

# Response of maize and potassium dynamics in Vertosols following potassium fertilization

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## Abstract

The application of potassium (K) fertilizer on maize and cotton crops grown on Vertosols in eastern Australia is yielding no response. The Vertosols contain abundant smectites and these 2:1 clay minerals often promote the fixation of K, making it unavailable for crop growth.

This study was undertaken to investigate the response of maize and K dynamics in two Vertosols following K fertilization. A glasshouse pot trial was conducted by growing four plants of *Zea mays* L. cv. Pioneer 3237. The samples were taken from Comet in Queensland and Quirindi in New South Wales, Australia. Both of these soils had a prior history of K deficiency in maize. The treatments consisted of factorial combination of four application rates of K (0, 20, 40 and 100 mg/kg) with two nitrogen (N) sources (NH<sub>4</sub> and NO<sub>3</sub>). All the treatments were replicated three times. Maize shoots of two plants from each pot were harvested at 46 and 79 days after sowing. Potassium fertilization had no significant effects on shoot dry matter yields, concentration and uptake of K and N in maize shoots. The nitrogen sources also had no significant influence on the K and N concentrations in the maize shoots.

The water soluble, exchangeable and non-exchangeable K pools were measured before and after the pot experiment. The water soluble K for both the soils decreased after the pot experiment. However, as expected, the exchangeable and non-exchangeable K levels for the Comet soil increased with K fertilization in samples taken after the pot experiment. The K dynamics for the Comet soil indicated that K was being released from mineral K to exchangeable and solution K pools. On the other hand, the exchangeable and non-exchangeable K levels for the Quirindi soil decreased, which resulted in less K being available for plants. The soil solution K for both the soils decreased after the pot experiment. In contrast to Comet soil, K was being fixed by smectite in the Quirindi soil. The Comet soil had slightly higher illite content than the Quirindi soil, where as the Quirindi soil contained more smectite. The small difference in the clay mineralogy of the two soils appears to be crucial to the fate of applied K and possibly explains the contrasting soil K dynamics.

## Key words

potassium fixation, ammonium fixation, illite, maize, non-exchangeable potassium, potassium forms.

## Introduction

Potassium (K) is usually the most abundant (~1%) major nutrient elements found in soil. Soil K is often sub-divided into water soluble, exchangeable, non-exchangeable and mineral forms. Potassium from water soluble and exchangeable pools is directly available for plant uptake. At low levels of exchangeable K and in certain soil types, non-exchangeable K can also contribute significantly to the plant uptake of K (Memon *et al.* 1988; Sharpley 1989). Exchangeable or available K, commonly measured by replacing with NH<sub>4</sub>OAc or NH<sub>4</sub>Cl, is held by negative charges on clay minerals and organic matter in soils. Non-exchangeable K is generally extracted using boiling nitric acid and consists predominantly of interlayer K<sup>+</sup> of non-expanded clay minerals such as illite and mineral or lattice K from K-minerals such as K-feldspars. A dynamic equilibrium exists between different forms of K in soils and the fate of applied K in soil is mainly governed by clay content and clay mineralogy of soil, and on the crops grown. Among swelling 2:1 layer silicates, vermiculite and beidellite have a higher K fixation capacity than montmorillonite (Ross and Cline 1984). Soil micas or illites have the capacity to fix or release K depending on the degree of weathering and some other factors (Tributh *et al.* 1987).

Vertosols in the north-west of Australia commonly have high levels of exchangeable K (> 400 mg/kg) down to depths of more than 1 metre (Wright 1998). Historically high removal rates by crops such as silage maize, lucerne hay and cotton have depleted soil K pools and K deficiencies have been observed in

