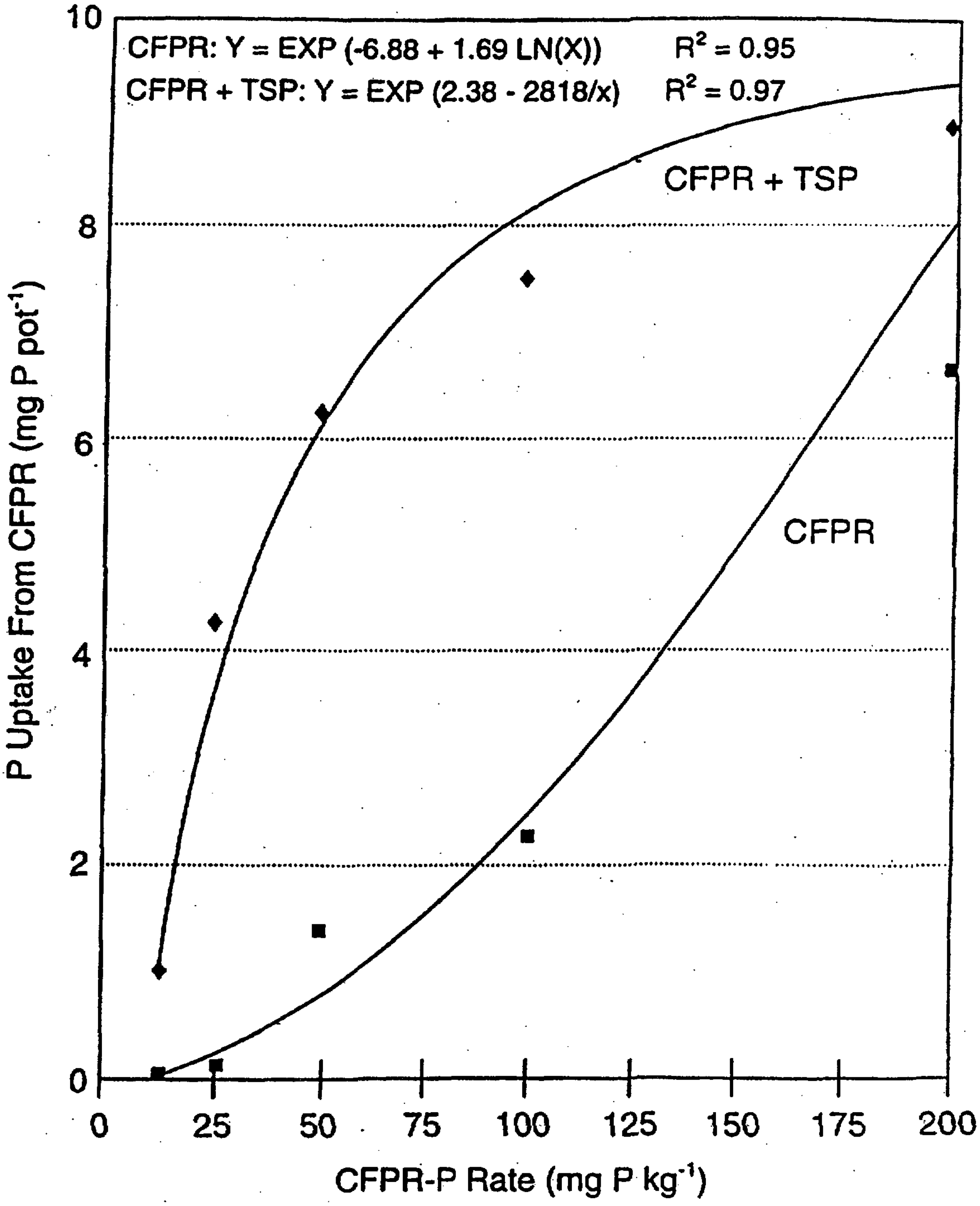

Fig. 1. Phosphorus uptake by maize from Central Florida phosphate rock (CFPR) alone or from CFPR in the mixture of CFPR and TSP (CFPR + TSP).

