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## Optimizing the Nutritional Status of a Typic Kandiusult of Kerala, India, Using Sorption Study

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**Abstract:** Nutrient sorption studies were carried out as a part of a mega project on “Yield maximization in cassava (*Manihot esculenta* Crantz) through systematic approach in fertilizer use” to find out the sorption characteristics of major, secondary, and micronutrients [i.e., phosphorus (P), potassium (K), sulfur (S), copper (Cu), zinc (Zn), manganese (Mn), and boron (B)] in a typic kandiusult of Kerala, India. The sorption curve fitted by using this study along with the results of preliminary soil analysis and critical level of these nutrients were used to optimize the nutritional status of this soil. Sorption study revealed that P, K, S, and B were limiting and others were sufficient for this soil. The quantities of the limiting nutrients required to optimize the soil nutritional status were estimated from the sorption curve as P, K, S, and B at  $136 \mu\text{g mL}^{-1}$ ,  $0.338 \text{ meq } 100 \text{ mL}^{-1}$ ,  $20 \mu\text{g mL}^{-1}$ , and  $6.025 \mu\text{g mL}^{-1}$ , respectively.

**Keywords:** Nutrient sorption, sorption solution, incubation, sorption curve, critical level, preliminary soil analysis

### INTRODUCTION

Sorption is one of the most important chemical processes in soil, which affects the fate and mobility of nutrients in the soil. Sorption studies were practical for

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some of the essential elements such as P, K, S, Cu, Zn, Mn, and B (Hunter 1980). These studies were conducted to determine whether any of the applied plant nutrients react (fix or complex) abnormally with the soil. This study was undertaken as part of a full-fledged research program on maximizing tuber yield in cassava (*Manihot esculenta* Crantz) through "Systematic approach in fertilizer use". In the "systematic approach" of evolving fertilizer optima for enhancing crop productivity, understanding the nutrient sorption characteristics of the soil of the experimental site is inevitable. This approach also envisages "the safe level of any one of the nutrients" in the soil because it should be maintained in the available pool of the soil at a level in which it is neither deficient nor toxic to crops, and this corresponds to 3 times the critical level of the nutrient in the soil (Hunter 1980). Moreover, the basic aspect of any soil fertility improvement program is related to the original nutritional status of the soil. Hence, the original program on maximum yield research aimed at realizing the yield potential in cassava comprised of arriving at the critical level of nutrients and understanding the nutrient sorption capacity and the preliminary chemical characteristics of the soil. Under the sorption study, if the extracted amount of any one of these nutrients at zero level of its addition was 3 times or greater than its critical level, this nutrient was considered nonlimiting and vice versa for limiting nutrients (Hunter 1980). The quantities of limiting nutrients required to optimize soil nutritional status were arrived at on the basis of the results of preliminary soil analysis, sorption curve, and critical level of nutrients.

## MATERIALS AND METHODS

Sorption studies were accomplished by adding various levels of the elements in solution to a soil sample, and after incubation, the samples were extracted to determine whether more of the element was available than was present in the original sample. Elements were added in solution in excess covering the soil, creating an anaerobic condition for a few hours. As the sample air dries, aerobic condition prevails, thus allowing the elements to react with soil under moisture regimens ranging from complete saturation to air dry, to simulate in a short time, the kinds of reactions expected under field conditions.

### Preparation of Sorption Solutions

There were four sorption solutions.

#### Solution A

It is prepared by dissolving the following chemical compounds in 200 mL of distilled/deionized water in separate containers and when these three were

mixed together and made up to 1 L, the resultant solution has the following elemental concentration as

Name of the compound	Weight (g)	Concentration ( $\mu\text{g mL}^{-1}$ )
MnCl <sub>2</sub> · 4H <sub>2</sub> O	7.20	2000
CuCl <sub>2</sub> · 2H <sub>2</sub> O	1.073	400
ZnCl <sub>2</sub>	2.08	1000

### Solution B

Solution B was prepared by first dissolving 3.51 g of KH<sub>2</sub>PO<sub>4</sub> in about 1.5 L of water and then added 100 mL of solution A to this and made up the volume to 2 L with distilled or deionized water. This contained the following elemental concentrations: P 400  $\mu\text{g mL}^{-1}$ , Cu 200  $\mu\text{g mL}^{-1}$ , Mn 100  $\mu\text{g mL}^{-1}$ , Zn 50  $\mu\text{g mL}^{-1}$ , and K 1.30 meq 100 mL<sup>-1</sup>.