crops on some Vertosols with exchangeable K > 300 mg/kg (Jonnie White pers. comm.). In some instances plant growth has not responded to moderate K application but has markedly improved with large K applications. Maize and cotton have a large biological demand for K with uptake of up to 5.2 and 3.7 kg K/ha/day, respectively during peak time (White 2000). Vertosols are commonly dominated by smectite clay mineral, which gives these soils a high potassium buffering capacity (PBC<sup>K</sup>). It is generally considered that soils with a high PBC<sup>K</sup> value, have adequate K supply for plant growth and a low PBC<sup>K</sup> suggests a need for frequent K fertilization (Sparks and Liebhardt 1981). The problem lies therein where these smectite rich soils simultaneously have a high K fixing capacity (Sharpley 1990). The high surface and layer charge density of the 2:1 clay minerals, including vermiculites and smectites, contributes to the fixation of applied K at the interlayer edges. This fixation process reduces the efficiency of applied K fertilizer since a large quantity becomes unavailable to plants. The chemistry of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> in soils is similar as both ions have low hydration energies and similar ionic radii and similar mechanism is responsible for the fixation of both NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> in the 2:1 clay minerals (Fanning *et al.* 1989). The limited number of fixation sites associated with some soils means that both the NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> ions compete for these sites when they are present in soil solution (Lumbanraja and Evangelou 1994). The consequence of this competition is that K<sup>+</sup> ions can become unavailable due to the presence of NH<sub>4</sub><sup>+</sup> ions.

The objectives of this study were to investigate the response of maize to applied K on Vertosols, and to evaluate soils K dynamics following K fertilization. The influence of NH<sub>4</sub> as a source of nitrogen on the K dynamics in soil was also evaluated.

### Materials and Methods

Soil samples (Vertosols) were taken from 2 locations in eastern Australia, Comet, in central Queensland and Quirindi, in north-west of New South Wales. The Quirindi soil had previously grown grain and silage maize. The Comet soil had grown silage maize and lucerne. Potassium deficiency has been observed in maize at both the locations. Soil samples were air-dried and passed through a 2 mm sieve before laboratory analysis. Soil pH and electrical conductivity were measured in soil water extracts using 1:5 soil solution ratios. The particle size analysis was determined by the International Pipette Method (Gee and Bauder 1986) after dispersing the soil in sodium hexametaphosphate solution. Exchangeable cations were extracted using 1 M NH<sub>4</sub>Cl (pH = 7) (Rayment and Higginson 1992). The resulting extractants were analysed for exchangeable Ca, Mg, Na, and K using a Varian SpectrAA 220FS atomic absorption spectrophotometer (AAS). The organic carbon content of soil was determined using the modified Walkley and Black method (McCleod 1975).

Measurement of the different K pools was carried out before and after the pot experiment to investigate the K dynamics of the soil. Soil solution K was extracted by shaking soil samples with deionised water using a soil solution ratio of 1:5 (Rayment and Higginson 1992). The exchangeable K was extracted by shaking 1 M NH<sub>4</sub>Cl for 1 h with a soil solution ratio of 1:20 (Rayment and Higginson 1992). The non-exchangeable K was extracted adding 25 ml of 1 M HNO<sub>3</sub> to 2.5 g of soil and boiling for 15 minutes (Helmke and Sparks, 1996). The total K was determined by a method described by Jackson (1958) which involved digesting 0.1 g of soil in a mixture of HF and HClO<sub>4</sub>. Potassium in different soil extracts was analysed using the AAS as described earlier.

### Glasshouse Experiment

A pot trial growing maize *Zea mays* L. cv. - Pioneer Hybrid 3237 was conducted in a glasshouse. Polythene lined plastic pots were filled with the two soils. On an oven dry basis, soil weights in each pot for Quirindi and Comet were 3.7 and 3.2 kg, respectively. The treatments consisted of a factorial combination of four K levels and two N sources. Potassium was applied at 0, 20, 40, 100 mg/kg with KCl. The 2 N sources, NO<sub>3</sub> and NH<sub>4</sub>, were applied at the rate of 35 mg/kg through NaNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, respectively. All treatments were replicated three times. A basal fertilizer application of 10 mg/kg P and 2.5 mg/kg Zn was applied initially to each pot through NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and ZnSO<sub>4</sub>·7H<sub>2</sub>O, respectively. Seven maize seeds were sown and were thinned to four plants after they reached a height of 5 cm. The plants were irrigated with deionised water on a regular basis to ensure that water was not a limiting factor. At 46 and 79 days after sowing, a harvest of the above ground material was made for two plants in each pot. The samples were dried at 60°C, weighed and ground. The roots could not be separated due to the extremely fibrous nature and due to the high clay content in both soils. The dry plant samples

were digested in a mixture of concentrated nitric and perchloric acid (Miller 1998) for K analysis using AAS. The plant nitrogen was analysed using a Leco CHN-1000 analyser.

