

Effects of Calcium and Magnesium on Phosphorus Availability in Ferralsols and Rice Production in Forest Zones of Côte d'Ivoire

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Abstract

Phosphorus bioavailability has long been a recurring problem in tropical acid soils. A pot experiment was carried out during three (3) successive rice production cycles at Adiopodoumé to evaluate the response of the NERICA 5 rice accession to various doses of calcium, magnesium and phosphorous. The experiment was conducted using a randomized split-plot design. The interactive effects of calcium carbonate (0, 25, 50 and 75 kg-Ca-ha⁻¹) and magnesium sulfate (0, 25, 50 and 75 kg-Mg-ha⁻¹) and Togo natural phosphate (0, 25, 50 and 75 kg-P-ha⁻¹) were determined at each production cycle. The results showed that single-dose natural phosphate supplementation for three cropping cycles resulted in an average enrichment of around 2 mg-P-kg⁻¹ after each trial following its continuous dissolution, with an increase in DSP (33.31% to 70.52%). The study revealed one strategy for managing and enhancing native P with cations and another for exogenous P: there would be a synergy of Ca/Mg on native P, whereas an antagonism would characterize the two parameters in phosphate fertilization.

Keywords

Soil Acidity, Native and Exogenous Phosphorus, Free Iron, Ca/Mg Balances, Rice Growing, Côte d'Ivoire

1. Introduction

Rice constitutes the basis of the diet in Ivory Coast. Its production was estimated at 1,713,589 tonnes of paddy in 2022 [1]. Almost all of this production is mainly ensured by rainfed rice cultivation, practiced almost 70% on plateau and on acidic soils [1]. Tropical acid soils are subject to phosphorus (P) deficiency and depletion of exchangeable soil cations (Ca²⁺, Mg²⁺ and K⁺) [1]. However, they are rich in aluminum (Al), iron (Fe) and manganese (Mn). The presence of the latter in tropical acid soils complex nutrients in the soil solution, often affecting agricultural resilience in these agro-ecosystems [2]. Among the basic cations, calcium (Ca) and magnesium (Mg) are probably the most important in managing soil acidity: the application of lime (Ca and Mg) [3] and the maintenance of optimum Ca/Mg ratios in acid soils are recommended, with justifications observed by [4] in rainfed rice.

Furthermore, recent studies in the rainforest zone of West Africa, notably in Côte d'Ivoire, have revealed no need for calcium applications in rainfed rice production, while yield reductions have been recorded for phosphate applications with magnesium (Mg) exclusion [5], as well as with the effect of increasing doses of Ca [6]. Consequently, phosphorus (P), calcium (Ca) and magnesium (Mg) are among the essential nutrients for rice production in acid soils under West African rainforests. In fact, phosphate ions (P_2O_4) have a synergistic effect on the accumulation of calcium (Ca) and magnesium (Mg) in plants, and reciprocally. This effect is associated with the ionic balance linked to the uptake of cations and anions in plants, as well as with the increased root growth sometimes observed with increased phosphorus (P) uptake.

Therefore, the determination of phosphorus (P), calcium (Ca) and magnesium (Mg) ratios (P/Ca/Mg) is important for rice nutrition in order to increase its yield in acid soil forest ecosystems, but there are limitations relative to basic theories for the development of such a strategy.

In fact, phosphorus (P) deficiency can be so limiting for plants in certain soils that cultivation is impossible, as in tropical regions [7]. Even when this element is relatively abundant in absolute terms, if it is total concentration is measured using powerful chemical extraction methods; it is strongly retained in insoluble form by various mineral and organic soil constituents [7]. The result for plants is the same as if it were rare, since they can only absorb the soluble orthophosphate form. This retention capacity by the solid matrix of the soil applies not only to native phosphorus naturally present in the bedrock, but also to exogenous soluble phosphorus supplied by chemical fertilizers in the form of orthophosphate [7]. As a result, it is possible to deepen knowledge in a controlled environment experiment, as was done by [8] in a pot experiment to improve nitrogen management.

Thus, the aim of this study conducted in pot is to 1) evaluate the effects of increasing doses of phosphorus (P), calcium (Ca) and magnesium (Mg) on rice production on a highly desaturated ferrallitic soil and 2) propose a better management strategy for phosphate fertilization practices in order to increase rice production in the rainforest zone of Côte d'Ivoire.

2. Materials and Methods

2.1. Experimentation Site

This study was conducted in pots under semi-controlled conditions at the experimental station of the Biotechnologies Central Laboratory (LCB) of the National Center for Agronomic Research (CNRA) in Adiopodoumé, Côte d'Ivoire (43 m altitude) (Figure 1).

It is a tropical rainforest zone, with a single-mode rainfall regime and an average annual cumulative rainfall of around 1531 mm [9].

The soil used for the experiment is a highly desaturated ferralitic type (Dystric Ferralsol). It was taken from fallow land over 10 years old at a depth of 20 cm.

2.2. Vegetable Material

The interspecific upland rice variety NERICA 5 was used for this study. This rice variety has a cycle that varies from 95 to 100 days after germination (JAG). Its average height can reach 120 cm, with tillering between 21 and 45 JAG. NERICA rice has a yield potential of 5 t \cdot ha⁻¹ [10].



Figure 1. Location map of Adiopodoumé (Experimentation site).

2.3. Experimental Setup and Treatments

The experiment was conducted using a randomized split-plot design with five (5) replicates (blocks). Three (3) sources of fertilizer were studied. Togo natural phosphate (35.4% P₂O₅ and 36.4% CaO), calcium carbonate-CaCO₃ and magnesium sulfate-Mg₂SO₄ (28% Mg) constituted the P, Ca and Mg sources respectively. Each fertilizer source was applied at four (4) different rates (0; 25; 50 and 75 kg P ha⁻¹). The blocks were subdivided into four (4) bands of 16 treatments corresponding to phosphorus (P). Each band is divided into four (4) sub-bands randomly receiving the different doses of calcium (Ca). Finally, the sub-bands received, in a random fashion, the different doses of magnesium (Mg). In total, each block consisted of 64 treatments, corresponding to 320 pots for each growing cycle.

