

Effect of Banded Fertilizers on Soil Solution Composition and Short-term Root Growth. III.* Monocalcium Phosphate with and without Gypsum

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Abstract

A layer of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (MCP) or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was spread over duplicate columns of six soils to simulate the effects of banded MCP or superphosphate (MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on soil solution composition. A separate column was set up without fertilizer addition for each soil to act as a control (background) treatment. The soils used were 0–10 cm samples from two Kurosols, a Ferrosol, a Vertosol, a Kandosol, and a 50–60 cm sample from the Kandosol. Prior to fertilizer addition, the columns were wet up to the water content at a matric suction of 10 kPa. Following 5 days of fertilizer–soil contact, soil sections were recovered at 5 mm increments from the fertilizer layer to a distance of 50 mm. Soybean (*Glycine max* (L.) Merr.) seedlings were grown for 48 h in each section and relative root elongation (RRE) was determined. Soil solution was then extracted from each section and analysed.

The distance of phosphorus (P) movement from both MCP and MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was better correlated with P buffer capacity determined at a solution P concentration of $3.2 \mu\text{M}$ than at $320 \mu\text{M}$. This suggests that the precipitation reactions which occur at the fertilizer site when MCP dissolves are independent of the soil, and it is only in soil sections further removed from the fertilizer source (i.e. with lower soil solution P concentrations) that the P sorption properties of the soil become important in determining the extent of P movement. The amount of inorganic P (P_i) in the soil solution was summed over all soil sections for each fertilizer source, and was correlated with citrate–dithionite extractable Fe and Al using step-up regression techniques. Citrate–dithionite extractable Fe was highly correlated with P_i ($r = -0.937$, $P < 0.001$), and the addition of citrate–dithionite extractable Al did not significantly ($P = 0.05$) increase the variation accounted for.

RRE decreased in proximity to the fertilizer. When RRE was plotted against the electrical conductivity of the soil solution, all data points fell below the regression line previously obtained for various salts (Moody *et al.* Aust. J. Soil Res. 1995, 33, 673–87), indicating that the reduction in RRE was not due solely to osmotic effects. Multiple regression analysis indicated that a combination of the activities of Al^{3+} (a_{Al}) and Mn^{2+} (a_{Mn}) explained 83% of the variation in RRE when both fertilizer sources were considered in all soils except the Kurosols. There was evidence of organic complexing of soil solution Al in the two Kurosols and so an accurate estimate of Al^{3+} activity could not be made.

For the soils other than the Kurosols, separate regressions of RRE against a_{Al} and a_{Mn} indicated a 10% reduction in RRE at activities of 1.9 and $70 \mu\text{M}$, respectively. Based on these activities, banding of MCP and MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ caused Al toxicity in all soils, and Mn toxicity in all soils except one of the Kurosols. Manganese toxicity occurred further from the fertilizer band than Al toxicity in the Ferrosol and the Kandosol. The dual occurrence of Al and Mn toxicities indicates that both factors need to be considered simultaneously when determining the effects of banded fertilizer on RRE.

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Introduction

The extensive use of superphosphate (a mixture of monocalcium phosphate (MCP) plus gypsum) as a phosphorus (P) fertilizer in agriculture has resulted in several studies of the chemical composition of the concentrated fertilizer solution, and its effects on soil constituents. Lindsay and Stephenson (1959*a*) characterized the effects of time on the composition of a saturated MCP solution in water, as well as measuring the dissolution process in soil and the chemical composition of the solution absorbed by filter papers at different distances from the fertilizer source. In other work, Lindsay and Stephenson (1959*b*) characterized the chemical composition of a 1:2 soil:fertilizer solution as it was reacted with successive samples of each of two soils. The results indicated that, at the low pH of the concentrated fertilizer solution, dissolution of Fe, Mn and Al occurred from the soil minerals, with the precipitation of various phosphate compounds. After contacting 10 successive soil samples, concentrations of Al and Mn in the extracted solution were as high as 700 and 15 mM respectively. At the fertilizer site, dicalcium phosphate dihydrate (DCPD) ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) precipitated first, and then slowly reverted to anhydrous dicalcium phosphate (DCP) (CaHPO_4). Lehr *et al.* (1959) found from 27% to 34% of the P added as MCP was left as a residue at the fertilizer site 9 days after soil-fertilizer contact; the amount of residue depended on soil type and moisture content.

Bouldin and Sample (1958) showed that, in two soils, the presence of soluble salts with MCP (they did not consider $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) decreased the fraction of MCP reverting to DCP at the fertilizer site, and increased or decreased (depending on the salt) the distance of P movement from the source, and the solubility of the reaction products. Fertilizer P uptake by oats (*Avena sativa* L.) was linearly related to the quantity of water-soluble P in the soil in contact with the fertilizer solution. However, Blanchar and Caldwell (1966) found that the roots of oats and maize (*Zea mays* L.) could only grow to within 2, 6 and 8 cm of a static band of MCP, MCP plus KCl, and MCP plus NH_4Cl , respectively. The band had been in contact with an acidic (pH 5.8 by an unspecified method) clay loam for a period of 14 days. They attributed the inhibitory effects to 'high salt concentrations'.

When considered *in toto*, these results present some interesting contrasts. The high concentration of Al in soil solution due to the dissolution of soil minerals in the very acidic conditions around MCP granules (Lindsay and Stephenson 1959*b*) could be expected to inhibit root growth close to the fertilizer source, and therefore restrict uptake of the fertilizer P. This toxicity, rather than 'high salt concentrations', may have been the reason for the poor root growth observed by Blanchar and Caldwell (1966). Yet the results of Bouldin and Sample (1958) suggest that it is simply the quantity of P in the soil solution which governs P availability, and this negates any possible inhibitory effect of soil solution composition on root growth and, as a consequence, P uptake. The rate of MCP used by Lindsay and Stephenson (1959*a*) was equivalent to $54.9 \text{ mg P cm}^{-2}$ soil, and that of Blanchar and Caldwell (1966), 116 mg P cm^{-2} . These rates are approximately equivalent, using the mathematical approach of Moody (1989),

to 50 and 106 kg P ha⁻¹ applied in 1 m bands; both are high rates. On the other hand, Bouldin and Sample (1958) used only one fertilizer pellet containing 30 mg P, and this does not simulate a fertilizer band which comprises a series of adjacent granules.