The statistical analysis was performed using Genstat Release 6.1 (VSN Int., 2002).

## Results

### General Soil Characteristics

Several relevant soil properties are given in Table 1. Many of the general soil properties such as pH, EC and organic carbon are similar for both the Comet and Quirindi soils. The CEC of Quirindi soil is higher than the Comet soil, due to the higher smectite and clay contents of the former.

The clay mineralogical composition of the 2 soils is similar (data not presented here) with the presence of smectite, illite and kaolinite. The Comet soil contains slightly higher quantities of illite and kaolinite than the Quirindi soil whereas the Quirindi soil had a higher smectite content than the Comet soil.

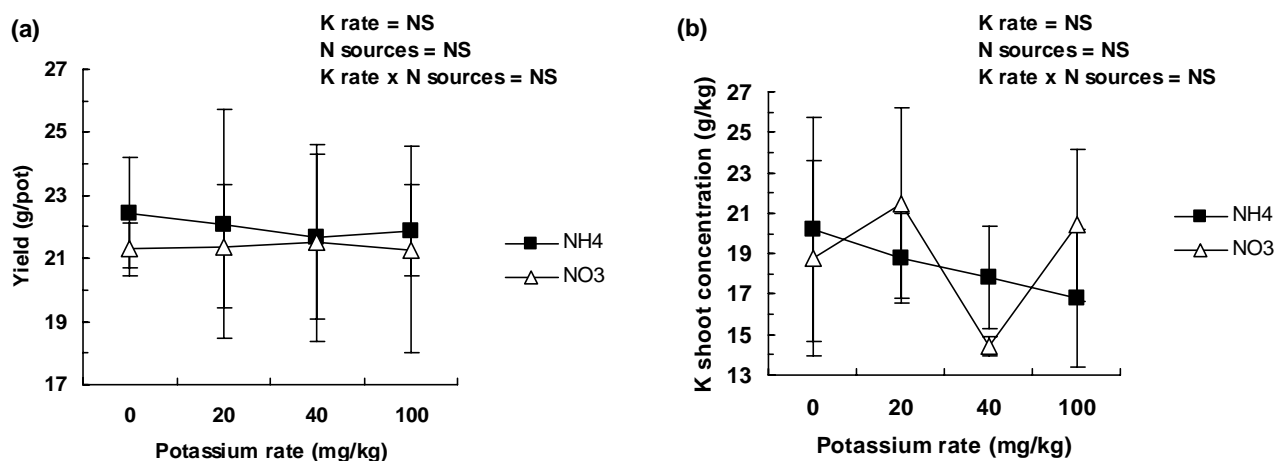
The random powder diffraction patterns for different size fractions showed that the clay minerals, including illite, mostly exist in the clay fraction with a very small amount was present in the silt fraction. Quartz and albite were the main minerals in the silt and sand fractions of the two soils.

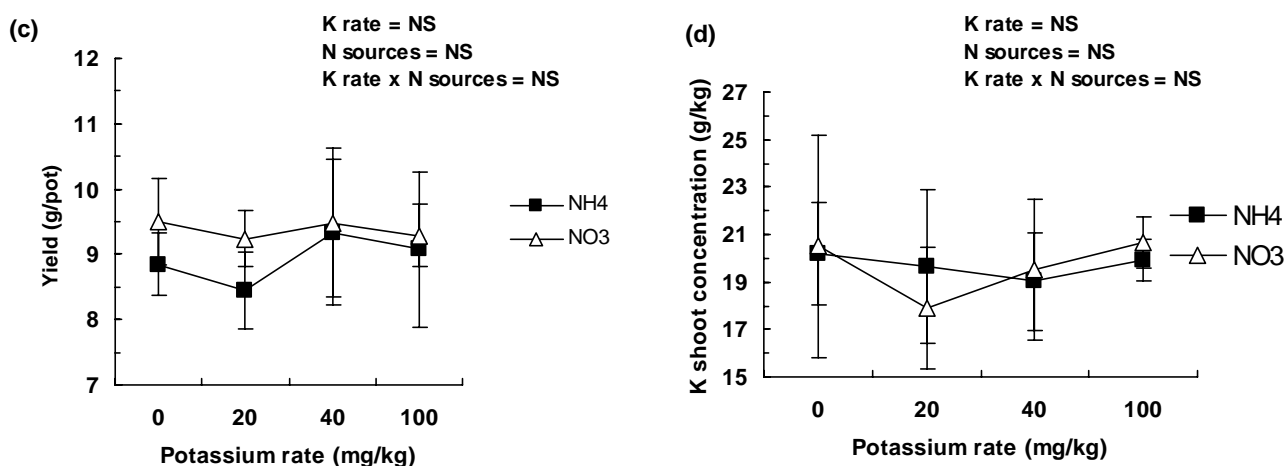
**Table 1. Chemical and physical soil properties of Comet and Quirindi soils**

