

# Kinetics of potassium release from Vertosols from northern NSW.

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## Abstract

Potassium release of four surface soils from cotton growing region of northern NSW was determined by continuous leaching with 0.01 M CaCl<sub>2</sub> and 0.01 M NH<sub>4</sub>Cl for 60 hr. The four samples represented two paired sites with similar soils but with the occurrence of premature senescence (PS) in cotton plants and no evidence for the occurrence of premature senescence i.e. Non-PS site. All soils contained abundant smectite and illite, kaolinite and interstratified minerals were present in small quantities. Cumulative K released by NH<sub>4</sub>Cl was higher than CaCl<sub>2</sub> for all the soils and it exceeded exchangeable K contents of the soils. Several mathematical models were fitted to the K release data but only Elovich and power function equations fitted the data adequately. The coefficients of these two equations were well correlated to different K forms. Discontinuities in the fitted equations indicate that K was released from different sites and possibly different mechanisms were involved. Further research is needed to determine the relationships between K release parameters and plant response to applied K.

## Key Words

Vertisols, kinetics, cotton soils, mica.

## Introduction

Potassium (K) is an essential plant nutrient and it is required in large quantities in cotton, often as much as nitrogen (N) or second only to N. Total soil K reserves of Vertosols, used for cotton growing in the northern NSW are high (1.68-2.32%) (Bedrossian and Singh 2004). Crop plants however, take K from solution and exchangeable fractions of soil, and often the amount of K in these pools is not high enough to meet crop demand. Consequently K is released from nonexchangeable and mineral fractions to maintain the equilibrium between different K pools in soil (Sparks 1987). The contribution of nonexchangeable K to plants is well recognised for a long time (Schmitz and Pratt 1953). The release of nonexchangeable K depends on several factors, and the amount and type of clay minerals are perhaps the most important of these factors (Martin and Sparks 1985). Smectites dominate the clay mineralogy of Vertosols in northern NSW and they are associated with small amounts of mica, kaolinite and an interstratified mineral (Singh and Heffernan 2002). The total layer charge of smectite in these soils is very high (0.55-0.67 mol(-)/(O10(OH)<sub>2</sub>)) and close to vermiculite, which means these soils may have a greater capacity to fix K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions than might be expected for Vertosols (Chen *et al.* 1989).

Vertosols in irrigated areas of northern NSW are predominantly used for cotton production. In the last few years cotton crop grown on these soils has shown premature senescence (PS) symptoms. Insufficient K in soil is implicated as the main contributing factor for the occurrence of PS in cotton. Cotton grown in soils with exchangeable K (1M NH<sub>4</sub>OAC extractable) levels greater than 150 mg/kg have shown PS symptoms (Wright 1999). Although exchangeable K is used widely to measure available K but it may not predict soil K availability accurately (Richards and Bates 1988). Bedrossian and Singh (2004) measured different K pools in soils from four paired sites with and without premature senescence, and plant availability of K could not be explained based on these measurements for some of the studies soils.

There is no information on the relationship between K release rates and the occurrence of K deficiency symptoms in field crops grown on these soils. Therefore, the research was undertaken to determine the K release kinetics from paired soils from PS and non-PS fields in northern NSW and to evaluate the relationships between K release parameters and the occurrence of PS symptoms in cotton.

## Materials and Methods

To evaluate the K release kinetics four surface soils (0-15 cm) were used. The samples were selected based on the results of a previous study on K forms and soil mineralogy of K (Bedrossian and Singh, 2004). The soils (Vertosols) used in this experiment were from the two paired soils (i.e. soils from PS

and Non-PS fields) at Moree and Pilliga in northern NSW. Soils were analysed for various chemical and physical properties using the methods described by Bedrossian and Singh (2004).

A continuous flow thin disk technique developed by Sparks *et al.* (1980) was used to study the kinetics of K release from the soil samples. The continuous flow method was selected because it provides data for the removal of desorbed species with time, which simulates K removal by plant uptake more closely than a batch technique (Bar-Tal *et al.* 1995). Soil samples were prepared for the experiment by first gently grinding samples to obtain < 1 mm fractions. This was done to obtain a uniform soil sample as only a small amount of soil was used in the kinetics study. The samples were then oven dried at 40 °C until constant weights were obtained.