2.4. Implementation of the Experiment

The experiment was conducted on three (3) different dates. It was conducted from March to June 2012 (trial 1), from March to June 2013 (trial 2) and from September to December 2013 (trial 3). In each trial, urea (30 kg·N·ha⁻¹) and potassium chloride (50 kg·K·ha⁻¹) were used as background fertilizer, then urea (35 kg·N·ha⁻¹) was also applied at tillering and heading of rice. Rock phosphate was only applied in the first trial. However, calcium carbonate and magnesium sulfate were applied to each trial.

Six (6) grains of rice were sown per pot at a rate of two (2) grains per planting. Ten (10) days after germination (JAG), the seedlings were pruned to reduce the number of plants to three (3) per pot. These plants were watered every two (2) days with a quantity of 20 mm of water in the absence of rain.

2.5. Soil Analysis

Before the trials were set up, a fraction of the soil was analyzed. Parameters assessed included particle size, pH, soil organic carbon, total nitrogen, assimilable phosphorus, total phosphorus, exchangeable aluminum and free iron, exchangeable bases and cation exchange capacity (CEC). After harvesting, soil samples were taken from each plot in each test cycle to assess the effect of treatments on soil physicochemical characteristics. Analyses were carried out for phosphorus saturation rate (PSR) and the parameters listed above, with the exception of granulometry, CEC and exchangeable bases.

Granulometry was carried out using the densimetric method with a Robinson pipette [11]. This method consists in separating soil particles according to their size. It provides a weighted breakdown of mineral particles less than 2 mm in diameter into different size classes.

Soil pH water and pH KCl were measured directly with a pH meter at a soil/ distilled water or soil/KCl (1 M) ratio of 1:2.5 (m/v) after stirring the suspension at 175 rpm for 30 minutes [12]. pH provides information on soil microbial activity and the degree to which plants assimilate chemical elements. From an agronomic point of view, it is therefore an indicator of soil fertility [13].

Organic carbon was determined after calcination of soil samples in a muffle furnace using the method in [14], then converted to organic matter (OM) using the factor 1.724 (OM = $C \times 1.724$).

Nitrogen determination was carried out using the Kjeldahl method [15]. This method consists of transforming organic nitrogen into ammonium sulfate in a sulfuric acid-concentrated medium (mineralization), then into ammonium hydroxide in the presence of excess sodium hydroxide (distillation) and into ammonium by titration with a sulfuric acid solution.

Assimilable phosphorus content was determined using the Dabin modified Olsen method [16]. This involved extraction of P by agitation and filtration, followed by spectrometric determination.

Exchangeable bases (Ca, Mg, K) were extracted with 1 M ammonium acetate buffered at pH = 7. Calcium and magnesium were quantified by atomic absorption. Potassium was measured by flame spectrophotometry [12] [17] [18].

The free iron content of the soil was assessed after extraction in a DTPA extraction solution according to the method of [19].

Exchangeable aluminum content was determined titrimetrically after extraction with potassium chloride [20].

Phosphorus saturation ratio (PSR) was determined by calculating the ratio of soil phosphorus content to soil aluminum content [21] [22].

2.6. Evaluation of Treatment Effects on Rice Grain Yields

At maturity, the rice was harvested and weighed at 14% moisture on a unit plot in order to determine the grain yield (RDG) for treatment. This yield was calculated according to the following relationship:

$$RDG = \frac{Grain_weight \times (100 - HUM)}{(Harvest_area \times 1000 \times 86)} \times 10000$$
(1)

*With: RDG: grain yield in t \cdot ha⁻¹; grain dry weight in g; humidity (HUM) in % and harvest area in m².

2.7. Statistical Analysis

The data collected were subjected to statistical analysis using SAS (Statistical Analysis System) software version 9.1. Mean values were classified using the least significant difference (LSD) method. Probabilities were evaluated at the threshold of $\alpha = 0.05$. Optimal doses of phosphorus (P), calcium (Ca) and magnesium (Mg) were determined by response surface curve analysis. Using linear mixed modulus analysis, the effects of phosphate and magnesium doses and their interaction were evaluated on grain yields (RDG).

3. Results

3.1. Soil Physicochemical Characteristics before Experimentation

Table 1 shows the results of physiochemical analyses of the soil taken from the 0

Soil characteristics	Value
Clay (g·kg ⁻¹)	210
Silt (g·kg ⁻¹)	310
Sand (g·kg ⁻¹)	480
Da (g cm ⁻³)	1.42
pH_{H2O}	4.6
pH KCl	4.1
$\Delta \mathrm{Ph}$	0.5
Organic carbon-C (g·kg ^{-1})	3.6
Total nitrogen-N (g⋅kg ⁻¹)	0.2
C/N	18
CEC (cmol·kg ⁻¹)	4.68
Pa (mg·kg ⁻¹)	3
Ca (cmol·kg ⁻¹)	5.5
Mg (cmol·kg ⁻¹)	3.9
K (cmol·kg ⁻¹)	0.2
Ca/Mg	1.41
Mg/K	19.5
K/CEC	0.043
Free Fe (cmol·kg ⁻¹)	25.5
Al exchangeable (cmol·kg ⁻¹)	3.58
DSP (%)	33.31

Table 1. Soil physicochemical characteristics at 0 - 20 cm depth before experimentation.

Da: Bulk density; CEC: Cation exchange capacity; DSP: Degree of phosphorus saturation.

- 20 cm layer and used for the experiment. It shows that the soil is sandy-loamyclayey (sand 48%; silt 31% and clay 21%). Apparent density (Da) was low (1.42 < 1.5 g/cm³), indicating good aeration and porosity of the soil, and therefore subject to good water storage capacity. Organic carbon (C) content is low (3.6 g·kg⁻¹ < 40 g·kg⁻¹), while total nitrogen (N) content is also low (<1 g·kg⁻¹) at 0.2 g·kg⁻¹, coupled with a high (18/1) C/N ratio (>10/1). Exchangeable cation contents for Ca, Mg and K were 5.5 cmol·kg⁻¹ (>2 cmol·kg⁻¹), 3.9 cmol·kg⁻¹ (>0.20 cmol·kg⁻¹) and 0.2 cmol·kg⁻¹ (>0.10 cmol·kg⁻¹) respectively, with a very low CEC (4.68 cmol·kg⁻¹) below the critical threshold (<20 cmol·kg⁻¹). Ca/Mg (1.41 < 10) and K/CEC (0.043 < 0.05) ratios are low. However, the Mg/K ratio of 19.5 is high (>2).

