# EXPERIMENTS ON EFFECTS OF PHOSPHORUS ON THE MANGANESE NUTRITION OF PLANTS

## III. THE EFFECT OF CALCIUM:PHOSPHORUS RATIO ON MANGANESE IN COTTON GROWN IN BUGANDA SOIL

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#### SUMMARY

In cotton grown in a manganese-rich Buganda soil the effect of phosphorus on the concentration of manganese in the plants depended on the ratio of Ca:P in the nutrient solutions applied. With mole ratios of Ca:P < 2 plant manganese concentration increased with all concentrations of added phosphorus. When the Ca:P ratio was 1:2 and 1:1, concentration of manganese was greater in plants grown with the smallest concentration (0.2 mmol/l) of phosphorus in the nutrient solution than in plants without added phosphorus or with more P. With Ca:P > 1, manganese concentration in the plants diminished as the concentration of phosphorus in the nutrient increased from zero.

The results indicated that in soils with much manganese a sigmoidal curve may describe response to triple superphosphate because its Ca: P ratio is too small for small dressings of the fertilizer to supply enough calcium to control harmful effects of manganese.

#### INTRODUCTION

The first of this series of papers<sup>7</sup> reported that monocalcium phosphate and its hydrolysis derivatives increased the concentration of manganese in ryegrass grown in a soil from Namulonge, Uganda; the second paper<sup>8</sup> showed that in cotton plants grown with nutrient solutions the ratio of Ca:P controlled concentrations of manganese in the plants. This paper reports an experiment that measured the effect of Ca:P on cotton grown in soil from Sendusu, Namulonge,

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without added manganese, to investigate the hypothesis that an unsuitable ratio of Ca:P caused the sigmoidal response curve when cotton was grown with triple superphosphate in the field at Namulonge<sup>4</sup>.

#### EXPERIMENTAL

A description of Sendusu soil was given earlier?. The experiment was in amber glass pots that contained 220 g of soil lying between two layers of a mixture of soil and quartz chippings, as in the earlier experiment with ryegrass<sup>7</sup>. Six delinted cotton seeds (Gossypium hirsutum var. BPA 68 from Uganda) were soaked in water overnight, then sown and covered with soilquartz mixture. The pots were covered, placed in saucers filled with deionized water, and put into controlled environment cabinets which were kept at 25°C during the 12 hour day and 20°C at night. When the seeds germinated the pots were uncovered; two days later the water in the saucers was replaced by nutrient solutions. The poorest seedlings in each pot were removed to leave four seedlings per pot. Nine days after germination temperatures in the cabinets were increased to 28°C during the day and 23°C at night; corresponding relative humidities were 66 per cent and 84 per cent. Light intensity was as in the previous experiment<sup>8</sup>. The experiment was harvested 49 days after sowing. The treatments, replicated four times, were all combinations of none and four concentrations of calcium with none and three concentrations of phosphorus so that the mole ratios of Ca:P varied from 1:8 to 4:1. The concentrations of Ca and P were:

Calcium, mmol/1: 0, 0.1, 0.2, 0.4, 0.8

Phosphorus, mmol/l: 0, 0.2, 0.4, 0.8.

Appropriate amounts of stock solutions that contained  $Ca(H_2PO_4)_2.2H_2O$ ,  $Ca(NO_3)_2.4H_2O$ ,  $NH_4H_2PO_4$  and  $NH_4NO_3$  were mixed to make the twenty solutions that were applied as treatments. All treatment solutions contained, mmol/l, 2.8N, 1.5K, 0.45Mg, 0.2S; and,  $\mu$ mol/l, 2.3B, 0.016 Cu, 3.8 Zn, 0.013 Mo. Details of the formulations were reported elsewhere<sup>6</sup>. Each treatment solution was adjusted to the pH of the soil (5.75) with 0.1 N NaOH or 0.1 N H<sub>2</sub>SO<sub>4</sub>. The saucers were filled with treatment solutions when necessary to maintain a constant supply of solution to the plants throughout the experiment.