Soil samples were used in their natural state as recommended by Springob and Richter (1998) and exchangeable K was not removed as has been suggested in several past kinetics studies (Havlin *et al.* 1985; Martin and Sparks 1983). To release K, 1 g sample of soil was placed between sand (~5 g) in a standard liquid chromatography column (Amersham Pharmacia Biotech XK 16/20 column) with a diameter of 16 mm. Whatman No. 40 filter papers were placed on both ends of the sand in the column to prevent any sample loss. Dry soil samples were used in order to delay hydration and the start of ion-exchange reactions until the electrolytic solution has come in contact with the soil in the column at the beginning of each run. Potassium from the samples was desorbed by continuously leaching with 0.01 M CaCl<sub>2</sub> for 60 hr. The leachates were collected using a Amersham Pharmacia Biotech Fraction Collector RediFrac with a carousel holding 95 plastic vials (5 ml capacity) leachates were collected at a rate of 1.25 ml/min for the first 6 hr, then 0.33 ml/min for the next 24 hr and finally 0.04 ml/min for the last 30 hr, using a Amersham Pharmacia Biotech P-1 Peristaltic Pump to maintain a constant flow of electrolyte solution. The time periods used in the experiment were determined based on a preliminary study on the soils used in the study and a previous study (Amer *et al.* 1955). Similar measurements were also made for all the samples using 0.01 M NH<sub>4</sub>Cl solution. The air temperature in the cabinet during the kinetics experiment was maintained at 23± 2 °C.

The leachate were analysed for K using a Varian Spectra AA 220FS atomic absorption spectrometer (AAS). Caesium chloride was added to obtain Cs concentrations of 2000 mg/L in the extracts as an ionising suppressant before AAS analysis.

**Table 1 General properties of the soil samples (0 – 15 cm) used in the study.**

Soil Property	Moree site		Pilliga site	
	Non-PS soil	PS soil	Non-PS soil	PS soil
pH (1:5, CaCl <sub>2</sub> )	5.88	5.68	7.36	7.16
EC (1:5 H <sub>2</sub> O, mS m <sup>-1</sup> )	35.1	3.1	18.4	16.1
OC (%)	2.4	2.6	2.4	1.2
Clay (%)	35	32	55	51
CEC (mmol <sub>c</sub> /kg)	29.7	193.3	356.9	324.5
Ca (mmol <sub>c</sub> /kg)	135.2	106.1	241.3	183.7
Mg (mmol <sub>c</sub> /kg)	5.7	6.0	12.0	11.0
Na (mmol <sub>c</sub> /kg)	25.3	25.0	26.4	35.3
<i>Clay mineralogy</i>				
Smectite (%)	76	83	66	68
Illite (%)	12	4	16	9
Kaolinite (%)	12	13	17	24
Water soluble K (mmol/kg)	0.019	0.007	0.068	0.023
Exchangeable K (mmol/kg)	2.02	2.30	17.57	5.65
Nonexchangeable K (mmol/kg)	5.91	4.78	42.43	16.19
Total K (mmol/kg)	256.2	74.5	344.7	184.7

## Results and discussion

Selected chemical and physical properties and clay mineralogy of the soils used in the study are given in Table 1. There is no systematic difference in soil pH, clay content and CEC between the soils at each site. Soil EC values were higher for the soil samples from the Non-PS fields than the PS fields of the Moree site. Organic carbon (OC) was higher in Non-PS sample than the PS sample from Pilliga. The CEC of samples from the Non-PS sites from both Pilliga and Moree sites were slightly higher than their corresponding samples from the PS sites.

Smectite was the dominant clay mineral in the studied soils. The K-bearing mineral illite was present in the clay fraction of all samples and its content was slightly higher in soils from the Non-PS fields than the PS fields for both Moree and Pilliga sites. The values of various K forms were generally higher in samples from the Non-PS fields than the PS fields from both Pilliga and Moree sites except that exchangeable K was higher in the PS sample than the Non-PS sample.

### Potassium release from soils

Potassium released by the two extractants (0.01 M  $\text{NH}_4\text{Cl}$  and 0.01 M  $\text{CaCl}_2$ ) over 60 hr periods were summed and plotted against time (Figure 1). The total quantity of K released over the 60 hr period using 0.01 M  $\text{CaCl}_2$  ranged from 1.60 to 17.65 mmol/kg. More K was released with 0.01 M  $\text{NH}_4\text{Cl}$  than 0.01 M  $\text{CaCl}_2$  from all soils, and the total K released varied between 2.49 and 19.98 mmol/kg. Initially K was released rapidly in all samples and then reached a plateau. The cumulative K released by  $\text{CaCl}_2$  and  $\text{NH}_4\text{Cl}$  solutions were found to be much higher in Pilliga than Moree soils (Figure 1) which is consistent with the exchangeable and non-exchangeable K contents of these soils.