### Solution C

By mixing the solution containing 21.76 g of K<sub>2</sub>SO<sub>4</sub> and 0.88 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O in 1000 mL distilled water, solution C was obtained with the following elemental composition: B 100  $\mu\text{g mL}^{-1}$  and S 4000  $\mu\text{g mL}^{-1}$ .

### Solution D

This solution contained B 5  $\mu\text{g mL}^{-1}$  and S 200  $\mu\text{g mL}^{-1}$  prepared by diluting 50 mL of solution C to 1000 mL with distilled water.

## Preparation of Sorption Treatment Solutions

There are two different types of sorption treatment solutions: one prepared from solution B containing P, K, Cu, Mn, and Zn and the other prepared from solution D containing only S and B. Five sorption treatments were made from solutions B and D by diluting these solutions as indicated in Table 1.

## Setting Up the Sorption Experiment

Plastic 50-mL containers were used to set up the incubation study. There were six treatments including one control and two replications. Sorption study of P, K, Cu, Mn, and Zn and that of S and B were done separately. In the first study, 12 plastic containers were numbered serially from 1 to 12 and kept in two rows as 1 to 6 and 7 to 12.

**Table 1.** Preparation of sorption treatment solutions

Sorption treatment solution no.	Solution (mL) B diluted to 100 mL	Concentration of elements in sorption treatment solutions ( $\mu\text{g mL}^{-1}$ )				
		P	Cu	Mu	Zn	K (meq $100\text{ mL}^{-1}$ )
1	5	20	1	5	2.5	0.065
2	10	40	2	10	5	0.130
3	20	80	4	20	10	0.260
4	40	160	8	40	20	0.520
5	80	320	16	80	40	1.04

Sorption treatment solution no.	Solution (mL) D diluted to 100 mL	S	B
2	10	20	0.50
3	20	40	1.00
4	40	80	2.00
5	80	160	4.00

Soil weighing 3 g [ $2.5\text{ mL (volume)} \times 1.2\text{ g cm}^{-3}$  (bulk density)] was taken in these containers. Because the plants grow in a volume of soil in the field, the volume is considered rather than the weight of the soil. Sorption treatment solution (2.5 mL) prepared from solution B was added to the above containers. Similarly in B and S also, the sorption treatment solution (2.5 mL) prepared from solution D was added in the plastic containers serially numbered from 13 to 24 kept in two rows as 13 to 18 and 19 to 24. On addition of the sorption treatment solutions to the soil, the containers were gently swirled to ensure complete mixing of the solution. Both sets of treatments were placed in a dust-free area and allowed to air dry for 3–6 days without any disturbance. On the 7th day, the samples were analyzed for the above elements by following the normal analytical procedures. The sorption curve was prepared by plotting the concentration of element extracted on the Y-axis against the concentration of element added on the X-axis. From the sorption curve, the optimum quantity of nutrients required is estimated on the basis of the critical level and preliminary soil analysis data. In the sorption curve, a broken line is drawn across the graph from 3 times the critical level point. This broken line will intersect the sorption curve at some point. A broken perpendicular line was drawn from the point of intersection to the X-axis. This point of intersection of the particular line with X-axis gives the amount of element to be added to the soil to provide an extractable or plant-available amount of 3 times the critical level. The data on initial soil analysis and their critical levels are given in Table 2.

**Table 2.** Preliminary soil analysis and critical level of nutrients

Nutrient	Initial value ( $\mu\text{g g}^{-1}$ )	Method	Critical level ( $\mu\text{g g}^{-1}$ )	References
P	6.95	Bray and Kurtz (1945)	8.23	Susan John (2003)
K <sup>a</sup>	0.0385	Hanway and Hiedal (1952)	0.11	Susan John (2003)
Cu	0.75	Lindsay and Norvell (1978)	0.20	Tandon (1993)
Zn	1.96	Lindsay and Norvell (1978)	0.60	Tandon (1993)
Mn	7.60	Lindsay and Norvell (1978)	2.00	Tandon (1993)
S	12.64	Tabatabai (1982)	10.00	Tandon (1993)
B	0.76	Berger and Troug (1940)	0.50	Tandon 1993

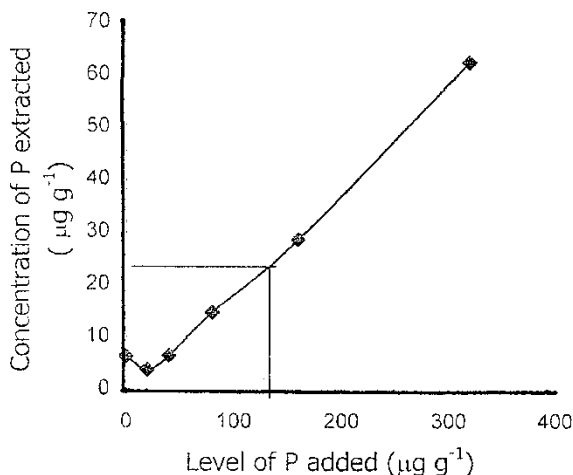
<sup>a</sup>K in meq 100 mL<sup>-1</sup>.