#### RESULTS

The results of the experiment are in Figures 1 to 4. Dry matter and chemical constituents of the plants are plotted against concentration of phosphorus in the nutrient solution; points at each ratio of Ca:P are joined so that effects of phosphorus at different ratios

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can be compared easily. At each concentration of phosphorus the vertical distances between points show the effects of calcium.

### Dry matter

Yields of total dry matter are in Fig. 1. Without added phosphorus yields were small, about 3 g/pot; the smallest concentration of phosphorus increased mean yield to 10.4 g but with more phosphorus the increment of yield was small. The effects of calcium were small.



Fig. 1. The effect of phosphorus applied without added calcium and at six mole ratios of Ca: P in solution, on total dry matter of cotton grown in Sendusu soil.  $\bigcirc$ , without added Ca. Mole ratios of Ca: P -  $\diamondsuit$ , 4:1;  $\bigtriangledown$ , 2:1;  $\Box$ , 1:1;  $\triangle$ , 1:2;  $\times$ , 1:4; +, 1:8.  $\bigcirc$ , Ca applied without P, mmol/l: a, 0.1; b, 0.2; c, 0.4; d, 0.8.

The vertical bar represents the standard error of a difference between two points.

### Plant manganese

Concentrations of manganese in the plants decreased in the order leaves > roots > stems, but the pattern of the curves relating the concentration of manganese to phosphorus in the nutrient solution was the same for each part, so only curves for leaves are shown in



Fig. 2. The effect of phosphorus applied without added calcium and at six mole ratios of Ca:P in solution, on concentration of manganese in dry matter of cotton leaves. ○, without added Ca. Mole ratios of Ca:P - ◇, 4:1; ▽, 2:1; □, 1:1; △, 1:2; ×, 1:4; +, 1:8. ●, Ca applied without P, mmol/: a, 0.1; b, 0.2; c, 0.4; d, 0.8.

The vertical bar represents the standard error of a difference between two points.

Fig. 2. Without added calcium, phosphorus increased the concentration of manganese from 0.024 to 0.103 per cent. With calcium the concentration of manganese in leaves was smaller, but when ratios of Ca:P were 1:8 and 1:4, at which there were only one and two treatments respectively, phosphorus increased manganese concentration. At all concentrations of phosphorus there were treatments with 1:2 and 1:1 ratios of Ca:P; at each of these ratios the smallest concentration of phosphorus increased concentration of manganese in the leaves, but more phosphorus lessened manganese concentration so that in plants given most phosphorus the concentration of manganese was less than in plants grown without added phosphorus or calcium. When Ca:P was 2:1 and 4:1 all concentrations of nutrient phosphorus diminished manganese in the leaves. Without added phosphorus calcium decreased the concentration of manganese, but the effects were small.

### Nutrient ratios in plants

Calcium:manganese. The size of the ratio of calcium:manganese in the plant parts diminished in the order stems > leaves >



Fig. 3. The effect of phosphorus applied without added calcium and at six mole ratios of Ca: P in solution, on the ratio of Ca: Mn in dry matter of cotton leaves. ○, without added Ca. Mole ratios of Ca: P - ◊, 4:1; ⊽, 2:1; □, 1:1; △, 1:2; ×, 1:4; +, 1:8. ●, Ca applied without P. mmol/l: a, 0.1; b, 0.2; c, 0.4; d, 0.8.

roots but, as with manganese concentration in the plants, the pattern of curves was the same in each part. In leaves (Fig. 3), without added phosphorus or calcium the Ca:Mn ratio was 90; calcium alone increased the ratio to 190 but phosphorus without calcium diminished the ratio to 10. With the smallest concentration of phosphorus the Ca:Mn ratio was about 40 without added calcium, and when Ca:P ratio in the nutrient was 1:2 and 1:1. More calcium increased the Ca:Mn ratio in the leaves to 85 and 130 when Ca:P in solution was 2:1 and 4:1 respectively.