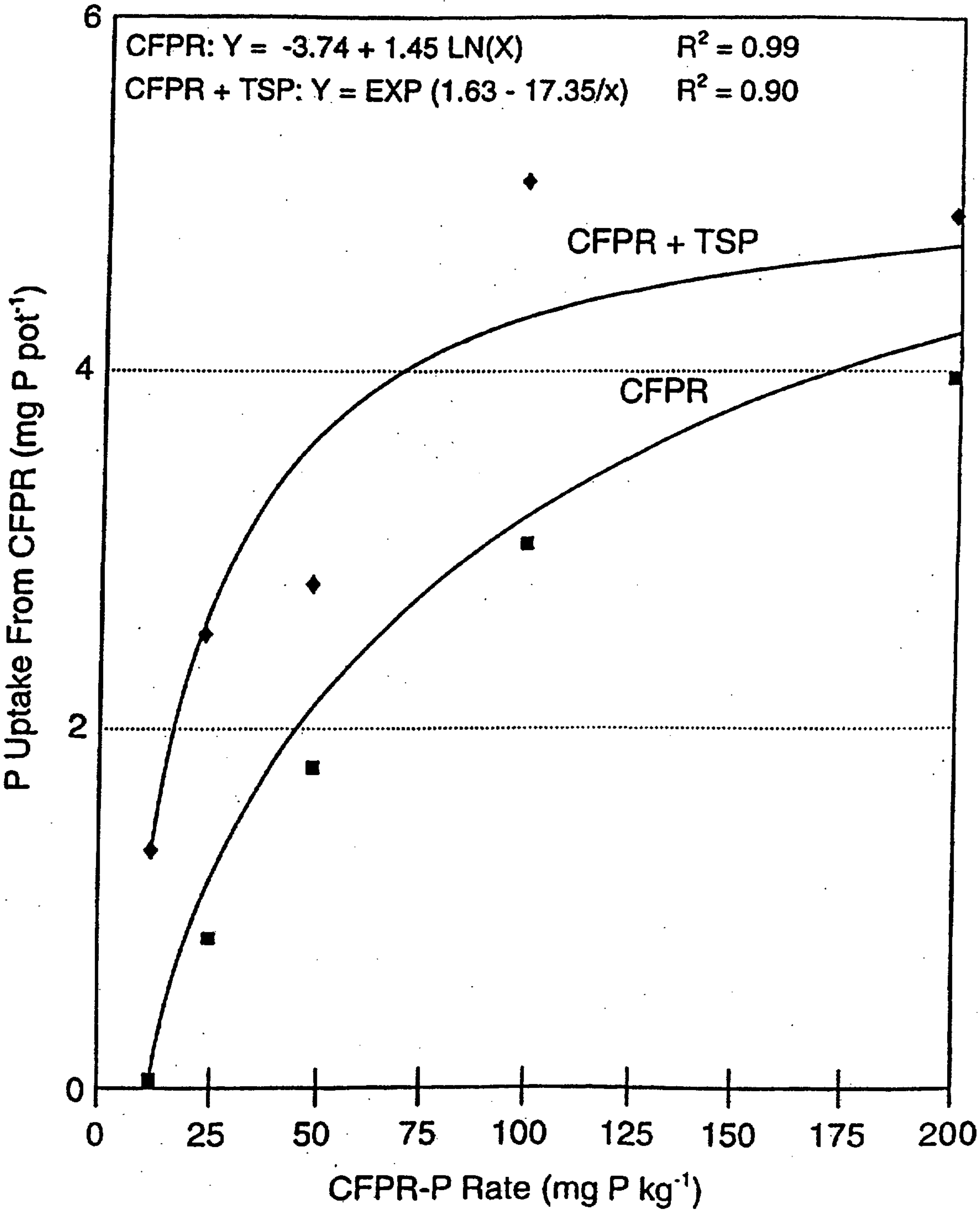

Fig. 2. Phosphorus uptake by cowpea from Central Florida phosphate rock (CFPR) alone or from CFPR in the mixture of CFPR and TSP (CFPR + TSP).

3. EXPERIMENT 2: MODIFIED OXIDE-IMPREGNATED PAPER STRIP TEST FOR SOILS TREATED WITH PHOSPHATE FERTILIZERS

3.1. Literature review and objective

The iron oxide-impregnated paper strip (Pi) test is a relatively new approach to evaluate available phosphorus (P) in soils [15, 16, 17, 18]. The Pi test was first introduced by Menon et al. [19] to measure available P in four soils pre-incubated with phosphate rock (PR) or triple superphosphate (TSP) before cropping with maize. Compared with other conventional soil tests (Bray I, Bray II, Mehlich I, Olsen, and resin), the Pi test had the highest correlation between dry-matter yield or P uptake and soil available P when all the soils P sources, and rates of application were pooled. Thus, the use of the Pi test has been suggested as an alternative to the conventional soil tests to measure available P in soils treated with PR-based fertilizers or TSP [18, 20-22]. In all of the studies, however, the ranges in plant yield or P uptake and Pi-P obtained with TSP were much wider than those obtained with PR. To evaluate critically whether PR and TSP follow the same relationship when crop response is plotted against Pi-P in soil, the ranges in crop response and Pi-P with PR and TSP should be approximately the same.

The objective of this study was to evaluate the use of the Pi test for available P from soils treated with PR and TSP. The emphasis of the study was to investigate whether the same relationship between crop response and Pi-P could apply to both PR and TSP.

3.2. Materials and methods

Two soil samples were collected from the surface (0-20 cm) layer of Hartsells silt loam and Hiwassee clay loam (Table I). Finely ground (-0.15 mm; -100 mesh) North Carolina (NC) PR and a commercial-grade, granular TSP were used. North Carolina PR had 130 g kg^{-1} of total P and 30 g kg^{-1} soluble P in neutral ammonium citrate. The total P of TSP was 201 g kg^{-1} of which 167 g kg^{-1} was water-soluble and 34 g kg^{-1} was citrate soluble.

Amounts of NC-PR and TSP were mixed with 4 kg of soil to give P rates at 0, 25, 50, 75, 100, 125, 150, 200, and 300 mg P kg^{-1}. The soils were then incubated for 2 weeks in the greenhouse with mean temperature approximately at 30°C. Soil moisture was maintained at approximately 80% of field capacity by watering daily.

After incubation, approximately 100 g of soil samples were taken from each pot for P analysis. Urea and KCl were then mixed with the incubated soils at 200 mg N kg^{-1} and 200 mg K kg^{-1}, respectively. Other nutrients were added to all the treatments at adequate levels. The pots were placed in a randomized block design with three replications for each treatment.

Six seeds of maize (variety Funks 4765) were planted per pot, and the plants were thinned to three plants per pot after germination. At 5 weeks after planting, the aboveground parts of the plants were harvested, dried in an oven at 60°C for 10 days, and weighed. The plant materials were ground using a Wiley mill, and the samples were digested with a mixture of H_2SO_4 and H_2O_2.

Phosphorus in the soils was extracted by Bray I and Pi tests. The Pi paper strips were prepared by neutralization of $FeCl_3$ with NH_3 vapor [15]. However, the Pi paper strips were washed with water to remove NH_4Cl before being used, as recommended by Chardon et al. [17]. For the Pi test, a 1.0-g soil sample was shaken with one Pi strip (without using a nylon sheath) in 40 mL of 0.01 M $CaCl_2$ solution for 16 hours. The Pi strip was then taken out and washed free of soil, and the P sorbed by the strip was dissolved in 40 mL of 0.1 M H_2SO_4 [15]. A modified Pi test, in which 0.01 M $CaCl_2$ was placed with 0.02 M KCl was used to study the effect of Ca^{2+} and K^+ ions on PR dissolution during soil extraction. The amounts of P in the plant digest and soil extracts were determined using the ammonium molybdate method with ascorbic acid as the reducing agent.

3.3. Results and discussions

There was no significant difference in dry-matter yield of maize obtained with NC-PR and TSP in Hartsells soil (Fig. 3a). In Hiwassee soil, TSP was more effective than NC-PR in increasing dry-matter yield (Fig. 3b).

There were two distinct lines when P uptake by maize was plotted against Bray I-P extracted from the two soils treated with NC-PR and TSP (Fig. 4). The NC-PR line above the TSP line suggests that the Bray I test underestimates available P from NC-PR with respect to TSP, as first reported by Barnes and Kamprath [23].