Soil Property	Comet soil	Quirindi soil
pH (1:5 H <sub>2</sub> O)	8.8	8.9
EC (dS/m) (1:5 H <sub>2</sub> O)	0.19	0.20
Organic carbon (%)	1.31	1.19
Clay (%)	44	57
CEC (mmol <sub>c</sub> kg <sup>-1</sup> )	491	687
Exchangeable NO <sub>3</sub> (mg/kg)	64	33
Exchangeable NH <sub>4</sub> (mg/kg)	53	57
Non-Exchangeable NH <sub>4</sub> (mg/kg)	330	243
Water soluble K (mg/kg)	9.4	8.2
Exchangeable K (mg/kg)	428	551
Non-Exchangeable K (mg/kg)	1506	1723
Total K (mg/kg)	11870	11631
Potassium buffering capacity (mmol <sub>c</sub> /kg)/(mmol/L) <sup>1/2</sup>	1122	1652

### Maize Glasshouse Trial

The application of K fertilizer to the Comet and Quirindi soils did not have a significant effect on the shoot dry matter yield of maize. This was evident at both the first (data not presented here) and second harvests of maize for the two soils (Figure 1). The dry matter yields were also similar for the N-sources for the two soils at both the harvests. Shoot yields were generally much higher for the Comet soil than the Quirindi soil.





**Figure 1. Effects of K rates and N-sources on dry shoot matter yield (g/pot) and concentration in maize shoots (g/kg) at the second harvest for the Comet (a,b) and the Quirindi (c,d) soils.**

The K concentration of the maize shoots grown on the Comet and Quirindi soil was not significantly influenced by K treatments at the two harvests (data presented for second harvest only; Figures 1b,d). The two nitrogen sources also had no significant effect on the K concentration at both harvests. Similar to K concentration, no significant response was observed in K uptake by maize shoot in the two soils. This lack of response was evident for both the harvests. The uptake of K was also not significantly influenced by N sources for the 2 harvests. The uptake of K by maize shoot for the two harvests was much higher for the Comet soil (370-534 mg/pot) than the Quirindi soil (217-258 mg/pot).

Different application rates of K had no significant effect on the N shoot concentration (data not presented here) in the two soils and at both harvests. The source of nitrogen also did not have any significant influence on the N shoot concentration in maize grown in the studied soils.

#### *Potassium dynamics in soil*

Potassium contents in various forms in the original Comet and Quirindi soils are presented in Table 1. Quirindi has 29% more exchangeable K and 14% more non-exchangeable K than the Comet soil. However, the soil solution and total K content was slightly higher in the Comet soil than the Quirindi soil.

#### *Soil solution K*

There was a small increase in soil solution K of the Comet soil which was not statistically significant (Figure 2a). Figure 4a also shows that the difference between N sources was also non-significant between the N sources for this soil. Potassium application significantly increased soil solution K in the Quirindi soil (Figure 2b). There was an increase of 23% over 0 to 100 mg/kg K application rates in the presence of NH<sub>4</sub>-N and the corresponding increase was 17 % for the NO<sub>3</sub>-N. The difference between the nitrogen sources was statistically non-significant.