The highly acidic pH_{H20} (4.6) is coupled with an insufficient assimilable phosphorus content (Pa-modified Olsen method) of 3 mg·kg⁻¹ well below the threshold of 10 mg·kg⁻¹). The soil is rich in free iron-Fe (25.5 cmol·kg⁻¹) and exchangeable aluminum-Al (3.58 cmol·kg⁻¹) characteristic of acid Ferralsol, while the degree of phosphorus saturation (DSP) of 33.31%, is above 20% (critical value).

3.2. Evolution of Soil Phosphorus (P), Calcium (Ca) and Magnesium (Mg) Contents

Figure 2 shows the evolution of average soil phosphorus, calcium and magnesium levels after each trial. With initial values of 3 mg/kg, 5.5 cmol·kg⁻¹ and 3.9 cmol·kg⁻¹, the average post-trial values respectively show an overall enrichment of the soil in phosphorus (P = 7.22; 8.13 and 10.02 mg·kg⁻¹) and magnesium (Mg = 4.12; 4.4 and 4.68 cmol·kg⁻¹) after each trial, while enrichment in calcium (Ca) (6.3 cmol·kg⁻¹) is observed only after the third trial.

This result is broken down by crop cycle and according to the doses of fertilizer applied, as shown in **Tables 2-4**.

For crop cycle 1 (**Table 2**), average phosphorus (P) values varied from 3.10 $\text{mg}\cdot\text{kg}^{-1}$ (0P-0Ca-0Mg) to 10.20 $\text{mg}\cdot\text{kg}^{-1}$ (50P-50Ca-25Mg). The same applies to magnesium (Mg), with average values ranging from 3.93 cmol·kg⁻¹ (0P-0Ca-0Mg) to 4.34 cmol·kg⁻¹ (50P-50Ca-25Mg). Calcium levels, meanwhile, were only high (5.52 cmol·kg⁻¹) for (0P-0Ca-0Mg) and relatively constant (5.5 cmol·kg⁻¹ before experimentation) for all the other treatments.

Table 2. Average soil	phosphorus,	calcium and	l magnesium l	levels after the	e first crop	cycle, c	lepending o	on the amount	of fertilizer
applied.									

			Soil P. Ca and Mg content										
Doses of	Doses	0	kg/Mg/ł	1a	25	kg/Mg/	ha	50	kg/Mg/	ha	75	kg/Mg/	ha
P (kg/ha)	of Ca (kg/ha)	P (mg/kg)	Ça (cmol/ kg)	Mg (cmol/ kg)	P (mg/kg)	Ça (cmol/ kg)	Mg (cmol/k g)	P (mg/kg)	Ça (cmol/ kg)	Mg (cmol/ kg)	P (mg/kg)	Ça (cmol/ kg)	Mg (cmol/ kg)
	0	3.10	5.52	3.93	3.10	5.51	3.93	3.20	5.51	3.94	3.30	5.50	3.93
0	25	3.90	5.49	3.94	3.40	5.48	3.94	3.40	5.48	3.94	3.40	5.47	3.94
0	50	3.40	5.48	3.94	3.60	5.46	3.94	3.60	5.46	3.94	3.50	5.50	3.96
	75	3.40	5.48	3.93	3.50	5.47	3.95	3.30	5.51	3.98	3.40	5.49	3.94
	0	7.90	5.35	4.11	8.00	5.33	4.12	7.90	5.34	4.10	8.20	5.31	4.15
25	25	8.30	5.31	4.15	8.30	5.30	4.18	8.30	5.31	4.26	8.30	5.30	4.16
25	50	8.20	5.31	4.17	8.50	5.27	4.20	8.50	5.28	4.24	8.40	5.29	4.23
	75	8.10	5.31	4.13	8.20	5.30	4.15	8.30	5.30	4.17	8.40	5.28	4.21
	0	9.70	5.21	4.26	9.70	5.21	4.27	9.70	5.21	4.26	9.60	5.22	4.25
50	25	9.60	5.22	4.26	9.60	5.22	4.27	9.70	5.20	4.27	9.60	5.21	4.26
50	50	9.80	5.19	4.27	10.20	5.17	4.34	9.90	5.18	4.29	9.70	5.22	4.28
	75	9.20	5.29	4.22	9.30	5.28	4.29	9.20	5.29	4.20	9.10	5.29	4.22
	0	7.70	5.37	4.10	7.60	5.38	4.10	7.60	5.38	4.11	7.60	5.39	4.10
	25	7.60	5.38	4.12	7.60	5.38	4.13	7.70	5.37	4.11	7.60	5.38	4.10
/5	50	7.40	5.40	4.10	8.70	5.25	4.24	8.60	5.26	4.20	7.50	5.39	4.13
	75	7.30	5.41	4.11	7.40	5.40	4.10	7.30	5.42	4.14	7.40	5.41	4.12

P: assimilable phosphorus (mg/kg); Ca: calcium (cmol/kg); Mg: magnesium (cmol/kg).



Figure 2. Evolution of average soil phosphorus, calcium and magnesium levels after each trial.

 Table 3. Average soil phosphorus, calcium and magnesium levels after the second crop cycle as a function of fertilizer doses applied.