Similar to the Bray I test, a plot of P uptake by maize against the Pi test with 0.01 M $CaCl_2$ resulted in two distinct lines for NC-PR and TSP (Fig. 5). The NC-PR line was above the TSP line, suggesting the Pi test with $CaCl_2$ also underestimates available P from NC-PR with respect to TSP to yield the same amount of P uptake. Thus, the conclusion drawn by Menon et al. [19] that the Pi test with $CaCl_2$ measured available P from PR and TSP similarly was incorrect, as evidenced from the present study. The explanation for the underestimation of available P from NC-PR with respect to TSP by the Pi test with $CaCl_2$ is that $CaCl_2$ decreased PR dissolution during the Pi extraction through the Ca common-ion-effect. Since the undissolved PR provided most of the P nutrient to the plant whereas reaction products of TSP in the form of Fe-Al-P provided available P, a decrease in NC-PR dissolution during the Pi extraction with $CaCl_2$ resulted in less available P from NC-PR than that from TSP. During plant growth, however, NC-PR and TSP were equally effective in providing available P to soil solution for plant uptake in Hartsells soil and 91% as effective as TSP in Waverly soil. Therefore, less available P was measured by the Pi test with $CaCl_2$ from NC-PR than from TSP for a given amount of P uptake.

If $CaCl_2$ was responsible for the underestimation of available P from NC-PR with respect to TSP by the Pi test, then the Pi test should be suitable to evaluate available P from NC-PR and TSP if $CaCl_2$ was replaced by KCl, which does not have the common-ion-effect on PR dissolution. This hypothesis was confirmed as a single line was obtained for both NC-PR and TSP when P uptake was plotted against Pi-extractable P with 0.02 M KCl (Fig. 6). Thus, the Pi test with 0.02 M KCl measured the same amount of available P from NC-PR and TSP to yield the same amount of P uptake from NC-PR and TSP.

The above discussions and conclusions on the use of the Pi test were based on P uptake data. Similar patterns were also observed when dry-matter yield data were plotted against available P extracted from NC-PR and TSP by the Pi test with $CaCl_2$ or KCl (data not shown). Therefore, it can be concluded that replacing $CaCl_2$ with KCl in the modified Pi test should be more suitable for evaluating available P from soils treated with PR and TSP. The other effective soil test for PR and TSP is the use of a mixture of cation and anion exchange resin membrane [24]. All other soil tests have been found unsuitable for PR and TSP treated soils [20, 21].

4. EXPERIMENT 3: EFFECT OF ACIDULATION OF HIGH CADMIUM CONTAINING PHOSPHATE ROCKS ON CADMIUM UPTAKE BY UPLAND RICE

4.1. Literature review and objective

Potential cadmium (Cd) uptake by food crops from applied phosphate (P) fertilizers has become an important environmental issue because of the potential health hazards to human life from consuming foods that may contain a significant amount of Cd. Numerous studies have investigated the Cd uptake by crops from P fertilizers [25,26]. In most of the studies, water-soluble P fertilizers such as TSP and DAP were used.

Reactive PR has been shown to be suitable for direct application to acid soils [4, 5, 27]. For those PRs that are not suitable for direct application because of their low reactivity, partial acidulation of PR is a technology that can produce agronomically effective P fertilizers [5, 28, 29]. Little information is available in the literature on Cd uptake by crops from either PR or partially acidulated PR (PAPR).

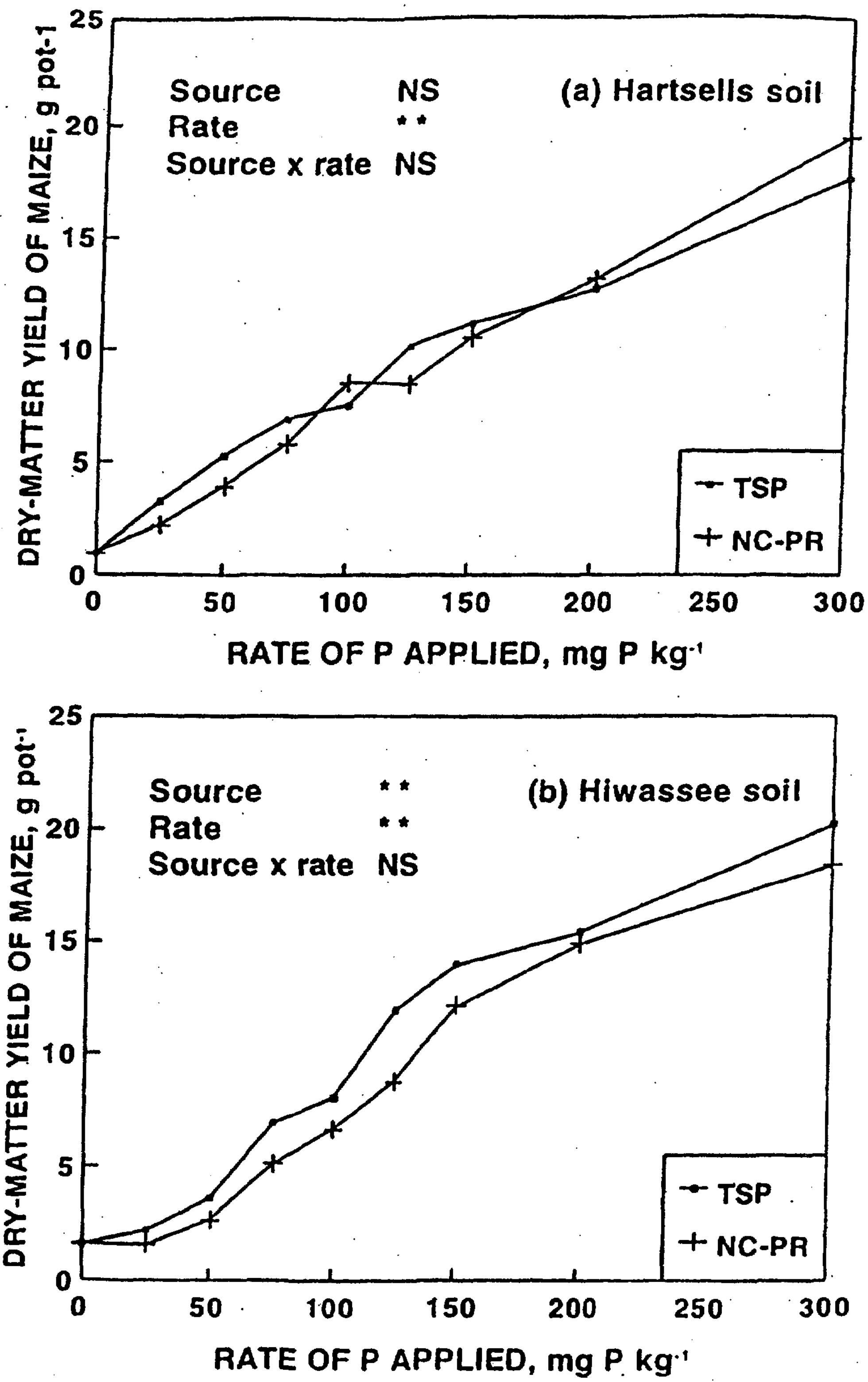

Fig. 3. Dry-matter yield of maize obtained with TSP and NC-PR in Hartsells and Hiwassee soils.