To reconcile the results from these two different methodologies, the procedure outlined in Moody (1989) was used to determine the effects, on soil solution composition and on short term root growth, of a fertilizer band applied at a rate relevant to row crop culture to six soils covering a wide range of mineralogy. The fertilizer sources investigated were MCP and MCP plus CaSO₄·2H₂O (in the same proportion as occurs in single superphosphate).

Materials and Methods

Soils

Six soils were used in this experiment. Soils 1–5 were the same soils described in Moody *et al.* (1995a), namely 0–10 cm samples from two Kurosol, a Ferrosol, a Vertosol, a Kandosol, and a 50–60 cm sample from the Kandosol. Soil 6 was the 0–10 cm layer of a Kurosol (Isbell 1993). Some properties of this latter soil were: pH (1:5 water), 5.1; organic carbon, 1.7%; clay, 6%; exchangeable Ca, Mg, Na and K, 0.2, 0.1, 0.05 and 0.1 cmol(+) kg⁻¹ respectively; exchange acidity, 0.1 cmol(+) kg⁻¹; P buffer capacities at solution P concentrations of 3.2 μM P (PBC_{3.2}) and 320 μM P (PBC₃₂₀), 119.3 and 1.1 L kg⁻¹, respectively; and citrate dithionite-extractable Fe (Fe_{cd}) and Al (Al_{cd}), 0.20% and 0.11%, respectively. Analytical methods used to derive these properties were described in Moody *et al.* (1995b).

Experimental Procedure

As described in Moody *et al.* (1995a), duplicate columns of each soil were set up for each fertilizer source. The soil columns were wet to the moisture content at 10 kPa matric suction. Either 7.526 g of MCP (Ca(H₂PO₄)₂·H₂O) or 7.526 g of MCP intimately mixed with 11.772 g of CaSO₄·2H₂O was spread over the surface of each soil column. These rates were calculated to supply the equivalent amount of P diffusing per unit surface area as would occur from 10 kg P ha⁻¹ applied as MCP or single superphosphate in bands 1 m apart (Moody 1989). Monocalcium phosphate was applied to soils 1–6, while MCP plus CaSO₄·2H₂O was applied only to soils 1, 2, 3 and 6. The fertilizer was allowed to contact the soil for 5 days at a temperature of 25±2°C. Another column was set up for each soil without fertilizer addition. This column acted as a control (background) treatment and was treated in the same way as the fertilized columns. Following incubation, soil was recovered in 10 successive 5 mm sections from the fertilizer source, and soybean (*Glycine max* (L.) Merr. cv. Forrest) seedlings were grown in each section in the dark for 48 h. Relative root elongation (RRE) was calculated as described in Moody *et al.* (1995a).

Soil solution was then extracted from each section by centrifuging (Aitken and Outhwaite 1987) and analysed for pH (pH_{SS}), electrical conductivity (EC_{SS}), Na, K, Ca, Mg, Al, Si, Mn, S, NO₃⁻-N, Cl⁻ and orthophosphate by using the methods described in Moody *et al.* (1995a, 1995b). Optical density at 330 nm (OD₃₃₀) of a 1+99 dilution of the soil solution was used as an index of dissolved organic C (Moody *et al.* 1995b). Activities of ions in the soil solution were determined using the iterative speciation program GEOCHEM (Sposito and Mattigod 1980; Parker *et al.* 1987). Statistical analysis of the amount of inorganic P in the soil solution comprised split plot analysis of variance with fertilizer source being treated as the main effect. Where presented, control (background) data are the means of the 10 soil sections comprising the control soil column. The distance from the fertilizer band corresponding to a reduction in RRE of 10% (i.e. 90% RRE) was interpolated by fitting, using least squares techniques, Mitscherlich equations to the RRE *v.* distance data.

Results

The pH_{SS} values, and Ca and P concentrations in the 0–5 mm section of the various soils are presented in Table 1. According to Lindsay and Stephenson

(1959*a*), the metastable triple point solution (MTPS) of MCP has a pH of 1.48, a P concentration of 3980 mM, and a Ca concentration of 1442 mM. Neither the pH nor Ca and P concentrations approached these values, and it is evident that dilution of the saturated fertilizer solution had occurred as it moved into the soil and reacted with soil constituents. In all soils, pH_{SS} was lower in proximity to MCP than to MCP plus CaSO₄·2H₂O (Table 1).

Table 1. Some chemical properties of the soil solution in the soil section 0–5 mm from bands of MCP or MCP plus CaSO₄·2H₂O in the six soils

| Soil | MCP | | | MCP plus CaSO ₄ ·2H ₂ O | | |
|------|------|-----------|------------|---|-----------|------------|
| | pH | P (mM) | Ca (mM) | pH | P (mM) | Ca (mM) |
| 1 | 2.89 | 387 | 419 | 3.36 | 536 | 549 |
| 2 | 3.90 | 62 | 30 | 3.94 | 123 | 86 |
| 3 | 3.74 | 159 | 94 | 3.86 | 216 | 145 |
| 4 | 3.41 | 216 | 197 | nd ^A | nd | nd |
| 5 | 3.32 | 333 | 347 | nd | nd | nd |
| 6 | 2.99 | 429 | 472 | 3.01 | 575 | 656 |

^A Not determined.

Extent of Phosphorus Movement

The extent of movement of P from MCP and MCP plus CaSO₄·2H₂O can be determined by reference to Table 2. Although P moved further from MCP plus CaSO₄·2H₂O than from MCP in the Ferrosol (soil 2), there were no differences for the other soils.