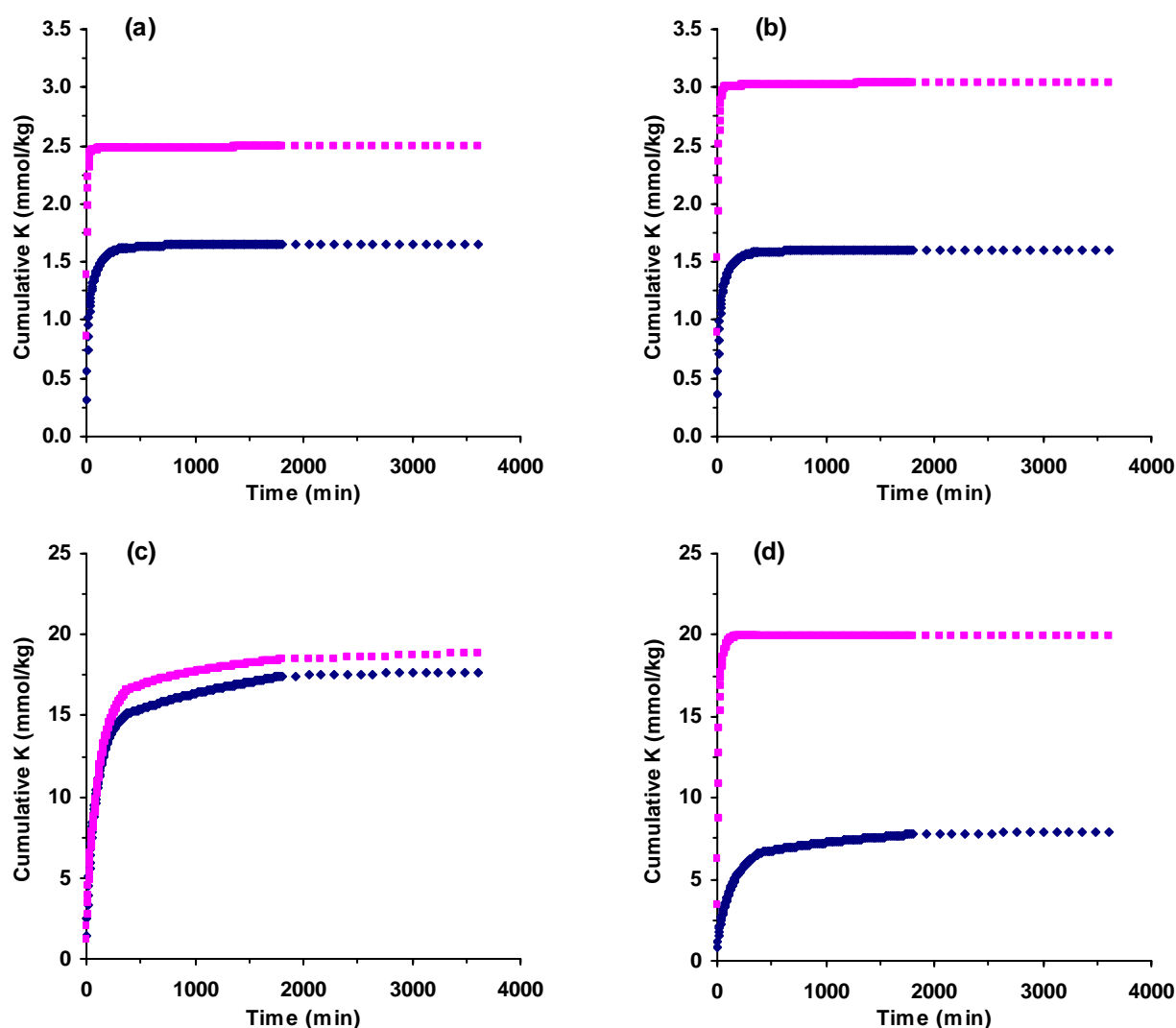


Figure 1. Cumulative potassium released from the studied soils with continuously percolated 0.01 M  $\text{CaCl}_2$  (◆) and 0.01 M  $\text{NH}_4\text{Cl}$  (■) solutions over 60 hr period. (a) Moree Non-PS, (b) Moree PS, (c) Pilliga Non-PS and (d) Pilliga PS.