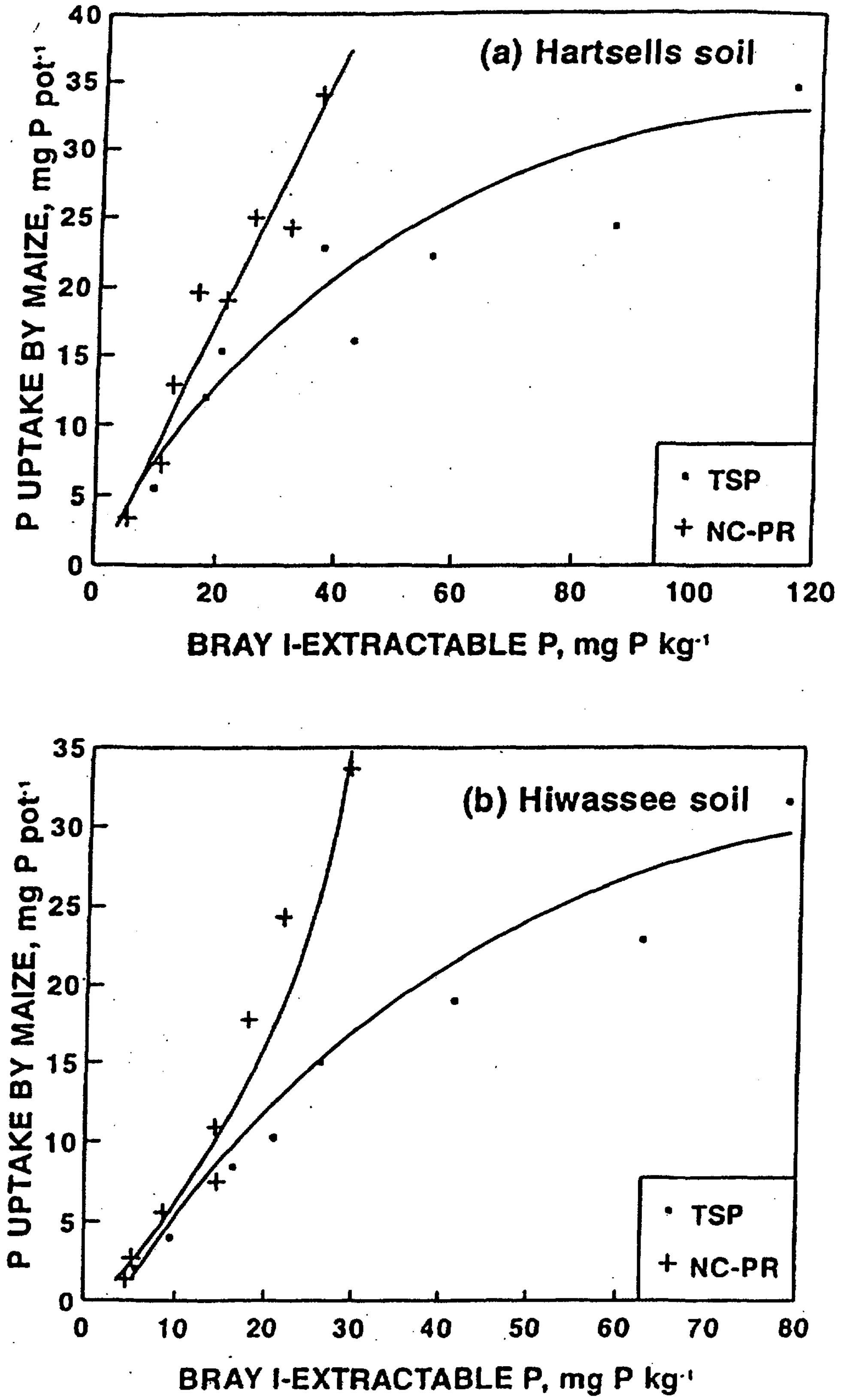

Fig. 4. Relationship between P uptake by maize and Bray I-extractable P in two soils treated with TSP and NC-PR.