The distance of P movement from MCP or MCP plus CaSO₄·2H₂O was correlated with PBC_{3.2} and PBC₃₂₀. Correlation coefficients (*r*) were -0.863 ($P < 0.001$, $n = 6$) and -0.763 ($P < 0.05$, $n = 6$) for MCP, and -0.987 ($P < 0.001$, $n = 4$) and -0.807 ($P < 0.01$, $n = 4$) for MCP plus CaSO₄·2H₂O, respectively.

Soil Solution Phosphorus

The amount of inorganic P (P_i) in the soil solution was summed over all soil sections for each soil and each P source, and mean values are presented in Table 3. For all soils, P_i was higher with MCP plus CaSO₄·2H₂O than with MCP alone.

The quantity of P_i in the soil solution for both P sources was regressed against Fe_{cd}, Al_{cd}, exchangeable Ca and Mg, and Al³⁺ activity in the soil solutions of the control (unfertilized) soils using step-up regression techniques. Of these parameters, Fe_{cd} was most highly correlated with P_i ($r = -0.937$, $P < 0.001$, $n = 10$), and the addition of any of the other parameters did not significantly ($P = 0.05$) increase the variation accounted for.

Cation Concentrations in Soil Solution

In all soils, trends in Ca and Na concentration with distance from the fertilizer band mirrored trends in K concentration, and Fig. 1 presents K and Mg data from soils 1, 4, 5 and 6 with both P sources. In general, soil solution cation (Na⁺, K⁺, Ca²⁺, and Mg²⁺) concentrations increased, and sometimes reached a plateau, as the fertilizer band was approached. However, in the case of the

Table 2. Orthophosphate concentrations (mm) in the soil solutions of the six soils at different distances from a simulated band of MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ after 5 days contact

Values in parentheses are standard errors

| Distance from band (mm) | MCP | | | | | | MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | | | | | |
|-------------------------|---------------|------------------|------------------|-------------------|-----------------|------------------|--|------------------|------------------|------------------|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| 0-5 | 387 (15) | 62.0 (5) | 159 (3) | 216 (7) | 333 (7) | 575 (12) | 536 (10) | 123 (9) | 216 (17) | 429 (25) | | |
| 5-10 | 255 (15) | 22.0 (1.9) | 101 (3) | 232 (3) | 171 (2) | 310 (9) | 410 (12) | 21.3 (2.3) | 103 (6) | 281 (18) | | |
| 10-15 | 127 (5) | 0.478 (0.009) | 44.2 (3.9) | 140 (3) | 54.2 (0.6) | 99.5 (7.8) | 133 (7) | 0.578 (0.031) | 36.1 (4.3) | 103 (11) | | |
| 15-20 | 46.2 (4.1) | 0.001 (0) | 2.81 (0.91) | 52.6 (4.9) | 16.1 (0.4) | 11.8 (1.3) | 33.9 (5.1) | 0.226 (0.041) | 3.26 (0.71) | 21.6 (2.1) | | |
| 20-25 | 7.94 (0.9) | <0.001 | 0.135 (0.003) | 11.7 (0.7) | 0.814 (0.09) | 0.049 (0.009) | 2.00 (0.39) | <0.001 | 0.158 (0.003) | 0.996 (0.101) | | |
| 25-30 | 0.001 (0) | <0.001 | 0.002 (0.001) | 1.51 (0.08) | <0.001 | 0.001 (0) | 0.001 (0) | <0.001 | 0.002 (0.002) | <0.001 | | |
| 30-35 | <0.001 | <0.001 | 0.001 (0) | 0.061 (0.008) | <0.001 | <0.001 | <0.001 | <0.001 | 0.002 (0.001) | <0.001 | | |
| 35-40 | <0.001 | <0.001 | 0.002 (0.001) | <0.002 (0.001) | <0.001 | <0.001 | <0.001 | <0.001 | 0.002 (0.001) | <0.001 | | |
| 40-45 | <0.001 | <0.001 | 0.002 (0.001) | 0.002 (0.001) | <0.001 | <0.001 | <0.001 | <0.001 | 0.002 (0.001) | <0.001 | | |
| 45-50 | <0.001 | <0.001 | 0.002 (0.001) | 0.002 (0.001) | <0.001 | <0.001 | <0.001 | 0.002 | <0.001 | <0.001 | | |
| Control | <0.001 | <0.001 | 0.002 (0.001) | 0.002 (0.001) | <0.001 | <0.001 | <0.001 | <0.001 | 0.002 (0.001) | <0.001 | | |

Kandosol surface soil (soil 4) with MCP, all cation concentrations were lower in the 0–5 mm section than in the 5–10 mm section (K and Mg data shown in Figs 1c and 1d). This is indicative of mass movement of the fertilizer solution into the soil as water vapour moves into the fertilizer band in response to the vapour pressure gradient (Lehr *et al.* 1959).

Table 3. Amount of inorganic P (mmol) in the soil solution summed over all soil sections for banded MCP and MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as fertilizer sources in the six soils

Least significant difference ($P = 0.05$) for soil \times fertilizer source is 1.9

| Soil | MCP | MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
|------|------|--|
| 1 | 22.3 | 28.3 |
| 2 | 3.0 | 5.2 |
| 3 | 14.6 | 15.7 |
| 4 | 20.4 | n.d. ^A |
| 5 | 12.2 | n.d. |
| 6 | 22.8 | 26.2 |

^A Not determined.

Although Na, K and Ca concentrations increased, or increased to a plateau, as the fertilizer band was approached in the Kandosol subsoil (soil 5) with MCP (Fig. 1c), and in the Kurosol (soil 1) with MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 1e), Mg concentrations tended to be lower in the 0–5 mm section than in the 5–10 mm section (Figs 1d and 1f). This contrasting trend of Mg compared with K suggests that precipitation of Mg phosphates was occurring in the 0–5 mm section of these soils.

