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Evaluating the Cu and Zn Status of Various Rice Soils of Peninsular Malaysia

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ABSTRACT

Malaysia is taking efforts to be self-sufficient in rice production. However, the country is facing low availability of Cu and Zn in its soils. Even though these elements are required in small quantities for normal plant growth, their role in maximising yield is very impressive. The present study was conducted to assess the micronutrient Cu and Zn contents in selected paddy soils of Malaysia. Investigations carried out showed that marine alluvium [Guar, Sedaka, Keranji, Kuala Kedah, Kangkong, Sedu, Rotan and Kundur (Kedah)] and reverine alluvium; [Chempaka, Lubok Itek, Lating, Batu Hitam and Machang soil series (Kelantan)] were low in Cu and Zn contents. All soils were acidic in nature, with their pH values ranging from 4.3 to 6.5. Based on the results, extractable Cu and Zn concentration of soil varied within the range of 0.09-1.70 and 0.51-2.10 mg kg⁻¹ in the soil series of Kuala Kedah and LubukItek, respectively. It was manifested that the micronutrient contents were below the critical level (Cu 0.1-1.0 mg kg⁻¹ and Zn 0.5-3.0 mg kg⁻¹)according to the method of extracting analysis; Mehlich-I. The sampling depth has shown a variation and the subsurface soil sampling exhibited lesser Cu and Zn contents as compared to the surface soil sampling. Findings of the research indicate that micronutrient deficiency occurs in the main rice regions of Malaysia, and this can be corrected by applying micronutrient fertiliser.

Keywords: Micronutrients, acidic soils, pH, copper, zinc, paddy

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INTRODUCTION

Malaysian rice production is facing many constraints. Among them, the availability of Cu and Zn in the soils is limited (Liew *et al.*, 2010). Even after realising the deficiency of micronutrients in some part of Malaysian soils, the micronutrient contents still have

to be investigated across the different soil series belonging to paddy fields. Though these elements are required in small quantities for normal plant growth, their role in maximising yield is very impressive. The incidence of Zn deficiency has been widely reported worldwide (Behera et al., 2011), including in Malaysia (Hafeezullah, 2010). It is mostly predominant in calcareous soils with high pH (Katyal & Vlek, 1985). It has also been reported to occur in heavily weathered and leached acid soils (Alloway, 2008). The micronutrients Cu and Zn are involved in several essential processes in plants, especially in cereals. Zinc is required in various biochemical processes in rice plant, such as synthesis of nucleotide and cytochrome, metabolism of auxin and production of chlorophyll; as well as enzyme activation and maintenance of membrane integrity. In particular, copper serves as effector, stabiliser and inhibitor, and also as catalyst of oxidation reaction. It is particularly important in N, proteins and hormone metabolism. At the same time, it is involved in photosynthesis and respiration mechanisms, which ultimately affect pollen formation and fertilisation (Dobermann & Fairhurst, 2000). Rice is sensitive to micronutrient deficiency; therefore, a lack of such nutrients in rice can cause a drastic decline in production.

Meanwhile, positive effects of Cu and Zn have been proven, particularly in cereals (Brennan, 1991; Penney *et al.*, 1991). The deficiency of micronutrients has become a major constraint to productivity, durability and unremitting life of the soils (Bell & Dell, 2008). Micronutrient availability in soil is subjective to numerous factors (Shuman, 1986); the vital one is soil pH (Corey & Schulte, 1973; Anderson & Christensen, 1988). Total quantity of micronutrients and their availability is entirely different. The analysis of total quantity of micronutrients cannot serve as an indicator of their availability to plants (McLaren et al., 1984). Besides that, the lack or excess of micronutrients in plant parts serves as a predictor in establishing the deficiency or toxicity level of an element. Therefore, it is of the utmost importance to determine the distribution of micronutrients in plant parts (Gupta et al., 2008). There are several extracting methods for determination of micronutrients. Critical values of each micronutrient may vary according to the extraction method. Particularly for rice soils, the critical values along with the method of analysis mentioned by Dobermann and Fairhurst (2000) are: 0.6 mg Zn kg⁻¹ (1N NH₄ acetate, pH 4.8), 0.8 mg Zn kg⁻¹ (DTPA method), 1.0 mg Zn kg⁻¹ (0.05N HCl), 1.5 mg Zn kg⁻¹ (EDTA method) and 2.0 mg Zn kg⁻¹ (0.1N HCl) whereas the critical values of micronutrients using the method of analysis, Mehlich-I are: Zn 0.5-3.0 mg kg⁻¹, 1.0-2.0 mg kg⁻¹ extracted with Mehlich-III, 0.2-2.0 mg kg⁻¹ extracted with DTPA and Cu 0.1-1.0 mg kg⁻¹ extracted with Mehlich-I and 0.1-2.5 mg kg-1 extracted with DTPA (Jones Jr, 2001).