			Soil P. Ca and Mg content											
Doses	Doses	0	kg/Mg/h	a	25	kg/Mg/	ha	50	kg/Mg/	ha	75	kg/Mg/	ha	
of P (kg/ha)	of Ca (kg/ha)	P (mg/kg)	Ca (cmol/ kg)	Mg (cmol/ kg)	P (mg/kg)	Ca (cmol/ kg)	Mg (cmol/ kg)	P (mg/kg)	Ca (cmol/ kg)	Mg (cmol/ kg)	P (mg/kg)	Ca (cmol/ kg)	Mg (cmol/ kg)	
	0	2.90	5.52	3.89	3.30	5.51	3.97	3.30	5.51	3.96	3.50	5.50	4.01	
0	25	3.60	5.49	4.00	3.50	5.48	4.13	3.50	5.48	4.11	3.60	5.47	4.14	
0	50	4.10	5.48	4.26	4.30	5.46	4.27	4.20	5.46	4.25	4.10	5.50	4.26	
	75	4.10	5.48	4.25	3.90	5.47	4.12	4.20	5.51	4.23	4.20	5.49	4.24	
	0	8.70	5.35	4.38	9.60	5.33	4.41	8.70	5.34	4.39	9.40	5.31	4.38	
25	25	9.40	5.31	4.40	9.70	5.30	4.43	9.60	5.31	4.42	9.70	5.30	4.40	
25	50	9.30	5.31	4.39	9.60	5.27	4.40	9.70	5.28	4.40	9.80	5.29	4.43	
	75	9.10	5.31	4.37	9.40	5.30	4.52	9.30	5.30	4.54	9.40	5.28	4.41	
	0	10.30	5.21	4.68	11.50	5.21	4.76	10.30	5.21	4.67	10.20	5.22	4.66	
50	25	10.20	5.22	4.65	10.00	5.22	4.64	10.40	5.20	4.69	10.20	5.21	4.64	
50	50	10.30	5.19	4.67	10.80	5.17	4.72	10.70	5.18	4.72	10.30	5.22	4.70	
	75	10.60	5.29	4.68	10.50	5.28	4.67	10.60	5.29	4.67	10.50	5.29	4.68	
	0	9.70	5.37	4.44	9.50	5.38	4.44	9.50	5.38	4.43	9.50	5.39	4.42	
75	25	11.10	5.38	4.74	8.50	5.38	4.36	8.70	5.37	4.37	8.80	5.38	4.35	
/5	50	8.30	5.40	4.33	8.30	5.25	4.34	8.40	5.26	4.32	8.40	5.39	4.33	
	75	8.20	5.41	4.34	8.30	5.40	4.35	8.20	5.42	4.33	8.30	5.41	4.35	

P: assimilable phosphorus (mg/kg); Ca: calcium (cmol/kg); Mg: magnesium (cmol/kg).

	Soil P. Ca and Mg content												
Doses	Doses	0	kg/Mg/ł	na	25	kg/Mg/	ha	50	kg/Mg/	ha	75	kg/Mg/	ha
of P (kg/ha)	of Ca (kg/ha)	P (mg/kg)	Ca (cmol/ kg)	Mg (cmol/ kg)									
	0	2.80	5.58	3.90	3.40	5.90	3.94	3.40	5.93	3.97	3.40	6.10	3.93
0	25	4.10	6.56	4.28	4.00	6.54	4.26	4.00	6.55	4.27	4.10	6.57	4.29
0	50	5.30	6.48	4.40	5.40	6.47	4.44	5.60	6.46	4.46	5.30	6.49	4.41
	75	5.30	6.50	4.42	4.00	6.56	4.25	5.40	6.48	4.46	5.40	6.49	4.45
	0	9.60	6.37	4.69	10.10	6.33	4.72	9.70	6.38	4.70	9.60	6.39	4.68
25	25	10.80	6.29	4.77	13.60	6.27	4.80	10.90	6.30	4.78	10.90	6.31	4.79
25	50	10.90	6.32	4.80	10.90	6.31	4.81	10.90	6.31	4.80	11.10	6.25	4.86
	75	11.30	6.26	4.84	11.50	6.27	4.84	11.40	6.27	4.83	11.50	6.28	4.82
	0	12.60	6.24	4.88	12.70	6.22	4.87	12.60	6.21	4.89	12.50	6.23	4.88
50	25	12.50	6.24	4.87	12.50	6.24	4.86	12.70	6.22	4.88	12.50	6.25	4.89
50	50	12.70	6.21	4.87	13.10	6.26	4.93	13.00	6.27	4.90	12.70	6.23	4.86
	75	12.70	6.22	4.85	14.50	6.13	5.11	12.80	6.24	4.88	12.60	6.23	4.86
	0	12.10	6.26	4.80	11.90	6.29	4.78	11.80	6.31	4.77	11.90	6.32	4.78
75	25	11.90	6.32	4.79	11.80	6.31	4.77	11.70	6.30	4.76	11.80	6.32	4.75
75	50	11.80	6.31	4.76	12.10	6.27	4.51	13.80	6.25	5.12	12.00	6.29	4.80
	75	11.70	6.30	4.75	11.60	6.30	4.74	11.50	6.31	4.73	11.60	6.31	4.75

Table 4. Av	erage soil	phosphor	us, calcium a	and magnesium	levels after	r the third	crop c	vcle as a	function	of fertilizer	doses applied	1.
		r r -									······································	

P: assimilable phosphorus (mg/kg); Ca: calcium (cmol/kg); Mg: magnesium (cmol/kg).

The mean values for cycle 2 (**Table 3**) varied for phosphorus (P) from 2.90 $mg\cdot kg^{-1}$ (0P-0Ca-0Mg) to 11.10 $mg\cdot kg^{-1}$ (75P-25Ca-0Mg) and 11.50 $mg\cdot kg^{-1}$ (50P-0Ca-25Mg). A similar trend was observed for magnesium (Mg), with mean values ranging from 3.89 cmol·kg⁻¹ (0P-0Ca-0Mg) to 4.76 cmol·kg⁻¹ (50P-0Ca-25Mg) from cycle 1 to 2. Calcium levels, meanwhile, remained high (over 5.5 cmol·kg⁻¹) for (0P-0Ca-0Mg) and reduced for all the other treatments.

Finally, for cycle 3 (**Table 4**), the mean values for phosphorus (P) varied from 2.80 mg/kg (0P-0Ca-0Mg) to 13.60 mg·kg⁻¹ (25P-25Ca-25Mg) and to 14.50 mg·kg⁻¹ (50P-75Ca-25Mg) from cycle 1 to 3. An increase from 3.90 cmol·kg⁻¹ (0P-0Ca-0Mg) to 5.12 cmol·kg⁻¹ (75P-50Ca-50Mg) was observed for magnesium (Mg). Calcium levels show an increase in this nutrient, with average values varying from 5.58 cmol·kg⁻¹ (0P-0Ca-0Mg), 6.55 cmol·kg⁻¹ (0P-25Ca-50Mg) and 6.57 cmol·kg⁻¹ (0P-25Ca-75Mg) for successive cycles.

3.3. Effect of Fertilizers on Grain Yield

Analysis of the response of rice to the interactive doses of P, Ca and Mg indicates a highly significant response for the linear and quadratic regression types (**Table 5**).