Soil Solution Silicon, Aluminium, Manganese, and Dissolved Organic Carbon

Total Si concentrations in the soil solutions of all soils increased as the band of MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was approached (data not presented); the maximum Si concentration of 9.08 mM occurred in the 0–5 mm section of soil 6 with banded MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In the Kurosols (soils 1 and 6), total Al concentration in the soil solution ranged up to 4.49 and 8.18 mM, respectively, as Si concentration increased in proximity to MCP. In contrast, total Al concentrations in soils 2–5 did not exceed 0.828 mM, even though Si concentrations reached 8.54 mM (Fig. 2). Because of the low soil solution pH near the fertilizer band (Table 1), Al solubilized by dissolution of aluminosilicates would be expected to precipitate as Al phosphates. However, as total Si in the soil solutions of the Kurosols (soils 1 and 6) increased, so did total Al (Fig. 2). Concomitant with the increase in total Al in the soil solution of these soils was an increase in OD_{330} (Fig. 3). Optical density at 330 nm in 1+99 dilutions of the soil solutions of soils 2–5 did not exceed 0.060, whereas it ranged up to 0.142 and 0.198 in soils 1 and 6, respectively. Coefficients of determination (R^2) for the quadratic equations describing the relationship between OD_{330} and the activity of Al^{3+} (a_{Al}) were 0.999 ($P < 0.001$, $n = 20$) for soil 1 and 0.995 ($P < 0.001$, $n = 20$) for soil 6.

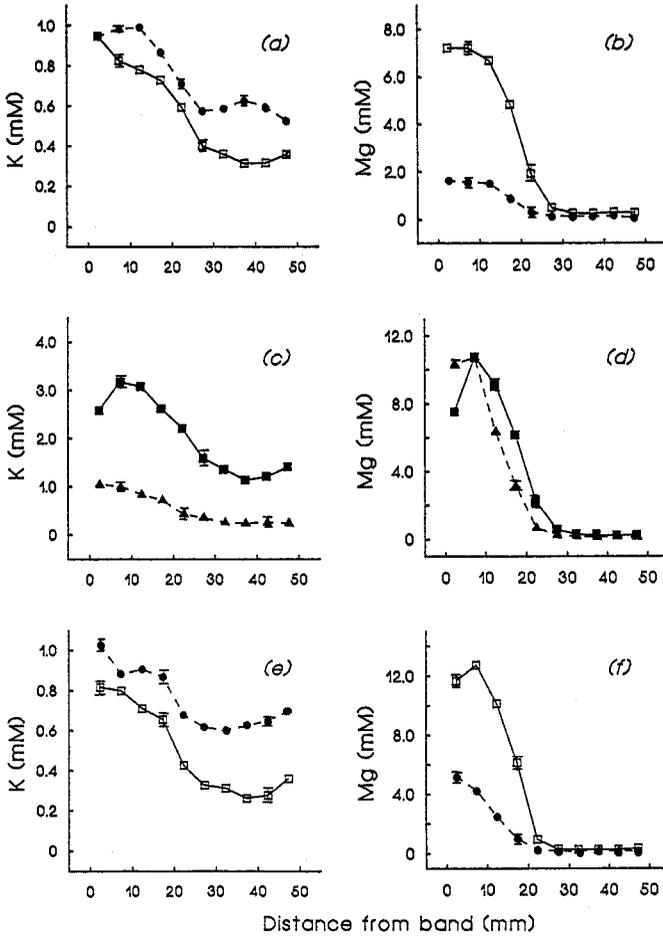


Fig. 1. Relationships between distance from bands of MCP (*a-d*) or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (*e, f*) and K and Mg concentrations in the soil solutions of soils 1 (□), 4 (■), 5 (▲) and 6 (●). Standard error bars are indicated for selected points.

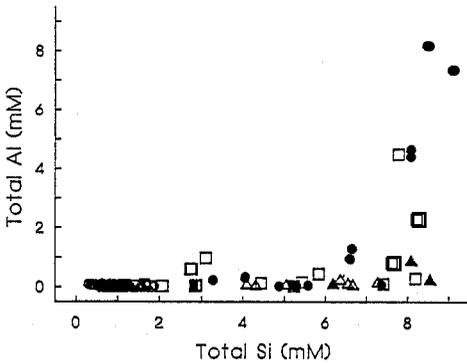


Fig. 2. Relationship between total Al concentration and total Si concentration in the soil solutions of soils 1 (□), 2 (○), 3 (△), 4 (■), 5 (▲) and 6 (●) with MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as banded fertilizer sources.

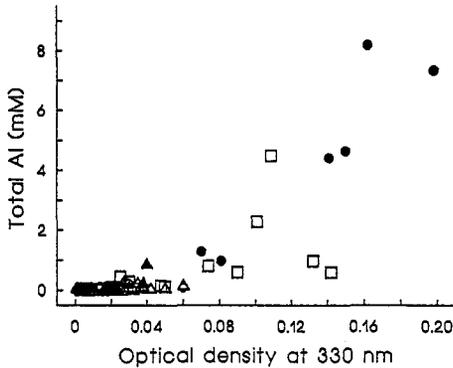


Fig. 3. Relationship between total Al concentration and optical density at 330 nm of the soil solutions of soils 1 (\square), 2 (\circ), 3 (\triangle), 4 (\blacksquare), 5 (\blacktriangle) and 6 (\bullet) with MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as banded fertilizer sources. Optical density was determined on 1+99 dilutions of the soil solutions.

In all soils, Mn concentration in the soil solution increased as the pH decreased in proximity to the fertilizer band, and this trend was particularly obvious in the Kandosol (soil 4) (Fig. 4). Background (control) concentrations of Mn were less than $8 \mu\text{M}$ in all soils except the Ferrosol (soil 2), where the mean background concentration was $28 \mu\text{M}$. Maximum Mn concentrations reached in proximity to MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were 0.304, 1.40, 0.970, 4.61, 0.706 and 0.047 mM in soils 1–6 respectively.