The interacting factors involved in the availability of micronutrients are crop selection, organic matter, pH and parent material, which may affect typical ranges

in the critical levels of micronutrients. Furthermore, the application of NPK fertilisers, along with intensive cultivation of high yielding varieties, has ultimately resulted in micronutrient deficiency in soils and plants (Cakmak, 2002). Micronutrient fertiliser practice is usually negligible in agriculture systems, particularly in Malaysian soils, due to their acidic nature. This is in spite of the chemical changes of rice fields that are somehow divergent against normal acidic soils. Flooding influences mainly the availability of essential nutrients due to depletion of O_2 and chemical changes, particularly in redox potential and pH, which eventually suppress the availability of Cu and Zn (Fageria et al., 2003). Malaysian soils are often acidic in nature, apart from the low availability of Mo, Cu and Zn (Ratnaprabha et al., 2011). Studies have proven the effects of micronutrient deficiency and the positive impacts of micronutrient fertiliser application in rice production in Malaysia (Hafeezullah, 2010; Saleem et al., 2010). Malaysian farmers emphasise on subsidised fertiliser without micronutrient fertiliser application, which eventually results in low rice production; however, the application of micronutrients has revealed its positive response on growth and yield of rice (Liew et al, 2010). Earlier investigations also reported the deficiency of some essential micronutrients that are required for normal rice growth on the riverine alluvium of Kelantan (Soo, 1975). However, attention was not given to these particular rice areas of Malaysia; it is known that continuous cropping results in micronutrient deficiencies. Incidences

of micronutrient deficiencies are due to intensive cultivation, leaching of nutrients and depletion of soil fertility because of the loss of top soil (Somani, 2008). Double cropping with high yielding varieties due to a well-developed irrigation systems is commonly observed in Malaysia (Ho et al., 2008). The long-term continuous cropping of high yielding varieties from the same piece of land causes obstacles in availability of soil micronutrients; hence, balanced fertiliser practice is a dire need for better crop production (Wei et al., 2012). The current study was designed to evaluate the status of the micronutrients Cu and Zn of various rice soils of Peninsular Malaysia, which can be used as a guideline for fertiliser application.

MATERIALS AND METHODS

Sampling Location

Soil samples were collected from 13 different soil series situated in the Northwestern (Kedah) and Northeastern (Kelantan) states of Peninsular Malaysia by applying the simple random soil sampling method. The soil samples were collected at two different depths (0-15cm and 15-30cm) of paddy fields. Further details in relation to the name of the soil series, location, taxonomy, texture of soil (estimated by the pipette method) and cropping practices in these soils are given in Table 1. The sampling sites are situated in the tropical climate with varied average annual precipitation. The temperature is relatively consistent throughout the course of the year, with a maximum of 32 $^{\rm o}\!C$ and a minimum of 23 °C.

Soil series	Latitude and Longitude	Taxonomy	Texture	Land use
Chempaka	N-05-97370, E-102-29944	Ultisol	Clay loam	Paddy-Paddy
Lubok Itek	N-05-94769, E-102-29465	Entisol	Clay loam	Paddy-Paddy
Lating	N-05-93200, E-102-27113	Ultisol	Sandy loam	Paddy-Paddy
Batu Hitam	N-06-22462, E-102-09477	Ultisol	Silty clay loam	Paddy-Paddy
Machang	N-05-76018, E-102-20285	Oxisol	Sandy clay loam	Paddy-Paddy
Guar	N-05-52098, E-100-27678	Inceptisol	Silty clay	Paddy-Paddy
Sedaka	N-05-53407, E-100-26313	Inceptisol	Silty clay	Paddy-Paddy
Keranji	N-06-08836, E-100-31481	Entisol	Silty clay	Paddy-Paddy
Kuala Kedah	N-06-13422, E-100.29527	Inceptisol	Silty clay	Paddy-Paddy
Kangkong	N-06-22744, E-100-26120	Entisol	Silty clay	Paddy-Paddy
Sedu	N-06-20451, E-100.33191	Entisol	Clay	Paddy-Paddy
Rotan	N-06-14233, E-100-31320	Inceptisol	Silty clay	Paddy-Paddy
Kundur	N-05-98005, E-100-43354	Inceptisol	Silty clay	Paddy-Paddy