The results for leaves of plants grown with solutions that contained Ca:P with ratios 1:2 and 1:1 were especially important because these ratios occur in common fertilizers, and because the curves had minima at the smallest concentration of phosphorus in the nutrient solution. Without added calcium and phosphorus the ratio of Ca: Mn was about 90; at both ratios the smallest phosphorus concentration diminished Ca:Mn in leaves to about 40; more calcium and phosphorus at 1:2 ratio increased the Ca:Mn ratio in leaves very little but solutions with Ca: P = 1:1 increased Ca:Mn to 140.

Phosphorus:manganese ratios. The ratios of P:Mn in leaves are shown in Fig. 4. Without phosphorus and calcium in the nutrient solution P:Mn in the leaves was 5; in stems and roots it was a little bigger. Calcium, without phosphorus, affected the ratio



Fig. 4. The effect of phosphorus applied without added calcium and at six mole ratios of Ca: P in solution, on the ratio of P:Mn in dry matter of cotton leaves.  $\circ$ , without added Ca. Mole ratios of Ca: P  $- \diamond$ , 4:1;  $\bigtriangledown$ , 2:1;  $\square$ , 1:1;  $\triangle$ , 1:2;  $\times$ , 1:4; +, 1:8.  $\bullet$ , Ca applied without P.

in leaves and roots very little, but it increased the ratio in stems to 18. Phosphorus without calcium increased the ratio in roots to 20, but it had no effect in stems and leaves. When phosphorus was given with calcium, the P:Mn ratio in all parts of the plant increased as the Ca:P ratio in the nutrient solution increased. With each Ca:P ratio in solution, P:Mn in the plants increased as more phosphorus and calcium were given. In leaves and roots the largest ratio was nearly 40; in stems it was 75.

Soil pH. Three times during the experiment pH was measured in the soil of each pot by putting a glass electrode into the layer of soil in the middle of the pot. Soil pH changed very little during the experiment; 35 days after sowing the mean pH was 5.63 and the largest difference between treatments was 0.27. Because soil pH varied little it is not likely that soil chemical processes affected the amounts of manganese available to plants with different treatments. The effects of calcium and phosphorus on plant manganese were therefore associated with mechanisms in the plants that controlled the amount of manganese taken up. This conclusion is supported by the results of the previous experiment<sup>8</sup> in which similar effects of calcium and phosphorus occurred in cotton plants grown without soil.

#### DISCUSSION

The experiment was designed to test the hypothesis that when calcium and phosphorus were added to soil from Namulonge, Uganda, the Ca: P ratio controlled manganese in cotton plants, as part of an investigation of the cause of the sigmoidal response of seed cotton and plant dry matter to triple superphosphate in the field<sup>4</sup>.

Cotton plants were grown for seven weeks. The curve relating yield of total dry matter to phosphorus in solution was not sigmoidal: all concentrations of added phosphorus, in all combinations with calcium, increased yield. This effect of phosphorus was similar to the effect of triple superphosphate on young plants in the field where six weeks after germination the response curve for dry matter was normal; but at harvest the curves for yields of seed cotton and total dry matter were sigmoidal.

However, although the response of dry matter in the pots was not sigmoidal, the results showed that the ratio of calcium to phosphorus in the nutrient solution controlled the effect of phosphorus on plant manganese; with some ratios this effect was sigmoidal. When the ratio was less than 1:2, concentration of manganese in the plants increased with all concentrations of phosphorus. But in solutions with 1:2 and 1:1 ratios of Ca:P, a small concentration of phosphorus increased manganese in the plants and more phosphorus diminished it.

The ratio of Ca:Mn in the plants was also controlled by Ca:P in the nutrient solution. In plants given more than the smallest concentration of phosphorus the critical Ca:P ratio was 1:2; with it Ca:Mn in the plants was small but where Ca:P was 1:1 the ratio of Ca:Mn in the plants increased greatly as more phosphorus and calcium were given.