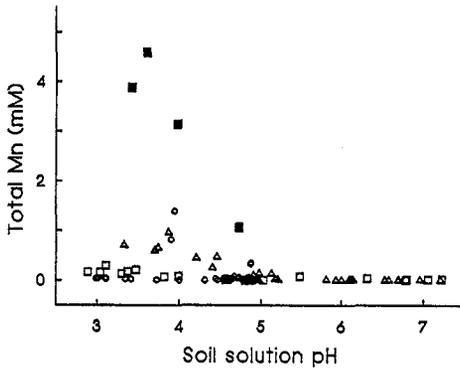


Fig. 4. Relationship between total Mn concentration and pH of the soil solutions of soils 1 (\square), 2 (\circ), 3 (\triangle), 4 (\blacksquare), 5 (\blacktriangle) and 6 (\bullet) with MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as banded fertilizer sources.

Relative Root Elongation

Mean root elongations measured in the six control soils 48 h after transplanting seedlings into the soil sections were 59 ± 3 , 74 ± 4 , 79 ± 4 , 65 ± 6 , 70 ± 5 , and 66 ± 2 mm for soils 1–6, respectively. Relative root elongation (RRE) was inhibited in proximity to the fertilizer bands in all soils; data from soils 3 and 6 are presented in Fig. 5. Reduced RRE in acidic soils has been attributed to osmotic effects, Al toxicity, H ion toxicity, or Ca deficiency (e.g. Ritchey *et al.* 1989). The possible effect of Mn toxicity on RRE has not been well documented (Scott and Fisher 1989).

The use of Ca compounds in our study eliminates Ca deficiency as a limitation to root growth in the vicinity of the fertilizer bands. It is therefore inferred that RRE has been reduced through osmotic effects, and/or one or more of Al, Mn or H toxicity.

The plot of RRE *v.* EC_{SS} (Fig. 6) for all soils and both fertilizer sources indicates that a factor in addition to an osmotic effect is the cause of reduced

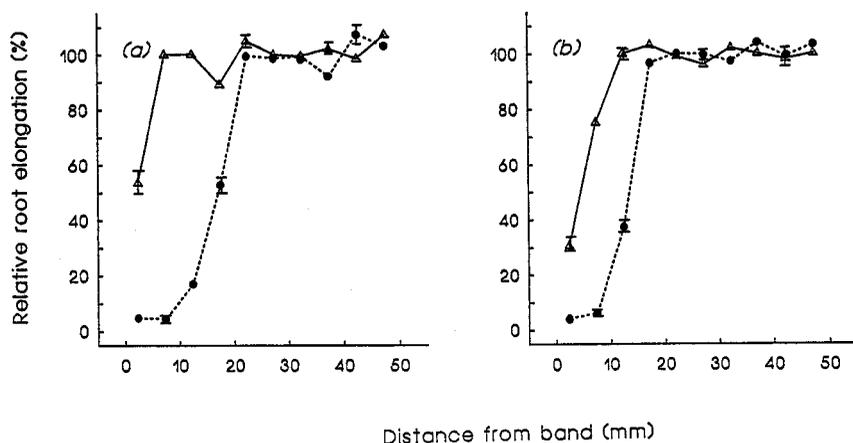


Fig. 5. Effect of distance from bands of (a) MCP or (b) MCP plus CaSO₄·2H₂O on relative root elongation of soybean cv. Forrest in soil 3 (△) and soil 6 (●). Standard error bars are indicated for selected points.

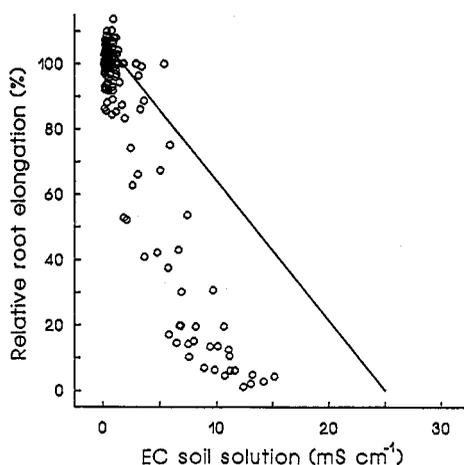


Fig. 6. Relationship between relative root elongation of soybean cv. Forrest and soil solution EC (EC_{SS}) for the six soils with MCP or MCP plus CaSO₄·2H₂O as banded fertilizer sources. Plotted regression line ($y = 107.7 - 0.043x$) is the relationship obtained at EC_{SS} < 25 mS cm⁻¹ using (NH₄)₂SO₄, NH₄NO₃, KNO₃ and Ca(NO₃)₂ as fertilizer sources (Moody *et al.* 1995a).

RRE; all data points fall below the RRE *v.* EC_{SS} regression line obtained for EC_{SS} < 25 mS cm⁻¹ when several soluble salts were used as banded fertilizer sources in the same soils (Moody *et al.* 1995a). Data for all soils and both MCP and MCP plus CaSO₄·2H₂O lay on a single response curve when plotted against soil solution pH (pH_{SS}) (Fig. 7). The Mitscherlich equation of best fit indicated that a 10% reduction in RRE occurred at a pH_{SS} of 4.5.