 TABLE 1

 Soil series, taxonomy, texture, GPS location and land use in particular areas



Fig. 1: Map of the Kedah and Kelantan showing the sampling locations

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Soil Sampling and Preparation

A total of 26 representative surface and subsurface soil samples (six from each soil series) were collected from the paddy fields to represent the 13 soil series, namely, Cempaka, Lubuk Itek, Lating, Batu Hitam, Machang, Guar, Sedaka, Kerenji, Kuala Kedah, Kangkong, Sedu, Rotan and Kundur of Kelantan (riverine alluvium) and Kedah (marine alluvium). The soil samples were air-dried, then ground using mortar and pestle and passed through a 2-mm sieve, before being placing in polyethylene bags for further analysis.

Soil Analysis

Soil pH was determined 1:1 with soil water ratio (v/w) using a pH meter (Jones Jr, 2001). Soil texture was determined by employing the pipette method (Gee & Bauder, 1986). Available Cu and Zn in soils were extracted by using Mehlich-I. (soil to solution ratio 1:5, soil 5g and 25 mL of double acids; 0.05 N HCl and 0.025 N H2SO4), with a shaking time of 15 minutes at 180 rpm using a mechanical shaker. The contents were then determined on Atomic Absorption Spectrophotometer (Jones Jr, 2001). This method is selected on the basis of its characteristics; this method is particularly designed for acidic soils (like Malaysian soils), specifically, soils with CECs less than 10 meq/100 g of soil and pH less than 7.0 and are relatively low in O.M (< 5%) contents (Davis et al., 1995).

Statistical Analysis

Descriptive statistics of the extractable Cu and Zn contents and pH were obtained. A correlation study was conducted to assess the relationships between pH, Cu and Zn. The collected data were analysed by using Analysis of Variance ANOVA in Completely Randomised Design (CRD), followed by Tukey's test for comparing means of the parameters using Statistic version 8.1.

RESULTS AND DISCUSSION

Soil pH

Findings on pH, Cu and Zn contents from 0-15 and 15-30 cm depths of various rice soils of Malaysia are presented in Tables 2 and 3, respectively. It is manifest from the data that all the soils collected from Kedah and Kelantan were found to be acidic in nature. The soil of Lubuk Itek (Kelantan) is slightly acidic in nature, with pH values ranging from 4.1 to 6.5. pH values are influenced by soil depths; as the sampling depth increases, so do the pH values. Standard error of mean for soil pH in the selected soil series indicated the acidity trend in all the soils from both regions, except for Lubuk Itek, with a pH value of 6.5 (Fig.2). A major reason behind the measurement of soil pH was to modulate the behaviour and micronutrient availability to plants in soil. This means pH value can affect the availability of trace elements (Öborn et al., 1995). Soil pH and redox potential are two most considerable factors in the flooded condition of paddy fields which effects on nutrient cycling.