#### *Exchangeable K*

The exchangeable K of the Comet soil slightly increased with the increasing application of K (Figure 2c); however this effect was statistically non-significant. The difference between N sources also non-significant in the Comet soil. In Quirindi soil exchangeable K increased significantly increasing rate of K application and exchangeable K was significantly higher for NH<sub>4</sub>-N (392.9 mg/kg) than NO<sub>3</sub>-N (351.2 mg/kg) in this soil (Figure 2d). At each level of applied K in the presence of NH<sub>4</sub>-N there was a significant interaction with the K level above and below (Fig. //). This was evident at K 40 mg/kg and K 100 mg/kg with values of 346 mg/kg and 429 mg/kg, respectively.

#### *Non-exchangeable K*

In Comet soil increasing rate of K application significantly increased the non-exchangeable K (Figure 2e). This was more prominent in the presence of NO<sub>3</sub>-N, with an increase of 238 mg/kg over control with the application of 100 mg/kg K. The non-exchangeable K levels remained similar for different K treatments with NH<sub>4</sub>-N. A significantly large difference existed in quantities of non-exchangeable K for the Quirindi soil between the different nitrogen sources (Figure 2f). The non-exchangeable K was significantly higher

in the presence of  $\text{NO}_3\text{-N}$  (mean= 1614 mg/kg) than the  $\text{NH}_4\text{-N}$  (mean = 1496 mg/kg). Application of K did not significantly change the non-exchangeable content of the Quirindi soil (Figure 2f).