Where nutrient ratios were 1:2 and 1:1 the curves relating concentration of manganese in the plants to added phosphorus were the inverse of the response curves to triple superphosphate in the field at Namulonge, so they were consistent with the hypothesis that excess of manganese diminished yields of crops with small dressings of triple superphosphate. Where the ratio of Ca:P was 1:2, the curve relating the ratio of Ca:Mn in leaves to P applied was similar to the field response curve, suggesting that yields at Namulonge were diminished by small dressings of triple superphosphate, which has mole ratio of Ca:P = 1:2, because they decreased the ratio of Ca:Mn in the crops. Thus, the crops may have taken up too much manganese, and had too little calcium in relation to available phosphorus to control the concentration of active manganese in the plants.

Optimum ratios of Ca: Mn in cotton are not known but in the leaves the ratio was 50 or less where the mole ratio of Ca: P in the nutrient was 1:2; the ratio of Ca: Mn increased to a maximum of 150 where more calcium was given. However, the ratio of calcium to total manganese in plants may be misleading if it includes manganese precipitated in plant tissue, as described in the second of these papers<sup>8</sup>; then concentration of mobile manganese may be more instructive than total manganese.

Ratios of P:Mn in the plants were related to the Ca:P ratio in the nutrient. With calcium in the nutrient solution, giving more phosphorus increased the P:Mn ratio; but without added calcium, phosphorus did not affect the ratio of P:Mn. These results indicate that without calcium, phosphorus and manganese were taken up together. It seems possible that crop failures associated with large concentrations of phosphorus in plants, sometimes attributed to toxicity of phosphorus<sup>9</sup> <sup>10</sup> <sup>13</sup>, may be caused by excess of a harmful cation taken up with phosphorus; then a phosphate fertilizer with large Ca:P ratio may prevent crop failure.

### Sigmoidal yield curves and phosphate fixation

There are few experimental data that show the cause of a sigmoidal yield curve with phosphatic fertilizer, but hypothetical causes based on fixation of phosphate<sup>11</sup> and on the geometrical distribution of granules and the phosphate that moves from them have been proposed<sup>12</sup>. All the hypotheses assumed that the cause of a sigmoidal curve was primarily a reaction of phosphate in soil; interactions with other nutrients in plants were secondary or ignored. Kellogg and Orvedal<sup>3</sup> stated that the response curve to phosphatic fertilizer is commonly sigmoidal, rather than parabolic, and that unless adequate amount of phosphatic fertilizer for the local kind of soil is used, the response to small applications is uneconomic. Kellogg and Orvedal, and Wilson<sup>14</sup>, considered that fixation of phosphorus in soil was the cause of poor responses to phosphatic fertilizers, and cited the experiments at Namulonge.

Although the Namulonge experiments showed that within two years added phosphate was converted to very slightly soluble compounds<sup>5</sup>, my results indicated that the intensity of phosphate in the soil solution was not small enough to cause the diminished yields with small dressings of triple superphosphate<sup>4</sup>. Yields of the final

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crop were linearly related to intensity of phosphate in the soil solution measured as  $pH_2PO_4^-$ , in plots without fertilizer and with all except the smallest dressings of fertilizer; with these yield was less than predicted from the values of  $pH_2PO_4^-$ . This result was very important: it indicated that soil phosphorus intensity with small dressings of fertilizer was adequate for a bigger yield and hence the cause of the sigmoidal yield curve was not fixation of phosphate. I suggested that with small dressings the crops could not absorb enough phosphate, or that adequate phosphate was not transported in the plants, because the concentration of another element was too large. The results of the pot experiments reported in this and the previous paper supported that speculation by showing that the ratio of Ca: P in triple superphosphate was too small to control the concentration of manganese in cotton. This experimental demonstration of the cause of a sigmoidal curve shows that despite reactions between phosphate and soil constituents, it may be more important to consider both ions and their ratio in a fertilizer in relation to other nutrients in the soil, to understand anomalous responses of crops to phosphate.

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