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	Soil corios		pH		Cu mg kg-1		Zn mg kg ⁻¹			
	Soll selles	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
1	Guar	4.25-4.52	4.37	0.13	0.75-0.92	0.81	0.09	1.00-1.67	1.39	0.34
2	Sedaka	4.24-4.42	4.31	0.09	0.54-0.65	0.58	0.05	1.10-1.51	1.33	0.21
3	Keranji	4.50-5.01	4.80	0.26	0.89-0.91	0.91	0.02	1.40-1.51	1.47	0.06
4	Kuala Kedah	5.00-5.65	5.29	0.32	0.10-0.12	0.11	0.01	0.88-0.92	0.90	0.02
5	Kangkong	4.10-4.69	4.61	0.11	0.69-0.76	0.73	0.03	1.00-1.60	1.23	0.32
6	Sedu	4.12-4.76	4.50	0.33	0.81-0.93	0.88	0.06	1.20-1.70	1.46	0.25
7	Rotan	4.32-4.98	4.75	0.37	0.88-0.91	0.89	0.01	1.30-1.63	1.49	0.17
8	Kudur	4.65-4.92	4.80	0.14	0.91-1.00	0.94	0.05	0.90-1.50	1.26	0.32
9	Chempaka	4.97-5.31	5.12	0.17	0.14-0.16	0.15	0.01	0.91-1.40	1.10	0.26
10	Lubok Itek	6.00-6.50	6.30	0.32	1.50-1.70	1.56	0.11	1.89-2.10	1.96	0.11
11	Lating	5.00-5.84	5.43	0.41	1.10-1.30	1.23	0.11	1.87-1.90	1.88	0.01
12	Batu Hitam	4.26-4.65	4.49	0.21	0.78-0.92	0.87	0.07	1.49-1.51	1.50	0.01
13	Machang	4.34-4.88	4.66	0.28	1.10-1.40	1.23	0.15	1.49-1.57	1.53	0.04

TABLE 2 Soil pH, extractable Cu and Zn contents in soils at depth of 0-15 cm



Fig. 2 : Standard error of soil pH selected soil series

	Soil coriog		рН		Cu mg kg ⁻¹		Zn mg kg ⁻¹			
	Soli series	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
1	Guar	4.31-4.62	4.49	0.16	0.69-0.73	0.71	0.02	0.98-1.10	1.02	0.06
2	Sedaka	4.15-4.87	4.58	0.37	0.65-0.70	0.67	0.02	1.11-1.21	1.14	0.05
3	Keranji	5.00-5.50	5.17	0.28	0.36-0.45	0.40	0.04	0.98-1.10	1.06	0.06
4	Kuala Kedah	5.50-6.10	5.80	0.30	0.09-0.11	0.10	0.01	0.51-0.56	0.53	0.02
5	Kangkong	5.39-5.67	5.51	0.14	0.58-0.61	0.59	0.01	0.98-1.00	0.96	0.05
6	Sedu	4.50-5.00	4.77	0.22	0.65-0.71	0.67	0.03	0.90-1.00	0.93	0.05
7	Rotan	5.03-5.56	5.22	0.29	0.67-0.71	0.69	0.02	0.89-1.00	0.93	0.05
8	Kudur	4.70-5.20	5.00	0.26	0.67-0.70	0.68	0.01	0.78-0.88	0.84	0.05
9	Chempaka	5.33-5.67	5.55	0.19	0.12-0.13	0.12	0.05	0.62-0.65	0.63	0.01
10	Lubok Itek	5.21-6.67	6.14	0.80	0.96-1.00	0.97	0.02	1.12-1.25	1.20	0.07
11	Lating	4.88-5.76	5.38	0.45	0.77-0.81	0.79	0.02	1.20-1.30	1.20	0.05
12	Batu Hitam	4.70-5.52	5.31	0.53	0.85-0.89	0.87	0.02	0.93-1.00	0.95	0.03
13	Machang	5.35-5.52	5.42	0.08	0.88-0.92	0.90	0.02	0.91-0.94	0.92	0.01

TABLE 3 Soil pH, extractable Cu and Zn contents in soils at 15-30 cm

Chemical changes mainly alter the pH and redox potential in the sub-merged condition of paddy fields and eventually affect nutrient availability (Fageria *et al.*, 2011).

A significant correlation was found between pH and soil available Cu and Zn from the samples that were taken from the surface depth. The results showed a positive correlation between soil pH and extractable Cu, and a significant correlation between soil pH and extractable Zn (Table 4).

TABLE 4

Correlation coefficient (r) among pH and extractable Cu and Zn

	pН	Cu	Zn
pН	1.00	0.74	0.51
Cu	0.74	1.00	0.034
Zn	0.51	0.034	1.00

These results are in accordance with Ghosh *et al.* (2009), who reported higher acidity from the surface of the soil samples than the subsurface soil. Furthermore, they also observed the significant negative correlation (-0.466 to -0.670) between DTPA extractable micronutrients and soil pH in subsurface soil sampling.