Bruce *et al.* (1988) found that the Al species toxic to soybean root elongation were Al³⁺ and AlOH²⁺. Inspection of the plot of RRE *v.* a_{Al} (Fig. 8) indicates that the data for soil 6, and to a lesser extent, soil 1, lie above the trend of the data for soils 2–5. For data from the latter soils, the Mitscherlich equation of best fit was

$$RRE = 1.13 + 101.61 \exp(-0.083a_{Al})$$

$$(R^2 = 0.721, \quad P < 0.001, \quad n = 120). \quad (1)$$

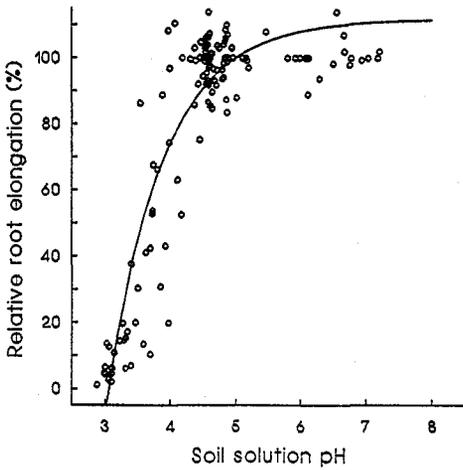


Fig. 7. Effect of soil solution pH on relative root elongation of soybean cv. Forrest with MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as banded fertilizer sources in the six soils. Plotted regression line is $y = 111.7 - 3767.3 \exp(-1.15x)$ ($R^2 = 0.836$, $P < 0.001$).

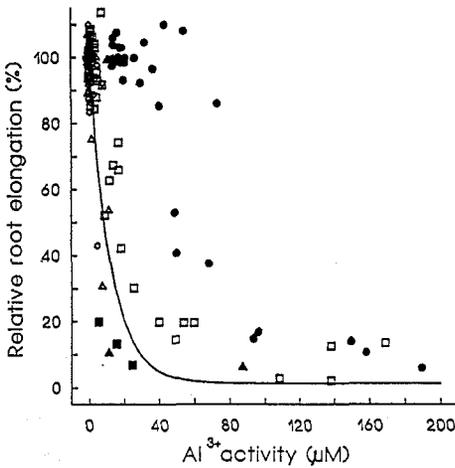


Fig. 8. Relationship between relative root elongation of soybean cv. Forrest and Al^{3+} activity in the soil solution of the six soils fertilized with MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Plotted regression line, using data from soils 2-5 only, is $y = 1.13 + 101.6 \exp(-0.0828x)$ ($R^2 = 0.721$, $P < 0.001$). (Soil 1, \square ; soil 2, \circ ; soil 3, \triangle ; soil 4, \blacksquare ; soil 5, \blacktriangle ; soil 6, \bullet .)

The coefficient of determination of a Mitscherlich fit between RRE and the activity of AlOH^{2+} (a_{AlOH}) was $R^2 = 0.673$ ($P < 0.001$, $n = 120$), suggesting that the Al^{3+} ion is probably the major causal species of the toxicity. These equations indicate that a reduction of 10% in RRE occurs at an a_{Al} of $1.6 \mu\text{M}$ and at an a_{AlOH} of $0.4 \mu\text{M}$.

It is not possible to eliminate H^+ ion toxicity as a contributory factor to the reduction in RRE, because the soil solution pH in proximity to the fertilizer band was less than 4.0 in all soils, and Foy (1992) stated that H^+ ion toxicity occurs at pH less than 4.0. Furthermore, for soils 2-5, there was a close correlation between soil solution pH and a_{Al} ($R^2 = 0.916$, $P < 0.001$, $n = 120$) and a_{AlOH} ($R^2 = 0.768$, $P < 0.001$, $n = 120$) when regression equations of the form $y = a \exp bx$ were fitted to the data. Both activities increased as pH decreased. However, inclusion of a pH_{SS} term with the Mitscherlich equation relating RRE to a_{Al} did not significantly ($P = 0.05$) increase the variation in RRE above that accounted for by a_{Al} alone.

It is possible that Mn toxicity, in addition to Al toxicity, may have contributed to the reduced RRE in proximity to the banded fertilizers; Mn activities in the

soil solution increased as the fertilizer band was approached (data not presented). When RRE (%) was regressed against the activity of Mn in the soil solution (μM) (a_{Mn}) of soils 2-5, the following quadratic equation of best fit was obtained:

$$\text{RRE} = 102.6 - 0.1879a_{\text{Mn}} + 0.00009a_{\text{Mn}}^2$$

$$(R^2 = 0.696, \quad P < 0.001, \quad n = 120). \quad (2)$$

At 90% RRE, a_{Mn} was $70 \mu\text{M}$.

Because both a_{Al} and a_{Mn} increased with the decrease in pH in proximity to the fertilizer, step-up multiple regression was used to account for the separate effects of Al and Mn toxicities on RRE. To allow for the curvilinear relationships between RRE and a_{Al} and a_{Mn} , a square term for each activity was included in the multiple regression. Because of the likely overestimation (due to unaccounted complexation) of a_{Al} in soils 1 and 6, only data from soils 2-5 were used. The multiple regression equation obtained was:

$$\text{RRE} = 103.8 - 2.80a_{\text{Al}} + 0.023a_{\text{Al}}^2 - 0.12a_{\text{Mn}} + 0.00006a_{\text{Mn}}^2$$

$$(R^2 = 0.826, \quad P < 0.001, \quad n = 120). \quad (3)$$

This equation accounts for 83% of the variation in RRE, whereas a_{Al} and a_{Mn} , when considered separately, accounted for only 72% and 70% of the variation, respectively. This indicates that Al and Mn toxicities have cumulative effects on RRE, and both factors must be considered when diagnosing the causes of reduced RRE.

Because, in soils 2-5, RRE was reduced by 10% at an a_{Al} of $1.6 \mu\text{M}$ and an a_{Mn} of $70 \mu\text{M}$, these two values can be used to diagnose whether an Al and/or Mn toxicity has been induced in the soils of this study through the placement of MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Table 4 indicates that in the Kurosols (soils 1 and 6) and Kandosol subsoil (soil 5), Al toxicity occurred at a much greater distance from the fertilizer than Mn toxicity (in fact, Mn toxicity was not recorded in soil 6), and is therefore the main factor reducing RRE in these soils. On the other hand, Mn toxicity affected RRE at a greater distance from the fertilizer than did Al toxicity in the Ferrosol (soil 2), Vertosol (soil 3) (MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatment), and Kandosol surface soil (soil 4). It is noteworthy that both Al and Mn toxicities co-existed in all soils except soil 6.