Larger amounts of K were released with  $\text{NH}_4\text{Cl}$  from the PS samples at both Moree and Pilliga sites than their corresponding Non-PS samples. Potassium released by  $\text{CaCl}_2$  solutions were similar for Non-PS and PS samples from Moree, whereas for Pilliga site Non-PS soil released more than twice the amount of K released from the PS soil. Ammonium ions (0.143 nm) has a crystalline radius similar to  $\text{K}^+$  ions

(0.133 nm) so it is more effective in removing a portion of  $K^+$  ions from the wedge zones in illite compared to larger  $Ca^{2+}$  ions (Rich, 1964). Several other researchers have observed that solutions containing  $NH_4^+$  ions extract more K than Ca and Mg based extractants from soils containing illite (Martin and Sparks, 1983; Richards and Bates, 1988).

### K Releases Kinetics

Although the data not presented here, seven equations (zero-order, first-order, second-order, Elovich, simplified Elovich, parabolic diffusion and power function) were applied to K release data obtained for the two solutions. These equations were fitted to the K release data separately to the three time periods with varied leachate collections and the combined K release data over the 60 hr period. Only simplified Elovich and power function equations described the K release data adequately for all three periods. Here we report K release kinetics data for the first 6 hr for the two simplified Elovich and power function equations. The simplified Elovich equation is expressed as:

$C_t = a + b \ln t$  where  $C_t$  is the quantity of K released at time  $t$ , and  $a$  and  $b$  are coefficients.

The linear form of power function equation can be written as:

$\ln C_t = \ln a + b \ln t$ ; and the expressions in this equation are similar to the Elovich equation.

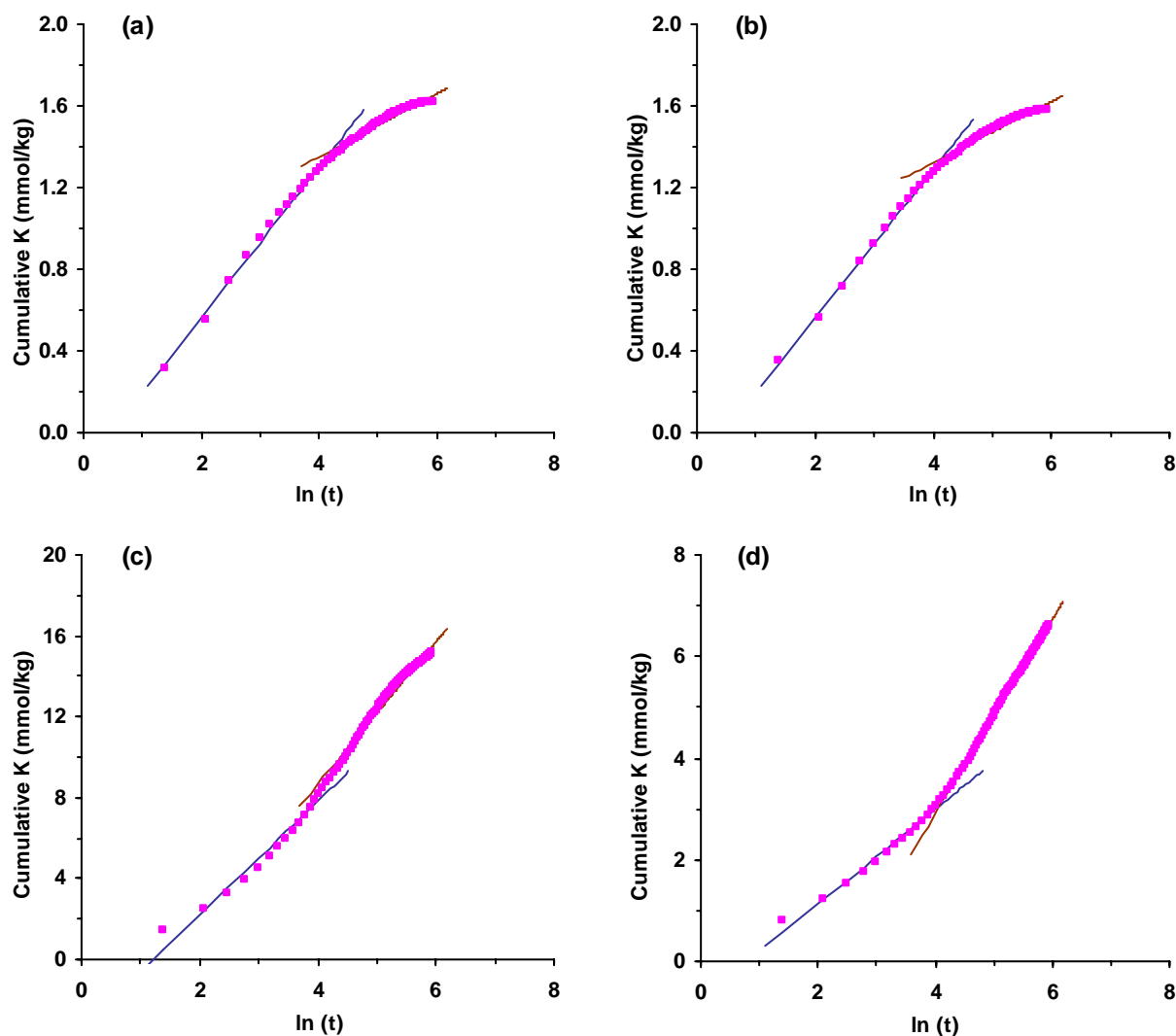
The kinetics parameters calculated for K release data (first 6 hr) are presented in Table 2. The results of statistical analysis showed that the two equations fitted better to the K release data obtained with  $CaCl_2$  than  $NH_4Cl$  for the soils used in the study.