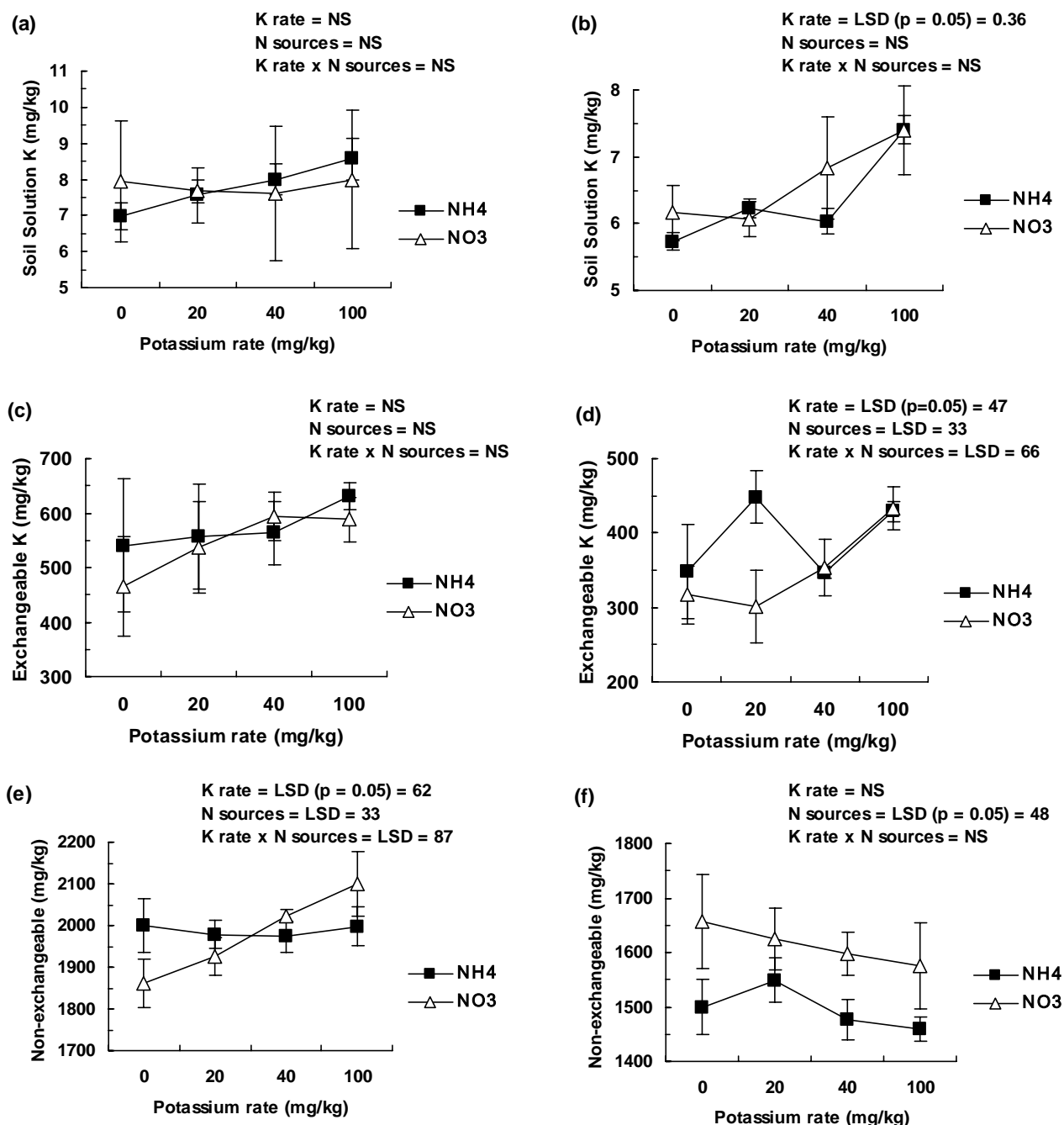


Figure 2. Effects of K rates and N-sources on soil solution, exchangeable and non-exchangeable K of the Comet (a, c and e) and the Quirindi (b, d and f) soils measured after the pot experiment.

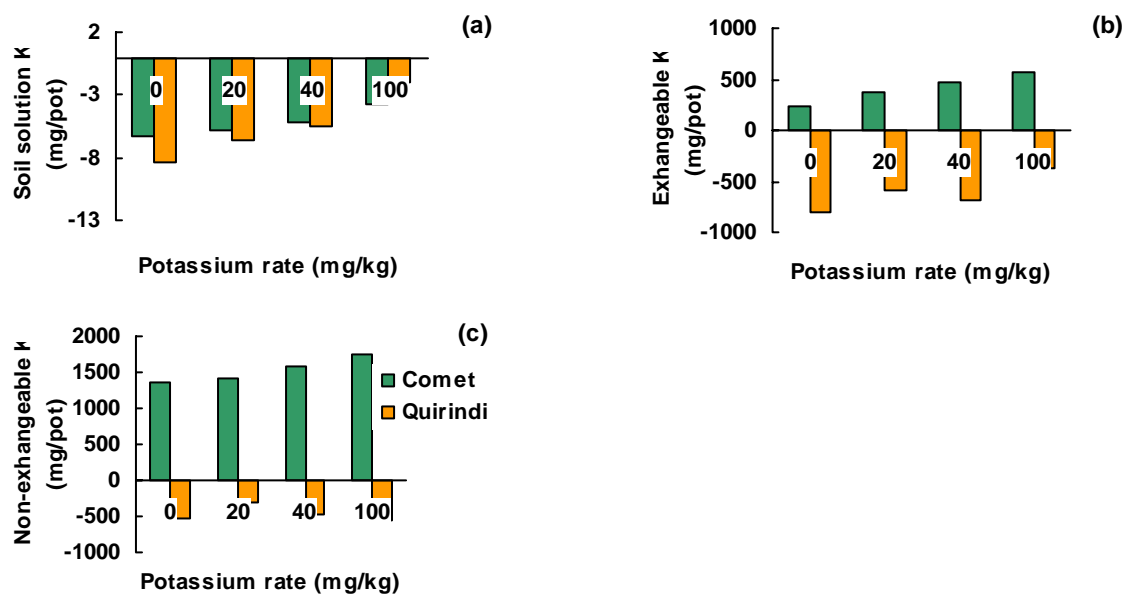
## Discussion

The trends in the dry matter yield of maize with K application were similar for the two soils. The non-responsive behaviour of maize in the pot experiment was a reflection of the soil K dynamics. Maize plants did not respond to the applied K for a number of reasons. The existing soil solution and exchangeable K were possibly adequate to supply the maize crop with sufficient levels of K. Commercial laboratories and agronomists in Australia currently use the critical value of 150 mg/kg (~4 mmol(+)/kg) for exchangeable K (Jonnie White pers. comm.). This conventional value is used as a benchmark for maize growing on Vertosols and soils are considered K deficient if the exchangeable K is below this threshold value. The exchangeable K levels (Table 1) were sufficient for maize growth in the studied

soils. The quantities of available K are not limiting, a growth response would not be expected. The dry matter yield data for the 2 harvests supports this hypothesis.