Regression	n Coef	ficients	$\Pr > F$
Linear	0.	2051	<0.0001
Quadratic	0.	2258	<0.0001
Cross produ	ct 0.	0016	0.5608
Total mode	el 0.	4324	<0.0001
Parameter	s Coef	ficients	Pr > t
Constants	1.	5141	<0.0001
Р	0.	0522	<0.0001
Ca	0.	0086	0.0007
Mg	0.	0060	0.0268
$P \times P$	-0	.0005	<0.0001
$P \times Ca$	-0.	00001	0.4696
$P \times Mg$	-0.	00002	0.2568
$Ca \times Ca$	-0	.0001	0.0012
$Ca \times Mg$	0.0	00001	0.6300
$Mg \times Mg$	-0.	00007	0.0121
$P \times Ca \times M$	g 4.63	$\times 10^{-8}$	0.8953
	Critic	al values	
Factor	Critical doses (kg/ha)	Optimal doses (kg/h	a) RDG (t/ha)
Р	48.49	41	
Ca	40.23	37	3.06
Mg	33.07	29	

Table 5. Characteristics of rice response to interactive doses of phosphorus, calcium and magnesium.

RDG: grain yield.

However, the coefficient for the quadratic trend (0.22) is higher than that (0.20) for the linear trend. The fertilizer coefficients remain low (1/1000) for both the linear and quadratic trends. No significant contribution from the interactions (P, Ca and Mg) was observed in the expression of yield, in contrast with P2, Ca2 and Mg2, whose respective coefficients were negative. This interaction shows quadratic trends for P, Ca and Mg with respective optimum doses of 41, 37 and 29 kg·ha⁻¹ for an average yield of 3.06 t·ha⁻¹ (**Table 5**).

3.4. Influence of the Degree of Phosphorus Saturation (DSP) and Cations

Table 6 shows the correlation between grain yield and the degree of phosphorus saturation, the Ca/Mg ratio and the aluminum and iron content of the soil after each crop cycle. There were highly significant correlations between all soil parameters and grain yield. The correlation values were negative for Ca/Mg and Al during each of the cycles, while DSP and Fe showed positive values.

Cycles 1 2	Deremeters	RDG con	rrelations
Cycles	Parameters	R ²	$\Pr > F$
	DSP	0.71	<0.0001
1	Ca/Mg	-0.77	< 0.0001
1	Al	-0.62	< 0.0001
	Fe	0.51	< 0.0001
	DSP	0.83	<0.0001
n	Ca/Mg	-0.85	< 0.0001
Z	Al	-0.46	< 0.0001
	Fe	0.83	< 0.0001
	DSP	0.77	< 0.0001
2	Ca/Mg	-0.78	< 0.0001
3	Al	-0.42	< 0.0001
	Fe	0.71	<0.0001

Table 6. Correlation coefficients between grain yield and degree of phosphorus saturation, Ca/Mg ratio and soil aluminum and iron content after each crop cycle.

RDG: grain yield; DSP: degree of phosphorus saturation; Al: exchangeable aluminum; Fe: free iron.

Tables 7-10 show the respective correlations between grain yield and the degree of phosphorus saturation, the Ca/Mg ratio, and the aluminum and iron content of the soil, depending on the doses of fertilizer applied. There were also very few significant correlations between all the parameters in the absence of P inputs and, to some extent, for the 0 kg·ha⁻¹ P and Ca treatments (**Table 7**). DSP was strongly (0.99) and significantly correlated with RDG for the 50 and 75 kg·ha⁻¹ Ca and Mg inputs respectively. The same was observed for Ca/Mg when the doses were 25 and 50 kg·ha⁻¹ respectively. On the other hand, with 75 kg·ha⁻¹ of Ca, there was a strong correlation (–0.99) between RDG and Al, with no Mg added. No significant correlation was observed for Fe without the addition of phosphorus. Strong correlations (0.99) were also observed between RDG and DSP at 25 kg P ha⁻¹ in the absence of Ca and Mg fertilizer and at 25 kg·ha⁻¹, respectively, for each of the two elements (**Table 8**).

Table 8 and **Table 9** show a significant correlation (0.99) between RDG and Ca/Mg was observed with 50 kg·ha⁻¹ and 25 kg·ha⁻¹ of Ca and Mg, respectively, as was the case for Fe for identical doses of Ca and Mg at 25 kg·ha⁻¹. In contrast, correlations (-0.99) were observed between RDG and Al under the effect of 75 kg Ca ha⁻¹ in combination with all doses of Mg, except for 0 kg·ha⁻¹. **Table 9** shows the correlation coefficients noted, respectively, between grain yield and the degree of phosphorus saturation, the Ca/Mg ratio and the soil aluminum and iron contents, under the effect of 50 kg P ha⁻¹ (phosphorus), for different doses of calcium and magnesium. There were strong significant correlations only for Fe, varying according to the Ca dose. **Table 10** shows than the highest dose of 75

Doses of P	Doses of Ca	a Doses of Mg	RD	G correlati	on coefficie	ents
(kg/ha)	(kg/ha)	(cmol/kg)	DSP	Ca/Mg	Al	Fe
		0	0.15 ^{ns}	0.93 ^{ns}	0.95 ^{ns}	-0.98 ^{ns}
	0	25	0.93 ^{ns}	0.43 ^{ns}	0.77 ^{ns}	0.54 ^{ns}
	0	50	0.54 ^{ns}	0.81 ^{ns}	-0.97^{ns}	0.84 ^{ns}
	P Doses of C (kg/ha) 0 25	75	0.30 ^{ns}	0.48 ^{ns}	-0.81 ^{ns}	0.62 ^{ns}
_		0	0.94 ^{ns}	0.79 ^{ns}	-0.96 ^{ns}	0.87 ^{ns}
	25	25	0.95 ^{ns}	0.24 ^{ns}	-0.72 ^{ns}	0.53 ^{ns}
	25	50	0.51 ^{ns}	0.99**	-0.85 ^{ns}	0.96 ^{ns}
0		75	0.82 ^{ns}	0.56 ^{ns}	-0.93 ^{ns}	0.82 ^{ns}
0		0	0.61 ^{ns}	0.74 ^{ns}	-0.99 ^{ns}	0.99 ^{ns}
	50	25	0.17 ^{ns}	0.82 ^{ns}	-0.50 ^{ns}	0.99 ^{ns}
	50	50	0.32 ^{ns}	0.87 ^{ns}	-0.38 ^{ns}	0.97 ^{ns}
		75	0.99*	-0.01^{ns}	-0.90 ^{ns}	0.57 ^{ns}
		0	0.92 ^{ns}	0.25 ^{ns}	-0.99*	0.79 ^{ns}
	75	25	-0.31^{ns}	0.64 ^{ns}	-0.89 ^{ns}	0.85 ^{ns}
	/5	50	0.88 ^{ns}	0.29 ^{ns}	-0.94 ^{ns}	0.79 ^{ns}
		75	0.80 ^{ns}	0.33 ^{ns}	-0.89 ^{ns}	0.85 ^{ns}

Table 7. Grain yield correlation coefficients for phosphorus saturation level, Ca/Mg ratio and soil aluminum and iron contents, respectively, under the effect of the 0 kg P ha⁻¹ dose, combined with the calcium and magnesium doses applied.