## RESULTS AND DISCUSSION

In this particular soil, among the seven elements for which sorption studies were carried out, the levels of P, K, B, and S extracted at zero level of their addition were lower than 3 times their critical level, hence, the quantities required to optimize their status in the particular soil were determined from the critical level and preliminary soil analysis data. The amounts of Cu, Zn, and Mn extracted at zero level of their addition were higher than 3 times their critical level and, hence, considered as nonlimiting (Table 3).

### Sorption of Phosphorus

The preliminary soil analysis of the experimental site had given an initial P status of  $6.95 \mu\text{g g}^{-1}$ . The critical level worked out was  $8.23 \mu\text{g g}^{-1}$  (Table 2). From the sorption curve fitted, it was found that  $136 \mu\text{g g}^{-1}$  P has to be added to maintain the soil P status to 3 times the soil critical level (Figure 1). Once the critical level of solution P can be worked out, the P sorption isotherm and current P level of the soil can be used to quantify the fertilizer P needed to raise the solution P to the desired level (Bhuiyan and Sedberry 1995). The low-P content of the soil of the experimental site is characteristic of red soils (typic kandiustults) having kaolinite as the specific clay type in association with hydrous oxides of iron and aluminum, which favors phosphate adsorption. Even with higher concentration of added P, the content of extracted P was comparatively lower. This can be attributed to the high phosphate adsorption, which in turn is modified by soil properties such as OH group of kaolinite and hydrated sesquioxides, free iron oxides and clay content (Dodor and Oya 2000), low-P and low organic matter content (Basak and Ghosh 1999). The content of P extracted increased invariably with increase in the concentration of added P. This is



*Figure 1.* Sorption curve for P.

in conformity with the findings that soil P availability increased with added P where the sorption was relatively higher in control and progressively decreased with increasing rates of fertilizer P (Indiati 2000).

### Sorption of Potassium

The critical level of soil K was estimated as  $0.11 \text{ meq } 100 \text{ mL}^{-1}$ , and the initial status of available K in the soil was found as  $0.0385 \text{ meq } 100 \text{ mL}^{-1}$ . From the sorption curve fitted, it was found that to maintain a K status of 3 times the critical level,  $0.338 \text{ meq } 100 \text{ mL}^{-1}$  of K has to be added. Moreover, the addition of varying levels of K ranging from  $0.065$  to  $1.04 \text{ meq } 100 \text{ mL}^{-1}$  to the soil and further incubation resulted in raising the K status much higher than the concentration of K added up to  $0.26 \text{ meq } 100 \text{ mL}^{-1}$  (Figure 2). However, there is a regular increase in K extracted with increase in the concentration of K added.

It is obvious that the K adsorption is affected by various factors such as type of clay, surface charge density, composition of associated minerals, rate of added K, pH, etc. (Shaviv et al. 1985). Because the kaolinitic clay minerals of the laterite soil type are having a low adsorption capacity to fix K, the extracted K is higher than the concentration of K actually added (Prasad et al. 1976). The acidic nature of the soil resulted in lower sorption, which increased with rise in pH. The decrease in K extracted compared with the concentration of K added can be substantiated by the fact that after K sorption along with a number of competing ions there is a continuous increase in the positive charge of the surface with a decrease in the vacant sites, resulting in maximum K adsorption (Mitsios et al. 1994). The adsorption