The K concentrations did not significantly change with K application for the two soils (Figure 1b,d). The results support the view that the maize plants had sufficient available K for plant growth. From a long term P and K applications study, Randall *et al.* (1997) reported that maize yields were optimised when leaf K concentrations occur between 11.4 and 22.9 g/kg. The concentration of K in maize shoots for all treatments occur within this range or above this range. It is important to consider that the trial was continued for 79 days after sowing. Further exhaustion of the soil K resource by growing maize to maturity could have led to yield responses due to applied K, considering that K deficiencies in maize have been reported at both these sites under field conditions.

One of the major aims of this study was to investigate the K dynamics of the soil following K fertilization. Measurement of the different K pools was carried out before and after the pot experiment. The content of K in the roots of the maize plants for both soils has not been accounted for due to the difficulty in extracting fine fibrous roots from the clayey soils. However, the total amount of K in plant roots was expected to be relatively small in comparison to the shifts in K between the soil K pools. There was a general decrease in soil solution K during the pot experiment (Figure 3 a,b) which can be attributed to plant uptake of K by the maize plants. The decline in soil solution K was greatest in control and was at its lowest at the highest application rate of K (Figure 3 a,b). The applied K readily moves into the soil solution pool, buffering soil solution K.



**Figure 3. Net gain or loss in (a) Soil solution K, (b) Exchangeable K and (c) Non-exchangeable K measured after the pot experiment in the Comet and the Quirindi soils.**

The exchangeable K pool in the Comet soil increased linearly at all K levels (Figure 3c). The observed increases in exchangeable K of Comet soil are well above amount of K added through K treatments indicating that K was released from the non-exchangeable and mineral K pools. The overall mean uptake of K by maize shoot was 475 mg/pot. Assuming that plant uptake of K was from the solution and exchangeable K pools, the maximum decrease in soil solution K was only 6.3 mg/pot. The uptake of K not decreasing the exchangeable K pool indicates that this pool is being buffered by the non-exchangeable K pool. Investigation of the non-exchangeable pool for the Comet soil indicates that there is a large increase in this pool as well (Fig. 3e). The average increase in non-exchangeable K in the Comet soil is 1526 mg/pot. With exchangeable K pool increasing simultaneously and K application not comparable to these large increases, the source for this K must be illite, the K containing mineral present in the soil. The higher total K value for the Comet soil compared to the Quirindi soil (Table 1) suggested that there is more illite in the Comet soil. Illite is an inherent source of soil K and its presence greatly influences the K supplying ability of a soil (Sparks 1987). The K dynamics of the Comet soil were such that the K moves

from the mineral K pool to the soil solution K pool. The Comet soil is supplying the maize plants with a luxury K uptake situation and the total plant K uptake values were generally twice than those of the Quirindi soil.

The major difference between the Quirindi and Comet soils starts at the exchangeable K pool. The exchangeable K pool decreased in the Quirindi soil, but increased in the Comet soil. The mean decrease in the exchangeable K pools across the K treatments of Quirindi soil was 613 mg/pot (Fig. 3b) and the mean plant uptake in this soil was 237 mg/pot. The large decrease in exchangeable K indicates that some K from the exchangeable pool had moved to the non-exchangeable and mineral pools. Examination of the non-exchangeable K pool in Quirindi soil indicated an average decrease of 465 mg/pot (Figure c). Although chemically definable K pools exist in soils, the transfer of K between the 2 pools may not always follow the same sequence. The movement of K into the mineral K pool was resulting in this K becoming fixed in the interlayer and frayed edges of illite and smectite. Sharpley (1990) observed a significant increase in K fixation in soils where smectite was the dominant clay mineral compared to mixed and kaolinite dominated soils. Zeng and Brown (2000) showed that wetting and drying cycles reduced plant growth and soil K supply, which contributed to the increased fixation and reduced mobility and plant availability of K.