RDG: grain yield; DSP: degree of phosphorus saturation; Al: exchangeable aluminum; Fe: free iron; ns: not significant; *: significant; **: highly significant.

Table 8. Grain yield correlation coefficients for phosphorus saturation, Ca/Mg ratio and soil aluminum and iron contents, respectively, under the 25 kg P ha⁻¹ dose combined with the calcium and magnesium doses applied.

Doses of P	Doses of Ca	Doses of Mg	RD	G correlati	on coefficie	nts
(kg/ha)	f P Doses of C) (kg/ha) 0	(cmol/kg)	DSP	Ca/Mg	Al	Fe
		0	0.99*	-0.07^{ns}	-0.3 ^{ns}	0.52 ^{ns}
	0	25	0.94 ^{ns}	-0.13 ^{ns}	-0.34^{ns}	0.63 ^{ns}
	0	50	0.96 ^{ns}	-0.07^{ns}	-0.35 ^{ns}	0.54 ^{ns}
-		75	0.61 ^{ns}	0.10 ^{ns}	-0.32 ^{ns}	0.52 ^{ns}
	25	0	0.75 ^{ns}	-0.10 ^{ns}	-0.94^{ns}	0.63 ^{ns}
25		25	0.99*	0.52 ^{ns}	-0.94^{ns}	0.99*
25	25	50	0.96 ^{ns}	-0.11 ^{ns}	-0.97^{ns}	0.82 ^{ns}
		75	0.92 ^{ns}	-0.03 ^{ns}	-0.97 ^{ns}	0.85 ^{ns}
		0	0.84 ^{ns}	-0.06 ^{ns}	-0.93 ^{ns}	0.62 ^{ns}
	50	25	-0.66 ^{ns}	0.99*	-0.07^{ns}	0.77 ^{ns}
	50	50	-0.50^{ns}	0.99 ^{ns}	-0.30 ^{ns}	0.90 ^{ns}
		75	0.75 ^{ns}	-0.07^{ns}	-0.99 ^{ns}	0.66 ^{ns}

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		0	0.98 ^{ns}	-0.39 ^{ns}	-0.98 ^{ns}	0.58 ^{ns}
	75	25	0.89 ^{ns}	-0.35 ^{ns}	-0.99*	0.79 ^{ns}
	/5	50	0.80 ^{ns}	-0.28 ^{ns}	-0.99*	0.81 ^{ns}
		75	0.88 ^{ns}	0.07 ^{ns}	-0.99*	0.84 ^{ns}

RDG: grain yield; DSP: degree of phosphorus saturation; Al: exchangeable aluminum; Fe: free iron; ns: not significant; *: significant.

Table 9. Grain yield correlation coefficients for phosphorus saturation, Ca/Mg ratio and soil aluminum and iron contents, respectively, under the 50 kg P ha⁻¹ dose combined with the calcium and magnesium doses applied.

Doses of P	Doses of Ca	Doses of Mg	RD	G correlation	on coefficie	nts
(kg/ha)	(kg/ha)	(cmol/kg)	DSP	Ca/Mg	Al	Fe
		0	-0.57 ^{ns}	0.21 ^{ns}	-0.99 ^{ns}	0.96 ^{ns}
	0	25	0.77 ^{ns}	-0.80 ^{ns}	-0.71^{ns}	0.26 ^{ns}
	0	50	-0.32 ^{ns}	0.23 ^{ns}	-0.99*	0.99*
		75	-0.26 ^{ns}	0.26 ^{ns}	-0.98 ^{ns}	0.99**
		0	0.19 ^{ns}	0.68 ^{ns}	-0.73 ^{ns}	0.90 ^{ns}
	25	25	-0.23 ^{ns}	0.35 ^{ns}	-0.95 ^{ns}	0.99**
	25	50	-0.26 ^{ns}	0.23 ^{ns}	-0.97 ^{ns}	0.99*
		75	-0.32 ^{ns}	0.22 ^{ns}	-0.97 ^{ns}	0.99 ^{ns}
50		0	-0.29 ^{ns}	0.28 ^{ns}	-0.96 ^{ns}	0.99*
	50	25	0.84 ^{ns}	0.95 ^{ns}	0.26 ^{ns}	0.16 ^{ns}
	50	50	0.01 ^{ns}	0.34 ^{ns}	-0.91^{ns}	0.99*
		75	-0.18 ^{ns}	0.36 ^{ns}	-0.88 ^{ns}	0.99*
		0	0.63 ^{ns}	0.04 ^{ns}	-0.97 ^{ns}	0.99 ^{ns}
	75	25	0.89 ^{ns}	-0.13 ^{ns}	-0.74^{ns}	0.98 ^{ns}
	/5	50	0.62 ^{ns}	-0.00 ^{ns}	-0.94 ^{ns}	0.98 ^{ns}
		75	0.36 ^{ns}	0.12 ^{ns}	-0.91 ^{ns}	0.99 ^{ns}

RDG: grain yield; DSP: degree of phosphorus saturation; Al: exchangeable aluminum; Fe: free iron; ns: not significant; *: significant; **: highly significant.

Table 10. Grain yield correlation coefficients for the degree of phosphorus saturation, Ca/Mg ratio and soil aluminum and iron contents, respectively, under the effect of the 75 kg P ha⁻¹ dose combined with the calcium and magnesium doses applied.