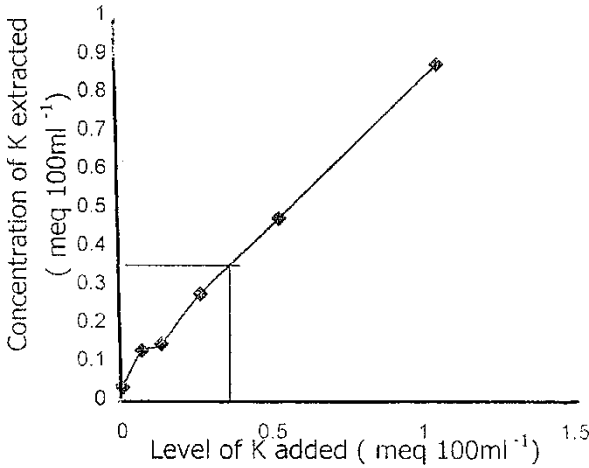


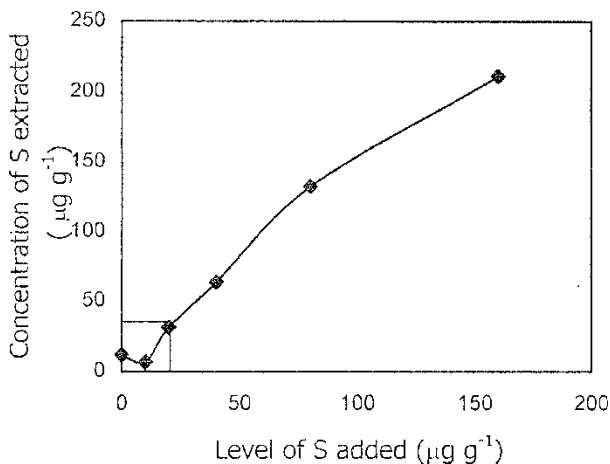
Figure 2. Sorption curve for K.

of K increased with the rate of added K irrespective of soil mineralogy (Sreenivasa Rao et al. 2000). Apart from sorption, desorption phenomena also affected the release of K to the soil solution. The medium availability of K in the soil solution on addition of different concentrations of K also could be due to the positive effect of clay and CEC on desorption of K (Choudhary and Prasad 1997) as kaolinites are intermediate in this property. The findings of the present study also corroborate the above reports.

**Sorption of Sulfur**

The preliminary analysis of the soil of the experimental site recorded a value of 12.64  $\mu\text{g g}^{-1}$ , and the critical level of sulfur was 10  $\mu\text{g g}^{-1}$  (Table 2). In this case, there was a necessity for application of S, because the initial level was less than 3 times the critical level. From the sorption curve, it is seen that 20  $\mu\text{g g}^{-1}$  of  $\text{SO}_4\text{-S}$  has to be added in this respect (Figure 3). For the  $\text{SO}_4$  adsorption isotherm, it was revealed that application of different concentrations of  $\text{SO}_4\text{-S}$  from 10 to 160  $\mu\text{g g}^{-1}$  resulted in raising the  $\text{SO}_4\text{-S}$  concentration in the soil solution accordingly. Except in the lowest concentration of 10  $\mu\text{g g}^{-1}$ , all the levels had shown a greater concentration in the extracted solution than that of the added concentration. Substantiating the results of the present study that in laterites with low pH during the 1st week of incubation an increase in water soluble  $\text{SO}_4^-$  can be seen, which is due to the release of  $\text{SO}_4$  that is strongly adsorbed by clay and hydrous oxides of iron and aluminum (Dahiya and Singh 1982). The increase in pH on incubation has been explained as due to release of  $\text{OH}^-$  ions on adsorption of  $\text{SO}_4$  (Johnson 1980). This increase in pH reduces sorption and increases the availability of plant available  $\text{SO}_4\text{-S}$ . The higher amounts of both amorphous and





**Figure 3.** Sorption curve for S.

crystalline iron and aluminum fraction present in laterite are other factors that favor sorption (Sammireddy et al. 2001).

Increase in pH causes desorption, resulting in greater soil solution levels. There is an increase in sorption with increased level of added  $\text{SO}_4$  (Douli and Jana 1993). The sorbed  $\text{SO}_4$  later is desorbed, and this in turn also is related to extractable soil aluminum content with a positive relationship between sulfate sorption capacity and free iron and aluminum sesquioxide (Sharpley 1990). This is also supported by the views that 95% of the  $\text{SO}_4$ -S sorption is completed within 60 min and then desorption starts, 70% of which in turn occurs within 30 min (Rajan 1978). The quantity of  $\text{SO}_4$  desorbed increased with the quantity of  $\text{SO}_4$  sorbed. Hence, the present observation of increased availability in the soil solution after incubation further confirms the above observation (Sammireddy et al. 2001).