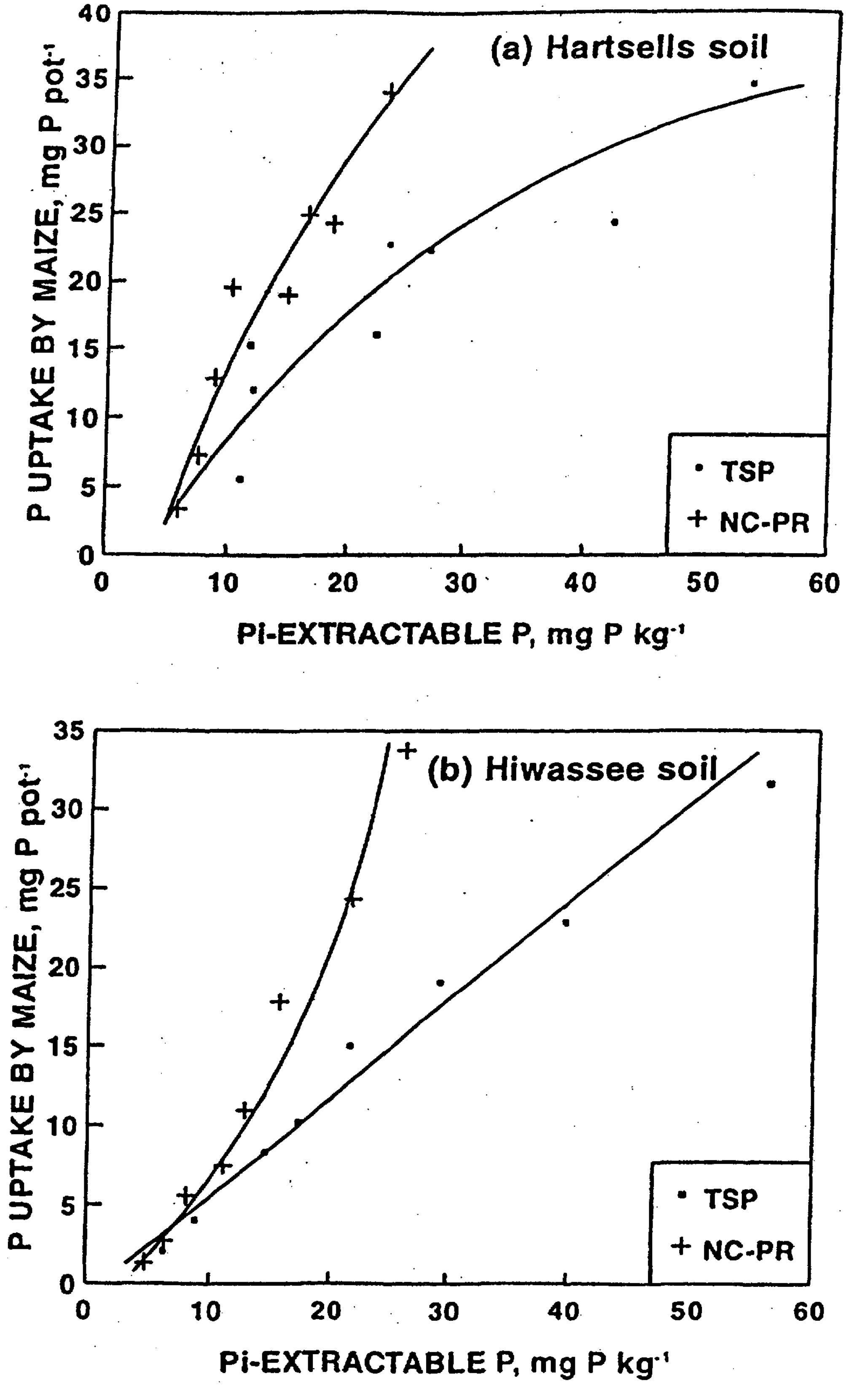

Fig. 5. Relationship between P uptake by maize and Pi-P (0.01 M $CaCl_2$) in two soils treated with TSP and NC-PR.

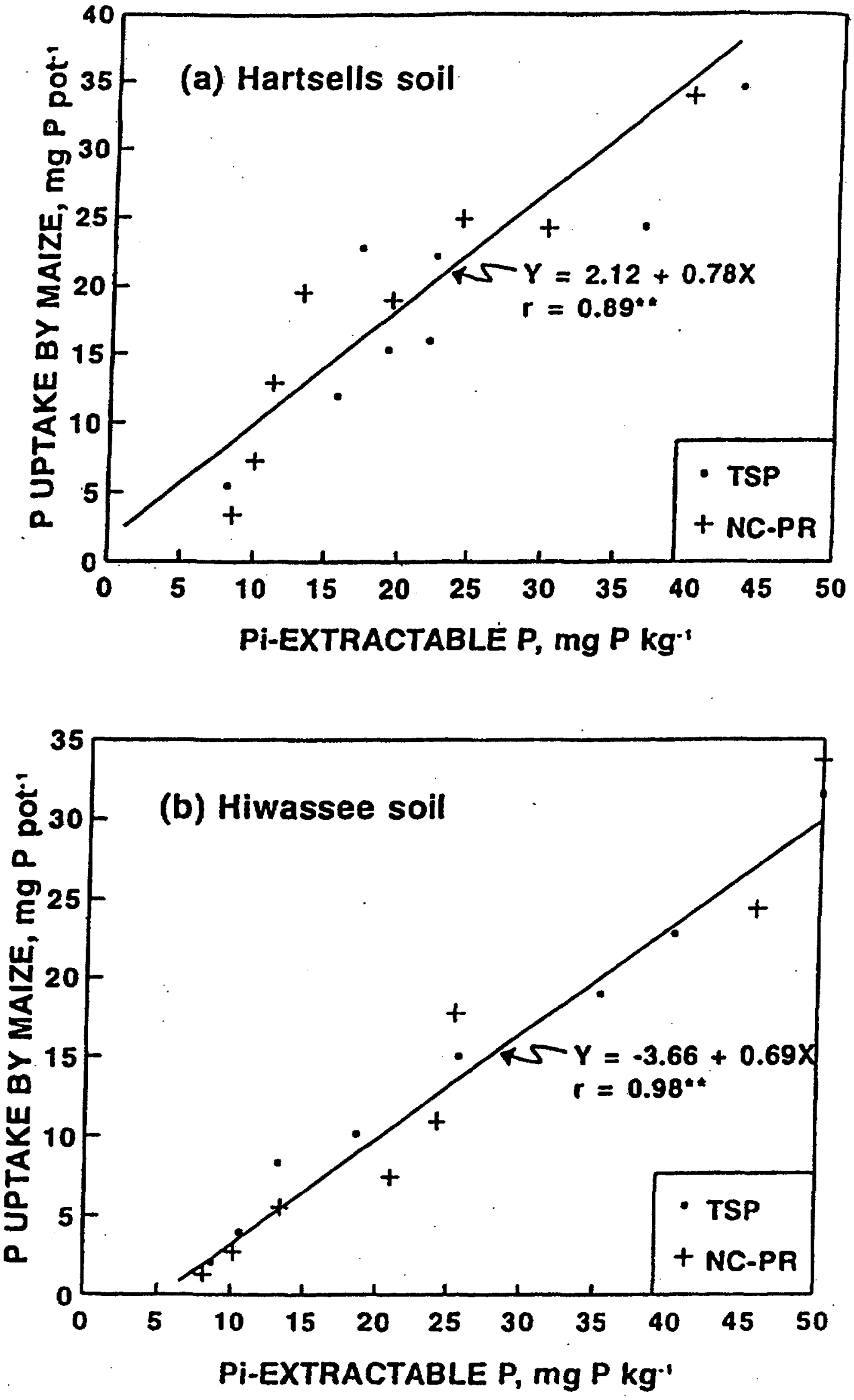

Fig. 6. Relationship between P uptake by maize and Pi-P (0.02 M KCl) in two soils treated with TSP and NC-PR.