Table 4. Soil sections (mm) in which soil solution Al activity exceeded $1.6 \mu\text{M}$ or soil solution Mn activity exceeded $70 \mu\text{M}$ due to the effects of banded MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the six soils

| Soil | MCP | | MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | |
|------|-------|-------|--|------|
| | Al | Mn | Al | Mn |
| 1 | 25-30 | 0-5 | 20-25 | 0-5 |
| 2 | 0-5 | 5-10 | 0-5 | 5-10 |
| 3 | 5-10 | 5-10 | 0-5 | 5-10 |
| 4 | 10-15 | 15-20 | n.d. ^A | n.d. |
| 5 | 15-20 | 10-15 | n.d. | n.d. |
| 6 | 45-50 | none | 45-50 | none |

^A Not determined.

Soil Properties Affecting Root Elongation

The distances from MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ corresponding to a 10% reduction in RRE are presented in Table 5. As indicated previously, this reduction is caused by osmotic effects and the toxic activities of Al, Mn and/or H. Step-up regression indicated that neither Fe_{cd} nor Al_{cd} concentrations in the control (unfertilized) soils were significantly ($P = 0.05$) correlated with these distances.

Table 5. Distance (mm) from the fertilizer band in the six soils at which relative root elongation of soybean cv. Forrest was reduced by 10%

| Soil | MCP | MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
|------|-----|---|
| 1 | 26 | 22 |
| 2 | 6 | 10 |
| 3 | 7 | 11 |
| 4 | 19 | n.d. ^A |
| 5 | 12 | n.d. |
| 6 | 24 | 17 |

^A Not determined.

Discussion

Extent of Phosphorus Movement

The tendency for P movement to be more restricted (Table 2), and P_i to be lower (Table 3), with MCP as the source than MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was also noted by Hamilton and Lathwell (1965) in a neutral silt loam soil. Sulfate ions from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would compete with orthophosphate for sorption sites and therefore increase P mobility in the MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatment. Solution P concentration and mobility of P in the MCP treatment would also be reduced because the lower pH in proximity to MCP than to MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ would favour increased precipitation of Al and Fe phosphates. The higher correlation of $\text{PBC}_{3.2}$ than PBC_{320} with distance of P movement is consistent with precipitation reactions occurring in proximity to the fertilizer independently of the P buffer capacities of the soils at the high solution P concentrations (>100 mM). This would be expected as Lindsay and Stephenson (1959a) found that the precipitation of DCPD from a saturated MCP solution occurred in the absence of soil. However, as the fertilizer P diffuses away from the fertilizer source, solution P concentrations become lower (<1 mM), and the P sorption properties of the soil then have an influence on the extent of further P movement.

These results are in contrast to those obtained by Moody *et al.* (1995b) for banded diammonium phosphate (DAP) and monoammonium phosphate (MAP) in the same soils. With these sources, PBC_{320} was better correlated with the distance of P movement than $\text{PBC}_{3.2}$. This occurred because the extent of the precipitation reactions taking place near the fertilizer band was determined by soil properties, and was not a consequence of the dissolution behaviour of MAP or DAP.

Soil Solution Phosphorus

The finding that Fe_{cd} , and not Al_{cd} , was correlated with P_i contrasts with an earlier study (Moody *et al.* 1995*b*) with MAP as the fertilizer source, where both Fe_{cd} and Al_{cd} were correlated with the quantity of P_i . However, the soil solution pH in proximity to the banded MAP ranged from 4.58 to 5.25 (depending on soil type) which is considerably higher than that found in proximity to MCP or MCP plus $CaSO_4 \cdot 2H_2O$ (Table 1). Therefore, in the presence of the latter two sources, clay mineral dissolution would be expected to be more extensive than that occurring in proximity to MAP. This is supported by a comparison of the maximum Si concentrations in the soil solution; for MAP, these were 4.4, 5.5, 5.2, 3.0 and 5.0 mM in soils 1–5 respectively (Moody *et al.* 1995*b*), whereas for MCP, the corresponding concentrations were 8.2, 5.6, 6.6, 8.2 and 8.5 mM. Under these conditions of extensive clay mineral dissolution, the initial Al_{cd} would not reflect the potential for Al release, and this explains the poor correlation between Al_{cd} and P_i . On the other hand, clay dissolution would not greatly increase the release of Fe, as the clay minerals of which it is a structural component are of limited occurrence in the soils of this study. The high correlation between P_i and Fe_{cd} when MCP or MCP plus $CaSO_4 \cdot 2H_2O$ is the fertilizer source is therefore a reflection of the importance of the sorption of P onto the surfaces of Fe hydrous oxides.

Soil Solution Silicon, Aluminium and Dissolved Organic Carbon

Although clay mineral dissolution would release Al and Si into the soil solution, solution Al concentrations in soils 2–5 did not increase because of precipitation of Al phosphates (Fig. 2). It was only in the Kurosols (soils 1 and 6) that solution Al concentrations increased with increasing Si concentrations. The relationship between OD_{330} and solution Al concentration (Fig. 3) indicates that the organic compounds released under the acidic, high ionic strength conditions near the fertilizer band can complex the Al released in the Kurosols and prevent its precipitation. As lower levels of organic compounds were solubilized in the other soils (Fig. 3), the complexing ability of these compounds cannot be compared with those solubilized in the Kurosols. However, Moody *et al.* (1995*b*) concluded that the organic compounds solubilized in the Kurosol (soil 1) and the Kandosol (soil 4) were more effective at complexing Al than those solubilized in the other soils with MAP and DAP as the fertilizer sources. It is noteworthy that, in the absence of high concentrations of NH_4^+ , OD_{330} near MCP or MCP plus $CaSO_4 \cdot 2H_2O$ did not exceed 0.14 in soil 1 whereas, in proximity to DAP and MAP, maximum values were 0.59 and 0.16, respectively (Moody *et al.* 1995*b*).