### Sorption of Boron

The status of B in the preliminary soil analysis was  $0.76 \mu\text{g g}^{-1}$ . Because the critical level fixed is  $0.50 \mu\text{g g}^{-1}$  (Tandon 1993) and the original soil status is less than 3 times the critical level, a need to apply B was observed (Figure 4). The sorption curve fitted showed the addition of  $6.025 \mu\text{g mL}^{-1}$  of B to optimize its status in the soil. It was also noticed in Figure 4 that the availability of B in the soil solution increases with increase in the concentration of added B, but the availability is very low compared with the concentration of added B at all the five levels of B added from 0.25 to  $6.025 \mu\text{g mL}^{-1}$ .

The extremely high adsorption of B by the soil of the experimental site can be attributed to the various soil properties such as pH, soil texture, soil

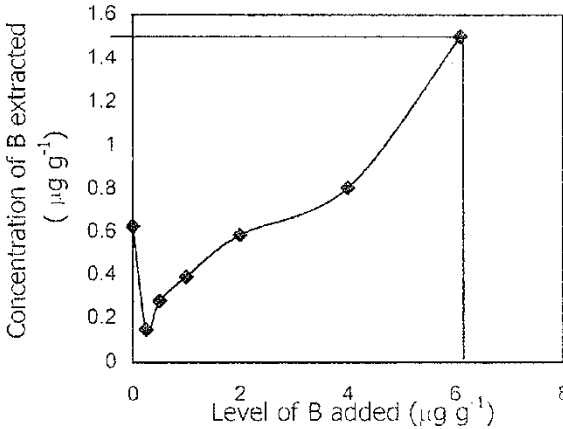


Figure 4. Sorption curve for B.

moisture content, oxides of iron and aluminum, clay minerals, etc. B adsorption by soils increased as a function of solution pH in the range of 3 to 9 (Lehto 1995) and adsorption maxima were significantly and positively correlated with solution pH (Evans 1987).

Soils containing predominantly kaolinitic type of clay minerals have higher adsorption for B (Goldberg and Glaubig 1986). Similarly, the incubation of the soil under saturated to a comparatively dried situation, with a reduction in moisture content is also one of the factors enhancing sorption (Mezuman and Keren 1981).

The iron and aluminum oxide content of the soil is also highly and significantly correlated with the B adsorption. Boron adsorbs as an inner sphere surface complex on aluminum oxide via ligand exchange of borate with surface hydroxyl groups in the clay particle edges (Toner and Sparks 1995). The properties (i.e., low pH, predominance of kaolinite clay with hydrous oxides of aluminum and iron, and reduction in moisture content on incubation) substantially favored the adsorption of B, resulting in a subsequent decrease in plant-available B in the soil solution, although there is an increase in extracted B with increase in the level of added boron.

### Sorption of Copper

For the experimental purpose, the critical level of Cu was taken as  $0.2 \mu\text{g g}^{-1}$  (Tandon 1993), whereas the initial status of Cu in the soil of the experimental site was  $0.75 \mu\text{g g}^{-1}$  (Table 2). Because the initial status is more than 3 times the critical level, there was no need to apply copper to this particular soil.

Addition of varying concentration ranging from 1 to  $16 \mu\text{g g}^{-1}$  Cu and further incubation resulted in a substantial increase in the availability of Cu

**Table 3.** Concentration of added and extracted nutrients on incubation ( $\mu\text{g mL}^{-1}$ )

Cu		Zn		Mn	
Added	Extracted	Added	Extracted	Added	Extracted
1	1.84	2.5	3.60	5	10.25
2	2.50	5	5.00	10	10.90
4	4.00	10	8.00	20	18.00
8	5.78	20	13.06	40	36.57
16	9.09	40	25.00	80	69.96
0	1.00	0	1.54	0	8.40
QN	NIL	NIL		NIL	

QN, quantity needed to optimize the soil nutrient status.

in the soil at the lower added level of 1, 2, and  $4 \mu\text{g g}^{-1}$ . However, at the higher levels of 8 and  $16 \mu\text{g g}^{-1}$ , the extracted Cu level was fairly lower than the concentration of Cu added. These results can be attributed to the various soil properties (i.e., pH, oxides and hydroxides, CEC, amount of organic matter, clay minerals, etc. (Saha et al. 1995; Scheidigger and Sparks 1996).