The non-exchangeable K for Quirindi was significantly less for  $\text{NH}_4\text{-N}$  source (mean = 1459 mg/kg) than  $\text{NO}_3\text{-N}$  (mean = 1575 mg/kg) source. The implications of these results are that  $\text{NH}_4^+$  ions possibly cause the collapse of interlayer space and stop the release of some of the non-exchangeable K during the extraction procedure. The mechanism of  $\text{NH}_4^+$  ions in preventing the release of non-exchangeable  $\text{K}^+$  ions has been demonstrated in past studies (Lumbanraja and Evangelou 1994; Springob 1999). The combined non-exchangeable and exchangeable  $\text{NH}_4^+$  for the Quirindi soil was 300 mg/kg, while the non-exchangeable  $\text{K}^+$  was 1723 mg/kg (Table 1). These values indicate that the quantities of  $\text{NH}_4^+$  ions required to cause a significant blocking affect can be small and similar observations were made by Springob (1999). The lack of yield response due to K application suggests that the duration of the experiment was not long enough to exhaust the available K of the soil. With less buffering of the exchangeable and soil solution K due to the  $\text{NH}_4$  interaction, K deficiency in crops may be experienced at later stages of growth.

The  $\text{NH}_4^+$  ions were not blocking the fixation of  $\text{K}^+$  ions in the Quirindi soil. We hypothesise that the  $\text{NH}_4^+$  and  $\text{K}^+$  ions were moving into the interlayer of the clay minerals in a synergistic manner. The application of K did not significantly affect the quantities of  $\text{NH}_4^+$  ions fixed by the Quirindi soil (data not presented here). This is contrary to the results of other researchers (Osborne 1976; Hinman 1966) who observed that  $\text{K}^+$  and  $\text{NH}_4^+$  ions compete for binding sites in the interlayers. In the smectite rich Quirindi soil there are many more binding sites than are needed by the small quantities of  $\text{K}^+$  and  $\text{NH}_4^+$  ions present in the system.

The general shift of K for the Quirindi soil is towards the mineral K pool from the exchangeable pool. This movement of K between different pools has obvious implications on its plant availability. The lower uptake and dry matter yield in Quirindi soils than the Comet soil supports the notion of K fixation in the interlayers of smectite.

The potassium buffering capacity ( $\text{PBC}^{\text{K}}$ ) of the Quirindi soil is higher than the Comet soil (Table 1), which can be attributed to the higher clay and smectite contents of the Quirindi soil. The 2:1 clay minerals with an interlayered structure, high surface area, and high lattice charge (e.g. illite, vermiculite, smectite) fix K to a greater extent than clay minerals of low charge (such as kaolinite) (Pal *et al.* 1999). Sparks and Liebhardt (1981) suggested that a high  $\text{PBC}^{\text{K}}$  value for a soil indicates a good supply of K for a long period of time and that a low  $\text{PBC}^{\text{K}}$  indicates a need for frequent fertilization. This is probably true for the Comet soil, but in the Quirindi soil its high  $\text{PBC}^{\text{K}}$  leads to higher K fixation and limits K availability to plants.

The magnitude and location of charge in the smectite is also important in relation to the adsorption and fixation of  $\text{K}^+$  and  $\text{NH}_4^+$  ions (Singh and Heffernan 2002). These authors observed the presence of high charge smectites in Vertosols from north-west of New South Wales, Australia. The Quirindi soil comes from the same area and possibly contains high a layer charge smectite. The high layer charge smectites,

which form by the weathering of mica, behave like vermiculites, and have greater affinity and fixation capacities for  $K^+$  and  $NH_4^+$  ions. The weathering of micas over time creates sites in the interlayer where applied K can be readily fixed.

The K dynamics observed in the two soils suggests that a substantial gain in understanding could be made if field trials were conducted that measured all of the K pools before and after cropping. These simple measurements in conjunction the mineralogical composition of the soil can provide a good overview of the K dynamics in soil.

### Acknowledgments

The authors wish to thank Jonnie White from AGROW Australia Pty. Ltd for her assistance with soil sampling and their financial support of the project. We also acknowledge the help of Adrian Nelson (Pursehouse Rural) in soil sampling.

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