Soil Available Cu

Cu and Zn in soils showed low contents of both micronutrients in all the 13 soil series. The average extractable Cu content in soils at 0-15cm varied from 0.11 to 1.56 mg kg⁻¹ and 0.10 to 0.90 mg kg⁻¹ at 15-30 cm depth. The extractable Cu content, as illustrated in Tables 2 and 3, decreased with the increase in soil depth. The sampling from different depths can specifically help to determine the areas where nutrient applications are warranted. Results are in accordance with Sharma *et al.* (2000), who testified that as the depth increased, the available Cu content would decrease. According to researchers, depth can only affect available Cu content, but total Cu will remain unfluctuating regardless of depth. Similar results were found by Sharma, Jassal, Sawhney and Sidhu (1999), who analysed total Cu in alluvial soils of Northwest India.

The surface soil samples recorded lower Cu content of marine alluvium soils (Kedah) as compared to riverine alluvium soils (Kelantan). The subsurface soil samples showed lesser content in comparison to the surface soil samples. Standard error estimates the accuracy among available Cu mg kg⁻¹ in the selected soil series (Fig.3). It is clear from the figure that the soil series of Lubok Itek (riverine alluvium) has more Cu content as compared to the rest of the soil series. The least content of available Cu was recorded at 0.1 mg kg-1 in the soil series of Kuala Kedah (marine alluvium), which falls at the critical level $(0.1-1.0 \text{ mg kg}^{-1})$ according to the extracting method Mehlich-I (Jones Jr, 2001). Higher available Cu content was observed in the soils of the riverine alluvium belt, except for the Chempaka soil series. The higher content of Cu in these soils may be due to the predominance of the higher content of Cu in the parent material. Spatial variability (variation across the distance) of soil available micronutrients is particularly due to the soil parent material, soil texture and specifically the clay contents in soil (Eriksson et al., 2010), all these parameters influence the micronutrient distribution. The

positive correlations between DTPA-Cu and OC, coarse clay and exchangeable K were also noticed; it was observed that available copper had inverse relationships with clay content, very fine sand and total Cu (Sharma et al., 2006). Therefore, the available Cu contents in this study were found to be lower in the marine alluvium soils due to their clay content. Overall, the comparison done through Tukey's test showed that the means with the similar letters for the Cu content were not significantly different, except for the Kuala Kedah and Chempaka soil series, as presented in Table 5. The evidence for the critical values of Cu and Zn content in these soils is mainly due to continuous cropping without any particular micronutrient application.

TABLE 5

hirteen	soil se	ries	u mg kg-1 among	;
0.11		Cu ma karl	Groups	

Soil series	Cu mg kg-1	Groups
	Mean	
Lubok Itek	1.27	a
Machang	1.06	ab
Lating	1.01	ab
Batu Hitam	0.87	bc
Kudur	0.81	bc
Rotan	0.79	bc
Sedu	0.78	bc
Guar	0.76	bc
Kangkong	0.66	c
Keranji	0.65	c
Sedaka	0.63	c
Chempaka	0.13	d
Kuala Kedah	0.10	d

Means followed by the same letters are not significantly different at p>0.05 by HSD

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Fig.3 : Standard error of available Cu mg kg⁻¹ in selected soil series.



Fig. 4 : Standard error of available Zn mg kg⁻¹ in selected soil series.

Soil Available Zn

The amount of Zn extracted by Mehlich-I ranged from 0.90-1.96 mg kg⁻¹ and 0.53-1.20 mg kg⁻¹ from the surface and subsurface soil samples, respectively. The results showed lower Zn content in the marine alluvium soils of Kedah; however, the Chempaka soil series from the riverine alluvium of

Kelantan also showed almost similar values of marine alluvium soils. Overall, the Zn content in the riverine alluvium soils is higher as compared to the marine alluvium soils, except for the Chempaka soil series (Fig.4). On average, a higher amount of Zn (1.65 mg kg⁻¹) was recorded from the soil series of Lubok Itek.

The results of the Zn content revealed the decreasing amount of Zn with subsurface soil sampling (Table 3). This is in line with the finding of Jobbágy and Jackson (2001), who studied the distribution of nutrients with depths and observed the fluctuating nature of nutrient content with depths, whereby they recorded that the subsurface horizon of soil initiated the deterioration in nutrient availability. It is manifested from the data that the average mean of the Zn content from the riverine alluvium soil recorded as slightly elevated compared to the marine alluvium soil. Meanwhile, the Kuala Kedah soil series showed the least amount of Zn as compared to the rest of the 12 soil series and was found to be significantly different (p<0.05) (Table 6).