Factors Affecting Relative Root Elongation

Bruce *et al.* (1988) used a slightly different method for calculating relative root growth responses than that used in this study, and it can be calculated that an RRE of 90% (as determined in the present study) is equivalent to 92% relative root length by the method used by Bruce *et al.* (1988). From the Mitscherlich equation of best fit presented in Bruce *et al.* (1988), pH_{SS} at 92% relative root length is 4.9, a slightly higher value than that obtained in our study (pH 4.5). Soil solution pH is a function of the activities of H^+ , Al^{3+} and hydroxy Al species. The close relationship between RRE and pH_{SS} across all soils indicates

that pH integrates the effects of Al, H and/or Mn toxicities on root growth near the fertilizer bands.

From the Mitscherlich equations of best fit presented in Bruce *et al.* (1988), values for a_{Al} and a_{AlOH} at 92% relative root length are 1.8 and 0.4 μM respectively. These values are in close agreement with those obtained for soils 2–5 in this study (1.6 and 0.4 μM respectively), and suggest that Al toxicity is contributing to reduced root elongation.

It is apparent from Fig. 8 that RRE data for the Kurosols (soils 1 and 6) lie above the regression curve obtained for soils 2–5. It is suggested that a_{Al} is overestimated in these soils because total Al in solution was measured and no allowances were made in the GEOCHEM speciation for organic ligands. This suggestion is supported by the higher concentrations of dissolved organic C in these soils and the close correlations between OD₃₃₀ of the soil solutions and a_{Al} . Because Bruce *et al.* (1988) measured monomeric Al in their study, they were able to ignore any organic complexing of Al. As the critical a_{Al} determined for soils 2–5 in the present work is similar to that obtained by Bruce *et al.* (1988), it is inferred that, in these topsoils, organic complexation of Al is negligible. The organic C contents of soils 2–5 varied from 0.2% to 3.4% (Moody *et al.* 1995a), while the contents of the Kurosols (soils 1 and 6) were 0.8% and 1.7% respectively. It is therefore not possible to infer the likelihood of significant organic complexation of Al from an examination of the organic C levels.

It is noteworthy that RRE data for soils 1 and 6 lay on the same soil solution pH response curve as the other soils (Fig. 7). This indicates that soil solution pH is a useful index of the biological effects of toxic Al monomeric species in solution when organic complexation of Al is present.

The possible effect of Mn toxicity on RRE has not been well documented (Scott and Fisher 1989), although MacFie *et al.* (1989) found that 4 and 8 days elapsed before root weights of two wheat (*Triticum aestivum* L.) cultivars were decreased by exposure to a nutrient solution of 500 μM Mn. In flowing solution culture, Edwards and Asher (1982) reported a 10% reduction in the whole plant dry matter yield of Wills soybean at a solution Mn concentration of 8.5 μM . This concentration is an order of magnitude lower than that reported here for a 10% reduction in RRE, and indicates that short term root elongation is much less sensitive to Mn toxicity than are plant growth processes over longer periods of time.

Neither Fe_{cd} nor Al_{cd} was significantly correlated with the distances from MCP or MCP plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ corresponding to a 10% reduction in RRE. This result is in contrast to the results obtained with DAP and MAP where Al_{cd} was highly significant (Moody *et al.* 1995b). Because the development of toxicities in the fertilizer zone of MCP is caused by the large decrease in soil solution pH, it is suggested that extractants used to indicate the potential for the development of Al and Mn toxicities should be acidic. The distances from MCP corresponding to 10% reductions in RRE were considerably less than those found for MAP or DAP; however, P did not move as far from MCP as it did where MAP or DAP were the P sources (Moody *et al.* 1995b).

Conclusions

Soils 1–5 were used by Moody *et al.* (1995a) to investigate the effects of banding various salts (namely $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , KNO_3 and $\text{Ca}(\text{NO}_3)_2$) on short term

root growth. It was shown in that study that only in the Kurosol (soil 1) did soil solution a_{Al} reach levels which could have restricted root elongation. The increase in a_{Al} in proximity to the soluble salts was due to the effect of increasing ionic strength as found by Bruce *et al.* (1989). However, it was concluded by Moody *et al.* (1995a) that osmotic effects, and not Al toxicity, were responsible for restricted root growth in the Kurosol. Using the same soils 1–5 and an additional Kurosol in the present study, Al toxicity has been identified as contributing to poor root growth in proximity to banded MCP and MCP plus $CaSO_4 \cdot 2H_2O$ in all soils. The increase in a_{Al} with these two fertilizers is primarily due to an effect of the reduced soil solution pH and not due to increased ionic strength.

The low soil pH in proximity to the fertilizer also caused an increase in soil solution Mn in all soils (albeit a small increase in soil 6 from 2 to 47 μM). This increased Mn activity reduced root elongation in addition to the Al toxicity effect. Short-term root elongation is less sensitive to Mn toxicity than other longer term growth parameters such as root weight and shoot growth. However, it is unlikely that the consequences of banding MCP or MCP plus $CaSO_4 \cdot 2H_2O$ would be manifested as a reduction in shoot growth because only a small proportion of the root system would be in a zone of high Mn.

While these results simulate a 'worst case' scenario (i.e. uni-directional diffusion and no mass flow of soil water), it is apparent that banded MCP and MCP plus $CaSO_4 \cdot 2H_2O$ can cause reduced root elongation through a combination of osmotic effects, and H, Mn and/or Al toxicity as a consequence of the low pH in proximity to the fertilizer band. As was demonstrated for banded DAP and MAP (Moody *et al.* 1995b), an evaluation of P availability from different fertilizers must take into account the effects of the fertilizer on soil solution composition, and therefore root growth, as well as the measurement of the chemical availability of the applied P.

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