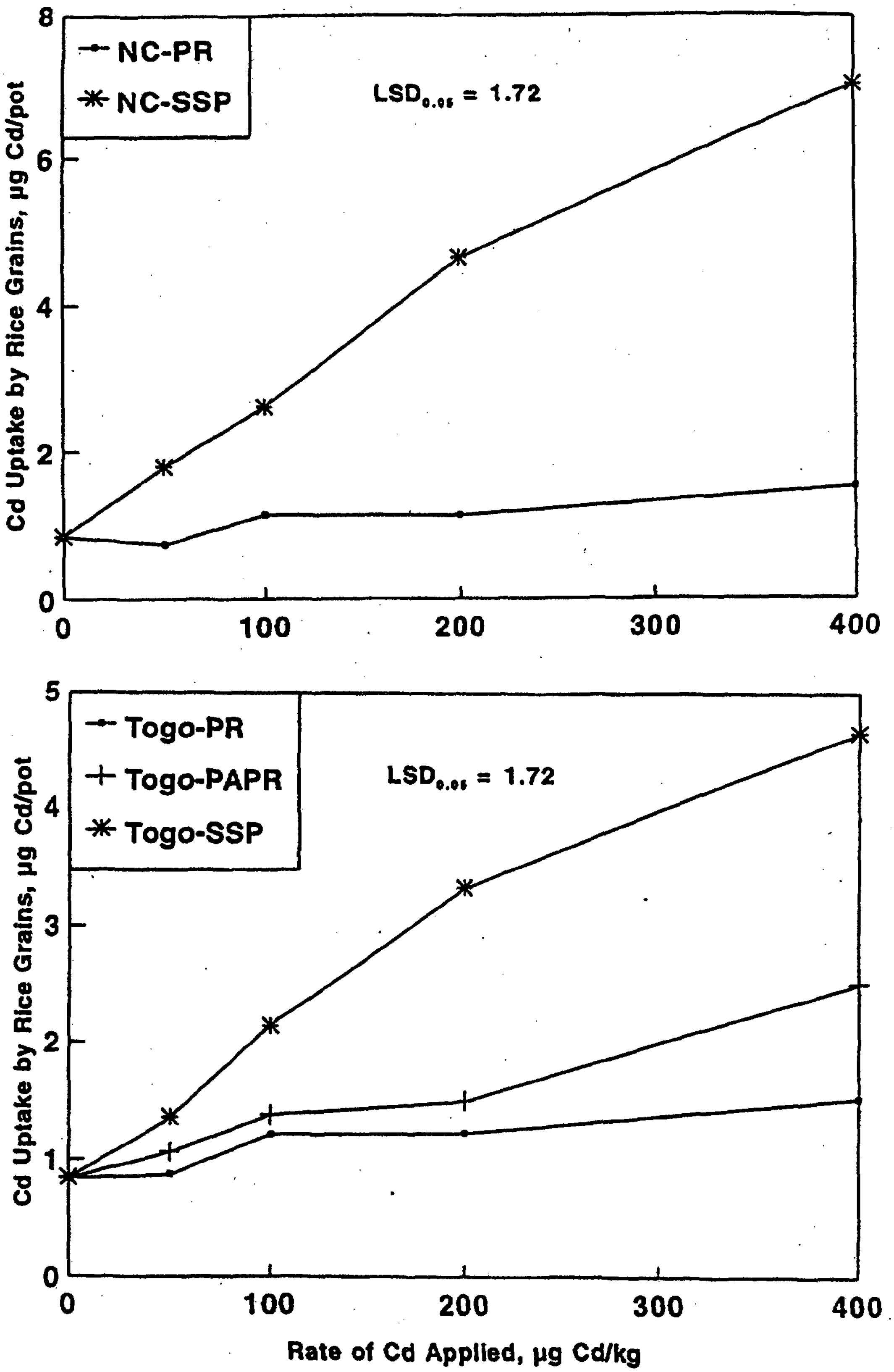

Fig. 7. Cd uptake by rice grains from (a) NC-PR and NC-SSP and (b) Togo-PR, Togo-PAPR, and Togo-SSP in Hartsells soil.