The pH and kaolinite mineralogy of the laterite soil has been responsible for the lower adsorption of copper (Choudhary and Khanif 2000; Pardo 2000). Furthermore, it was observed that the acidic pH and low organic matter content tend to reduce the sorption capacity of the soil for Cu (Biback 1994; Yuan and Lavkulich 1997). The greater availability of Cu observed in the soil solution in the present study can be an interplay of the above factors and confirms the observations made by the above workers. The increased availability of copper in the soil solution at lower concentration of added copper can also be supported by the views that at the beginning of incubation under submergence, more than 85% of the applied Cu was transformed into water-soluble plus exchangeable form (Saha and Mandal 2000). Cu adsorption by kaolinite increased with increasing initial concentration of copper as well as increasing levels of added copper (Choudhary and Khanif 2000).

### Sorption of Zinc

The soil of the experimental site had an initial Zn status  $1.96 \mu\text{g g}^{-1}$ , whereas the critical level of Zn is  $0.6 \mu\text{g g}^{-1}$  (Table 2). This evidently indicates that there is no need of addition of Zn. Furthermore, with the application of different levels of Zn, the concentration of Zn extracted showed that at lower levels ( $2.5 \mu\text{g g}^{-1}$  and  $5 \mu\text{g g}^{-1}$ ), the extracted Zn content is slightly higher or

almost the same as that of added Zn. But at higher levels of added Zn, the extracted Zn is substantially lower than the concentration of added Zn. However, with increase in the level of added Zn, there is an increase in the concentration of extracted Zn (Table 3). These observations on incubation of soil with different levels of Zn can be attributed to the fact that sorption of Zn is governed mainly by pH. The low pH of the soil under investigation might have reduced sorption, thus increasing the availability in the soil solution (Guadalix and Padro 1995).

Submergence brings about the dissolution of Zn to  $\text{Zn}(\text{OH})^{-1}$ , thus raising the pH. Greater sorption observed at higher levels of added Zn is due to increased sorption with rise in pH. Maximum sorption of Zn takes place at or just above a pH of 5.5, thus reducing its levels in the soil solution.

Other factors, such as hydrous oxides of iron, aluminum, and manganese of the soil, also have high affinity for Zn and contribute to the greater sorption in a laterite soil (Rupa and Tomar 1999). The trends in Zn adsorption isotherm in this study agrees with the findings that there is increased Zn adsorption with increasing concentration of added Zn (Chai and Ritchie 1990).

### Sorption of Manganese

In the Mn adsorption isotherm, the initial concentration of Mn in the soil was found to be  $1.96 \mu\text{g g}^{-1}$ , and the critical concentration was  $0.6 \mu\text{g g}^{-1}$  (Table 2). Because the initial status was more than 3 times the critical level there was no necessity of applying Mn to the particular soil (Table 3). For the effect of different concentrations of Mn on soil sorption after incubation, there was an increase in the concentration of extracted Mn with increasing levels of added Mn. However, at lower levels ( $5$  and  $10 \mu\text{g g}^{-1}$ ), the quantity extracted was quite higher than the quantity added. Submergence of soil can reduce manganese to divalent  $\text{Mn}^{2+}$  and thus increase its concentration in the soil solution (Ponnamperuma 1972). In the acidic laterite soils high in manganese and low in organic matter, the  $\text{Mn}^{2+}$  concentration in the initial stages of submergence can be as high as  $90 \mu\text{g g}^{-1}$  and a subsequent fall to as low as  $10 \mu\text{g g}^{-1}$ . The fall in the soluble  $\text{Mn}^{2+}$  levels over the period is due to drying, which favors sorption of Mn by the sesquioxides present in abundance in laterites. The dominating influence of sesquioxides in  $\text{Mn}^{2+}$  sorption at higher levels of Mn addition also observed (Dahiya and Singh 1982).

Manganese availability during the initial stage of incubation could be due to low pH ( $<5.5$ ) observed in acid laterite soils. The effect of native Mn and added  $\text{MnO}_2$  is also important, because this can retard the initial soil reduction and, hence, counteract the adverse effect of  $\text{Fe}^{2+}$  and other reduction products, thereby reducing the availability of Mn in soil solution as observed at higher levels of Mn addition.

## CONCLUSIONS

This type of sorption study carried out can be very useful in getting a realistic estimate of the quantities of nutrients to be added to optimize the nutrient status of a soil. Based on the information on preliminary nutrient status of the soil, critical level of the nutrients, the sorption curve fitted for the various nutrients under study will give a correct estimate of whether a particular nutrient is required or not and, if required, the correct quantity to be added to optimize the soil nutrient status. While formulating treatments for field experiments, the quantities to be added can be precisely arrived at by these types of studies and this can eliminate the overuse and underuse of fertilizers.

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