Doses of P Doses of Ca Doses of Mg			RDG correlation coefficients				
(kg/ha)	(kg/ha)	(cmol/kg)	DSP	Ca/Mg	Al	Fe	
75	0	0	0.91 ^{ns}	-0.52 ^{ns}	-0.96 ^{ns}	0.85 ^{ns}	
		25	0.68 ^{ns}	-0.65 ^{ns}	-0.87 ^{ns}	0.73 ^{ns}	
		50	0.88 ^{ns}	-0.31 ^{ns}	-0.98 ^{ns}	0.90 ^{ns}	
		75	0.90 ^{ns}	-0.30 ^{ns}	-0.99 ^{ns}	0.92 ^{ns}	

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	25	0	0.95 ^{ns}	-0.92 ^{ns}	-0.70 ^{ns}	0.27 ^{ns}
		25	0.96 ^{ns}	-0.21 ^{ns}	-0.99 ^{ns}	0.67 ^{ns}
		50	0.99*	-0.28 ^{ns}	-0.99 ^{ns}	0.67 ^{ns}
		75	0.99*	-0.26 ^{ns}	-0.99 ^{ns}	0.67 ^{ns}
		0	0.91 ^{ns}	-0.39 ^{ns}	-0.98 ^{ns}	0.62 ^{ns}
	50	25	0.86 ^{ns}	0.99 ^{ns}	-0.38 ^{ns}	0.97 ^{ns}
	50	50	0.99 ^{ns}	-0.21 ^{ns}	-0.40 ^{ns}	0.96 ^{ns}
		75	0.98 ^{ns}	-0.31 ^{ns}	-0.99 ^{ns}	0.68 ^{ns}
		0	0.96 ^{ns}	-0.34 ^{ns}	-0.99 ^{ns}	0.62 ^{ns}
	75	25	0.80 ^{ns}	0.35 ^{ns}	-0.75 ^{ns}	0.98 ^{ns}
	/5	50	0.99 ^{ns}	-0.17 ^{ns}	-0.99**	0.62 ^{ns}
		75	0.99*	-0.30 ^{ns}	-0.99**	0.62 ^{ns}

RDG: grain yield; DSP: degree of phosphorus saturation; Al: exchangeable aluminum; Fe: free iron; ns: not significant; *: significant; **: highly significant.

kg Ca ha⁻¹ is characterized by the absence of any significant correlation, whereas the lower doses (0, 25 and 50 kg·ha⁻¹) show significant correlations with an exceptional aspect for 0 kg Mg ha⁻¹, in combination with 50 kg·ha⁻¹, respectively, for P and Ca (Table 10).

4. Discussion

4.1. Management Strategies for Native and Exogenous Phosphates

Before the trial, the concentration of phosphorus in the soil was 3 mg/kg, whereas it was 3.10, 2.90 and 2.80 mg/kg after the three successive cropping cycles with no fertilizers applied. Referring to the phosphorus measurement errors of plus or minus 0.53, we can state that there was no decrease in the stock of assimilable phosphorus (Pa) under this condition, while the degree of saturation decreased from 33.31 to 30.96; 31.87 and 30.62% depending on the cycles, for an average biomass of around 25 g/pot.

This suggests a greater quantity of Fe and Al cations on the absorbent complex, particularly for Fe (31.49, 34.56 and 42.59 cmol·kg⁻¹), whose concentrations increased, unlike Al, whose effect was linked to its saturation rate on the pH, which varied from 4.6, 4.5 and 4.4.

This leads to increasing acidification of the soil during the three successive cropping cycles. This process of chemical degradation in agroecology is well known and characterized in Asian countries, which are major rice producers, as it is a major constraint induced by cropping systems [23], unlike the work carried out in Africa, which focuses mainly on the effects of this acidity [24] [25].

This is why the results obtained here are so scientifically relevant, revealing that this would be achieved at a rate of 1/10 pH per crop cycle without the addition of P, Ca and Mg fertilizers, despite the addition of N and K. The evidence of

an increase in soil Fe-free content brings us back to the holistic concept of the buffering effect of organic matter (RCOO--) to absorb the effect of this cation [26].

The correlation results observed between RDG and soil parameters reveal the possibility of managing native phosphorus in the soil, in that DSP was positively correlated with RDG, particularly for specific doses of Ca (50 kg·ha⁻¹) and Mg (75 kg·ha⁻¹). This specificity highlights the importance of the Ca/Mg ratio, which would be optimum at 2/3 in this case. Furthermore, it was the application of 25 kg Ca ha⁻¹ and 50 kg Mg ha⁻¹, corresponding to a ratio of 1/2, that produced a significant correlation for the Ca/Mg balance of the soil.

Ultimately, the initial balance of 1/1 in the soil studied would have had to be reduced to 5/3 (1 + 3/3) to achieve a good influence of DSP on grain production, whereas the optimum balance would be 3/2 for a direct effect of Ca/Mg. This analysis highlights, on the one hand, the importance of magnesium in the soil studied and, on the other hand, a difference in cationic equilibrium depending on the crop.

In fact, Mg is strongly correlated with DSP and soil Ca/Mg standards have long been established for most tropical crops [27] [28] [29] with satisfactory values of 1.5 to 5, including 2 - 4 for Arabica coffee in Kenya [30].

The results of this study set this ratio at 1.6 specifically for upland rice growing. There is a strategy here for managing P deficiency without adding phosphate fertilizer, but by acting on the Ca/Mg balance, bearing in mind that tropical soils are very rich in total phosphorus. As proof of this, an increase in DSP was noted with increasing doses of Ca or Mg in the absence of phosphate fertilizer (control). Roughly speaking, it was the low doses (<50 kg·ha⁻¹) of P, in combination with Ca and/or Mg, that influenced DSP, while the higher doses did the same with Al and Fe.

Finally, during the experiment, there was a parallel increase in soil P and Mg levels after the different crop cycles, whereas Ca levels only increased after the third cycle. However, Ca had a greater linear trend (0.47) compared with a slope of 0.28 for Mg, and the best relative ratios (Ca/Mg) were 1/2 and 1/3 without the addition of P in the third cycle. However, the residual P content of the soil applied reached 11.10 mg·kg⁻¹ (75P-25Ca-0Mg) and 11.50 mg·kg⁻¹ (50P-0Ca-25Mg) for 25 kg/ha Ca or Mg against the absence of the other.

We can easily deduce from this that the management of native P with cations differs from that of its fertilization: there would be a synergy of Ca/Mg on native P, whereas an antagonism would characterize the two in phosphate fertilization.