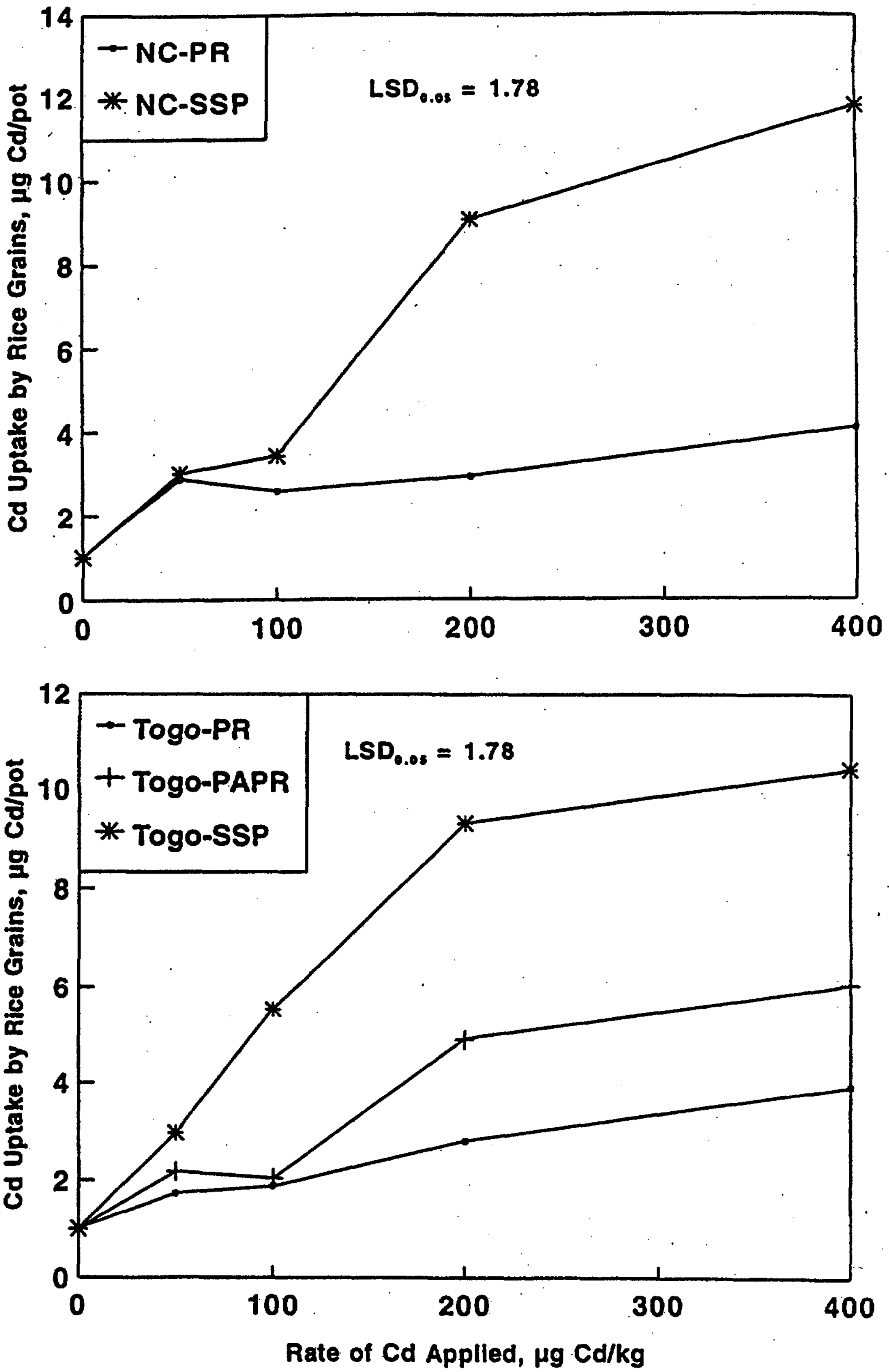

Fig. 8. Cd uptake by rice grains from (a) NC-PR and NC-SSP and (b) Togo-PR, Togo-PAPR, and Togo-SSP in Hiwassee soil.

The objective of this study was to investigate the effect of acidulation of PR on Cd uptake by an upland rice crop. Two PRs having high Cd content were used in this study. In this study, the application of a large amount of water-soluble P as reagent-grade of KH_2PO_4, which does not contain Ca and Cd, and using the P fertilizers containing Cd as sources of Cd under the conditions where P was not a limiting factor on the plant growth, eliminated the confounding effect of P and Cd uptake [30].

4.2. Materials and methods

The NC-PR that was used was unground with a particle size distribution of 85% in the range between 1.18 mm and 150 mm and 15% smaller than 1.18 mm. Togo-PR was finely ground through 1.18 mm. PAPR and SSP were produced by acidulating ground (smaller than 1.18 mm) Togo and NC PRs with H_2SO_4 at 50% (only Togo-PR) and 100% levels in a nongranular run form. The P and Cd contents of P fertilizers are shown in Table V. Two acid soils, Hartsells and Hiwassee (Table I), were used in the greenhouse experiment.

TABLE V. PROPERTIES OF P AND Cd CONTENTS OF P FERTILIZERS USED

P Source	Total P	H_2O-P	Citrate-P	Total Cd	DTPA-Cd
	------------ (%) ------------			------ (mg Cd/kg) ------	
NC-PR	13.3	0.0	2.8	47.0	0.2
NC-SSP	6.3	5.8	0.5	24.7	18.7
Togo-PR	16.0	0.0	2.0	54.0	1.7
Togo-PAPR	12.3	4.8	1.8	35.7	6.8
Togo-SSP	9.2	8.7	0.5	31.5	19.7

Phosphate fertilizers in amounts required to give total Cd rates of 0, 50, 100, 200, and 400 □g Cd/kg were mixed with 4 kg of soil. All of the treatments also received 200 mg P/kg as KH_2PO_4. Constant rates of other nutrients were added at adequate levels to each pot. The pots were placed in a randomized block with three replications for each treatment. Ten rice seeds were planted and thinned to one seedling per pot. Soil moisture was maintained at 80% of field capacity by watering daily. The rice crop was grown to maturity and harvested.

Rice grain samples were taken from all the treatments whereas rice straw and root and soil samples were taken only from the check (no Cd added) and 400 □g Cd/kg treatments. After harvesting the aboveground plant parts, soil in the pots was carefully washed with water on a screen to obtain soil-free root samples. The plant samples (grain, straw, and root) were dried in a forced-air cabinet at 65°C for 10 days followed by grinding. To determine Cd, Ca, and P uptake by plant, the ground plant samples were ashed in the furnace at 400°C. The ash was then dissolved with 5 N HNO_3 at 50°-60°C. Cadmium in the soil samples was extracted with a DTPA solution, as described by Baker and Amacher [31]. Cadmium and Ca in the ashed plant samples and soil DTPA extracts were determined by using an inductively coupled plasma (ICP) spectrometer. Phosphorus concentration in the ashed plant samples was determined by using the ammonium molydate-ascorbic acid method.

4.3. Results and discussions

Analysis of variance (ANOVA) of rice yield data showed that source and rate of P were statistically nonsignificant (data not shown). Thus, there was no P response as expected since all the treatments including the check received a very high rate of P (200 mg P/kg) as KH_2PO_4. Therefore, it would be expected that there should be no confounding effect of P and Cd uptake by upland rice.

Uptake of Cd by rice grains on Hartsells and Hiwassee soils increased with the rate of Cd applied to the soils. The increase of Cd uptake was most pronounced with NC-SSP and Togo-SSP followed by Togo-PAPR. NC-PR and Togo-PR resulted in the lowest Cd uptake (Figs. 7 and 8). This corresponds with the findings that DTPA-Cd levels in NC-SSP and Togo-SSP were higher than those in NC-PR and Togo-PR (Table V).

Table VI shows Cd uptake by rice roots, straw, and grains from various Cd sources at the 400 μg Cd/kg rate. It can be seen that most of the Cd take-up was retained in rice roots and straw. In Hartsells soil, Cd uptake by rice grains was less than 3% of total Cd uptake by rice. In Hiwassee soil, the value was less than 10%. Data in Table VI indicate that Cd uptake by rice increased as the degree of PR acidulation increased. Acidulation of PR also increased DTPA-extractable Cd in soils, and there was a significant relationship between Cd uptake by rice and soil DTPA-Cd (data not shown).