TABLE 6

Soil series	Zn mg kg ⁻¹	Groups
	Mean	
Lubok Itek	1.58	a
Lating	1.57	a
Keranji	1.27	ab
Sedaka	1.24	ab
Batu Hitam	1.23	ab
Machang	1.22	ab
Rotan	1.21	ab
Guar	1.20	ab
Sedu	1.20	ab
Kangkong	1.09	ab
Kudur	1.05	ab
Chempaka	0.87	b
Kuala Kedah	0.71	b

Comparison of the mean micronutrient Zn mg kg⁻¹ in 13 soil series

Means followed with the same letters are not significantly different at p>0.05 by HSD

The effect of pH on the micronutrient availability was also noted, whereby the strong acidic soil series of marine alluvium (Sedaka) with a pH value of 4.31 contained Cu and Zn contents of 0.63 and 1.24 mg kg⁻¹, respectively whereas the soil series of riverine alluvium (LubukItek) with the pH value of 6.50 showed comparatively elevated contents of Cu and Zn 1.56 and 1.96 mg kg⁻¹, respectively. The results also revealed higher Cu and Zn contents in the soils having pH values above 5. A similar finding was also noted by Ghosh, Sarkar and Sahoo (2009), who described the relationship between micronutrient cation and physical and chemical properties of soils in West Bengal. They reported that the surface soils were more acidic compared to subsurface soils; simultaneously, the extractable micronutrients decreased with increasing depth.

There was a positive correlation coefficient (r) between both micronutrients, Cu and Zn (Table 4). However, studies by Sherma et al. (2006) indicated a negative correlation for the soil for available Zn and percentage of coarse clay in soil texture. Malaysian soils were found to be deficient in essential micronutrients, as previously reported (Hafeezullah, 2010; Liew et al., 2010; Saleem et al., 2010). According to Dobermann and Fairhurst (2000), the results obtained in this study are also similar to the critical values retrieved from the analytical method Mehlich-I and also from the rice crop growth point of view. There are low contents of Cu and Zn in almost all the rice soils in Kedah and Kelantan. Trace element availability in acid soils is a constraint for crop productivity. These regions have low rice productivity due to very trace or low availability of these micronutrients in the soils.

It is important to understand the factors inducing the deficiency of such crucial micronutrients; soil pH, organic matter, soil texture accentuated Cu and Zn mining are of vital importance. Soil calcareousness, low soil organic matter, sandy soil texture and most importantly, the mining of Zn by high yielding varieties have been reported (Rashid & Ryan, 2004). The main rice growing areas of Malaysia are continuously cultivated with rice but are not supplied with micronutrient fertiliser. Due to the continuous mining of such nutrients through high yielding varieties, deficiency of these crucial nutrients will eventually occur. Healthier rice production and soil fertility status are possible if these soils are supplied with the required amounts of Cu and Zn, along with the recommended NPK fertilisers and package of management practices.

CONCLUSION

All the soil samples taken from the main rice growing areas of Malaysia were acidic in nature and had low available Cu and Zn contents. The micronutrient contents were found to be different in both of the regions; marine and riverine alluvium. However, the marine alluvium soils had lower micronutrient contents and the lowest amounts of both Cu and Zn were recorded in the soil series of Kuala Kedah (marine alluvium), with the values that are below the critical level of Mehlich-I. Thus, it was perceived that soil depth and pH effects on the micronutrient availability and more contents were observed in the surface soil samples. Soil acidity influences micronutrient content, with slightly acidic soil series containing more Cu and Zn compared to strongly acidic soils. Therefore, there were low yields of rice due to the imbalance in fertiliser practices, which can eventually overcome micronutrient deficiencies. Therefore it is suggested to sample the soil of main rice growing areas of Malaysia for the determination of micronutrients, and as the contents are found to be at critical values, the particular micronutrient should be applied in the form of inorganic fertilisers. Besides fertiliser application, the appropriate agronomic practices should strictly be followed for better crop production.

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