4.2. Balances in Relation to Iron and the Degree of Phosphorus Saturation in Mineral Nutrition

A soil's degree of phosphorus saturation (DSP) is one of its properties relating to its ability to store nutrients for plant mineral nutrition. It is expressed as the ratio of available P to the sum of iron and aluminum oxides. In other words, it is defined as the ratio of P-adsorbed to P-sorption capacity. It is a valuable indicator for agriculture and environmental management, as it determines the soil's ability to store the P supplied ($20\% \le \text{DSP} \le 30\%$) and therefore warns of the possibility of pollution, particularly through eutrophication.

Previous studies elsewhere have already revealed an exponential relationship between P and DSP, whereas the relationship between rock phosphate doses and DSP is quadratic [31]. Similar investigations in the Ferralsol environment could help to improve phosphorus management in a rational way that protects the environment.

The P/Ca/Mg ratios with a positive impact on soil quality in terms of this parameter (DSP) were recorded for 0/1/1; 1/1/1; 1/3/2; 3/0/ (cycles 1, 2 and 3). It can be deduced from this that the addition of P is not compulsory to improve the PSD with a good Ca/Mg balance.

On the other hand, Mg in variable proportions between P and Mg (3/1; 3/2 and 1/1) is required to improve the DSP without Ca.

This indicates the predominance of Mg over Ca in improving soil quality with respect to phosphorus. This assertion is all the more accurate when we refer to the positive correlations observed between RDG and DSP following the example of Fe-free, whereas Ca/Mg and Al indicate the opposite: it took 25 and 75 kg Mg ha⁻¹ to positively influence P export by rice at different respective doses of P and Ca.

It is therefore with good reason that ternary N-P-K fertilizers, widely used in Côte d'Ivoire, are coupled with Mg [32] and the work of [25] recommended Mg in the composition of bottom dressing for upland rice cultivation in the forest zone of Gagnoa, while [33] [34] did the same for lowland rice cultivation in central Côte d'Ivoire.

The results obtained highlight the effect of liming on soil acidity [35] when pH values increase with the addition of Ca and Mg, whereas this value was lower without the addition of these elements. This can be explained by an isomorphic substitution between Al³⁺ and the cations Ca²⁺ and Mg²⁺ for 1 or 2 atoms, with an excess of positive charge [6] [36] [37] [38]. Electrical equilibrium can then be ensured by a bond with an anion such as $H_2PO_4^-$. Hence the depressive effect of the P-Ca-Mg treatments on the Al content of the soil, although the respective doses are not regular, and this is due to the existence of HPO_4^{2-} , which would require more cations than $H_2PO_4^-$. On the other hand, the 2/3/1 balance of P-Ca-Mg seems to be beneficial to soil iron enrichment, in parallel with that of P in the soil.

This result confirms the findings of [24] [39] regarding the importance of iron for P recovery, even though iron is known to fix P. This other contradiction can be explained by the existence of the ferric form of iron (Fe³⁺) in the flooded environment [40] [41], even though Fe³⁺ has no toxic effect on rice, unlike Fe²⁺ in the flooded environment [5]. In fact, in addition to the quantity needed to complex P, iron is thought to contribute to good rice nutrition by boosting enzymatic activity [40] and to be capable, through isomorphic substitution, of displacing Al and/or Mn, which have an effect on rice at low doses [41].

It is therefore pure logic to observe a reduction in Al content over the crop cycles while there was an enrichment in Fe. On the contrary, a low Fe-free content (<200 ppm) can lead to a deficiency (iron chlorosis) in rice nutrition by becoming a limiting element, especially at the 3 - 5 leaf stage during episodes of water stress [42].

In the light of these analyses, there is a plausible interest in iron nutrition alongside Ca and Mg for the management of soil acidity and remediation of the toxic elements Al and Mn.

The predominant Fe^{3+} in the soil will be reduced to Fe^{2+} in the rhizosphere for uptake by the plant. It contributes to the transport of electrons for photosynthesis and respiration, as well as to catabolism reactions (H2O2) and the synthesis of $2NH_2$ from H_2N-NH_2 with the need for ATP, hence phosphorus [40] [42] [43] [44]. There is evidence of a relationship between iron and Ca, Mg, N and P.

Consequently, the role of iron in the mineral nutrition of rice, particularly for phosphorus in an acid environment, should be confirmed and studied in greater depth in a future study. This perspective should remove the ambiguity raised by such an assertion: iron oxides are supposed to fix P [44] [45] whereas soil richness in free iron seems to improve the availability of the same nutrient according to the results presented in this work.

The results obtained in the present study show that rice grain yield increases with soil content in free iron, with a significant correlation (R) of the order of 0.51 - 0.71. This was more consistent for some equilibria than for others [45]. This was more consistent for certain P/Ca/Mg balances, including the 1/1/1 ratio, particularly for the 50 kg P ha⁻¹ dose. This is further confirmed by the high total P export of around 11 to 12 kg/ha.

In view of these analyses, the originality of this study on P nutrition in rice can be confirmed, pending a more detailed study on iron, the central element in this nutrition.

5. Conclusions

The results of the study revealed that the DSP and Ca/Mg values, initially 33.31% and 1.41, respectively, varied from 70.52% and 1.35 at the end of the experiment, indicating two opposite trends under the effect of the treatments. Overall, strong positive influences of DSP and Fe were noted on RDG in contrast to Ca/Mg and Al. Specifically, low doses ($<75 \text{ kg}\cdot\text{ha}^{-1}$) of Ca had a positive influence on the increase in grain yield for 50 kg P ha⁻¹, whereas an opposite effect was observed with Al for 25 kg P ha⁻¹. A significant correlation (0.99) between RDG and Ca/Mg was observed with 50 kg $\cdot\text{ha}^{-1}$ and 25 kg $\cdot\text{ha}^{-1}$ of Ca and Mg respectively, as was the case with Fe for identical doses of Ca and Mg at 25 kg $\cdot\text{ha}^{-1}$. On the

contrary, negative correlations (-0.99) were observed between RDG and Al under the effect of 75 kg Ca ha⁻¹ in combination with all doses of Mg, except for 0 kg \cdot ha⁻¹.

The respective optimum doses of P, Ca and Mg were 41, 37 and 29 kg·ha⁻¹ for an average yield of 3.06 t·ha⁻¹. However, studies need to be carried out on the effectiveness of these doses of fertilizers in the farming environment and efficient forms of application (organic, mineral (solid, liquid)). Endogenous and exogenous phosphorus (P) management strategies were recommended, as was the role of iron in rice mineral nutrition.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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