The results of Cd uptake suggest that if unacidulated PRs (e.g., NC-PR) and partially acidulated PRs (e.g., Togo-PAPR) are as effective as fully acidulated P sources (e.g., SSP) under certain soil and crop conditions [5, 29], these water-insoluble and partially water-insoluble P sources are not only more cost effective, but also they may contribute less Cd uptake by crops than the use of water-soluble P sources. In a previous study, it was observed that rice grain yields obtained with NC-PR, NC-SSP, Togo-PAPR, and Togo-SSP were about the same at a rate of 200 mg P/kg applied to Hiwassee soil (Table VII). Both Cd uptake by rice grains and Cd concentration in grains followed the order of NC-SSP > NC-PR and Togo-SSP > Togo-PAPR (Table VII). The Cd concentration in grains obtained with NC-SSP was approximately twice more than that obtained with NC-PR. Similar results were observed with Togo-SSP and Togo-PAPR.

Table VIII shows total uptake of Cd, Ca, and P by rice plant (root, straw, and grain) from NC-PR and Togo-PR. Similar to Cd uptake, uptake of Ca and P was higher from NC-PR than that from Togo-PR. Because the reactivity of NC-PR is higher than that of Togo-PR (Table V), it suggests that Cd is associated with Ca and P in the same apatite structure, rather than as a discrete Cd mineral (e.g., $CdCO_3$). The presence of Cd in apatite structure is most likely through the isomorphic substitution of Cd^{2+} for Ca^{2+} [32]. Data in Table VIII points out that highly reactive PR (e.g., NC-PR) provides not only more available P but also more available Cd as compared with the low-reactive PR (e.g., Togo-PR). However, there was no significant difference in Cd concentration in grains of upland rice using NC-PR and Togo-PR on both soils, whereas Cd concentrations in roots were higher with NC-PR than those with Togo-PR in both soils (Table IX). Concentration of Cd in rice straw was higher with NC-PR than that with Togo-PR in Hiwassee soil. It should be pointed out that potential Cd toxicity to human health from Cd-contaminated food crops is based on Cd concentration in edible parts of crops rather than on total Cd uptake by crops. Table IX shows that both highly reactive NC-PR and low-reactive Togo-PR resulted in the same quality of rice grains in terms of Cd contamination with respect to human health.

TABLE VI. CADMIUM UPTAKE BY RICE, ROOT, STRAW,
AND GRAIN AND DTPA-EXTRACTABLE Cd IN SOILS AT 400 □g Cd/kg RATE

		Cd Uptake				
Soil	Cd Source	Root	Straw	Grain	Total	Soil DTPA-Cd
		------------ (□g Cd/pot) ------------				(□g Cd/g)
Hartsells	Check	21.4	12.0	0.84	34.2	0.023
	NC-PR	51.1	17.6	1.5	70.2	0.055
	NC-SSP	204	195	7.0	406	0.123
	Togo-PR	37.9	16.3	1.5	55.7	0.027
	Togo-PAPR	98.3	54.2	2.5	155	0.088
	Togo-SSP	194	133	4.6	331	0.166
	($LSD_{0.05}$)	(26.9)	(21.1)	(2.2)	(31.0)	(0.010)
Hiwassee	Check	1.2	9.4	1.0	11.6	0.011
	NC-PR	52.5	57.4	4.1	114	0.094
	NC-SSP	12.	181	11.8	313	0.106
	Togo-PR	23.2	31.8	3.9	58.9	0.025
	Togo-PAPR	54.7	95.7	6.0	156	0.067
	Togo-SSP	137	189	9.6	336	0.136
	($LSD_{0.05}$)	(14.9)	(23.9)	(5.6)	(22.5)	(0.015)

TABLE VII. RICE GRAIN YIELD AND Cd UPTAKE FROM VARIOUS P SOURCES ON HIWASEE SOIL

P Source	P Rate (mg P/kg)	Cd Rate (□g Cd/kg)	Grain Yield[1] (g/pot)	Cd Uptake by Grain[1] (□g Cd/pot)	Cd Concentration in Grain[1] (□g Cd/g)
NC-PR	200	70.5	25.3 A	1.68 B	0.066 B
NC-SSP	200	79.0	24.5 A	3.25 A	0.135 A
Togo-PAPR	200	57.8	27.6 A	1.44 B	0.051 B
Togo-SSP	200	69.3	25.6 A	2.88 A	0.114 A

[1] Values followed by same letter in each column are not significantly different ($P = 0.05$).

TABLE VIII. TOTAL Cd, Ca AND P UPTAKE BY RICE PLANT (ROOT, STRAW, AND GRAIN) FROM TWO PRs AT 400 □g Cd/kg RATE

	Cd Uptake[1]		Ca Uptake[1]		P Uptake[1]	
PR Source	Hartsells	Hiwassee	Hartsells	Hiwassee	Hartsells	Hiwassee
NC-PR	70.2 A	114 A	339 A	276 A	166 A	236 A
Togo-PR	55.7 B	58.9 B	265 B	207 B	125 B	170 B

[1] Values followed by same letter in each column are not significantly different ($P = 0.05$).

TABLE IX. CADMIUM CONCENTRATION IN ROOT, STRAW, AND GRAIN OF RICE PLANT OBTAINED FROM TWO PRs AT 400 □g Cd/kg RATE

		Cd Concentration[1]		
Soil	Cd Source	Root	Straw	Grain
		(mg Cd/kg)		
Hartsells	NC-PR	1.568 A	0.304 A	0.056 A
	Togo-PR	1.055 B	0.273 A	0.054 A
Hiwassee	NC-PR	2.021 A	0.995 A	0.216 A
	Togo-PR	0.624 B	0.518 B	0.159 A

[1] Values followed by same letter in each column are not significantly different ($P = 0.05$).

5. CONCLUSIONS

Use of the ^{32}P isotope dilution technique is a powerful tool to study the agronomic efficiency of PR as enhanced by water-soluble P. The modified iron oxide-impregnated paper strip (Pi test) by replacing 0.01 M $CaCl_2$ with 0.02 M KCl is an effective soil P test for both PR and water-soluble P. Acidulation of Cd-containing PR clearly increases Cd uptake by crops. If unacidulated PR or partially acidulated PR are agronomically as effective as fully acidulated PR, these water-insoluble or partially water-soluble P sources may also contribute less to Cd uptake by crops than the use of water-soluble P sources.

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