**Table 2. Intercept and slope values for simplified Elovich and power function equations used to describe K release data during the first 6 hr 20 min for the soils. Coefficients of determination ( $r^2$ ) and standard error of the estimate (SE) for the two equations are also given.**

	$CaCl_2$					$NH_4Cl$				
	Time (min)	$a$	$b$	$r^2$	SE	Time (min)	$a$	$b$	$r^2$	SE
<b>Simplified Elovich: <math>C_t = a + b \ln(t)</math></b>										
Moree Non-PS	0 - 68	-0.180	0.370	1.00	0.019	0 - 40	-0.066	0.711	0.99	0.060
	68 - 380	0.730	0.155	0.96	0.015	40 - 380	2.416	0.010	0.59	0.004
Moree PS	0 - 56	-0.170	0.365	1.00	0.013	0 - 56	-0.115	0.805	0.99	0.071
	56 - 380	0.726	0.149	0.96	0.015	56 - 380	2.928	0.016	0.74	0.004
Pilliga Non-PS	0 - 72	-3.426	2.811	0.97	0.420	0 - 84	-3.969	2.823	0.96	0.467
	72 - 380	-5.396	3.516	0.98	0.217	84 - 380	-11.575	4.797	0.99	0.224
Pilliga PS	0 - 72	-0.720	0.928	0.98	0.103	0 - 52	-6.332	6.384	0.99	0.533
	72 - 380	-4.753	1.914	1.00	0.024	52 - 380	16.659	0.594	0.76	0.156
<b>Power function: <math>\ln(C_t) = \ln(a) + b \ln(t)</math></b>										
Moree Non-PS	0 - 32	0.145	0.625	0.98	0.073	0 - 40	0.520	0.452	0.95	0.079
	32 - 380	0.775	0.130	0.94	0.021	40 - 380	2.416	0.004	0.59	0.002
Moree PS	0 - 40	0.184	0.527	0.98	0.050	0 - 56	0.598	0.431	0.93	0.091
	40 - 380	0.826	0.114	0.94	0.017	56 - 380	2.929	0.005	0.73	0.001
Pilliga Non-PS	0 - 192	0.891	0.533	0.98	0.063	0 - 148	0.586	0.623	0.99	0.044
	192 - 380	5.377	0.175	0.99	0.003	148 - 380	3.148	0.282	0.99	0.009
Pilliga PS	0 - 152	0.457	0.473	1.00	0.022	0 - 40	1.331	0.735	0.99	0.065
	152 - 380	1.002	0.318	1.00	0.003	40 - 380	15.986	0.040	0.73	0.012

The plots of both Elovich and power functions equations showed discontinuity in slopes (two slopes in each graph) which is more obvious in K release curves for  $NH_4Cl$  (Figures 2 and 3). The coefficients  $a$  and  $b$  for the two sections of the equations were quite different (Table 2). The discontinuity in K release data for the two extractants occurred at different times and the time ranged between 32 and 192 minutes.

The value of coefficient  $a$  in the two equations indicates to some extent soluble and exchangeable K where as the coefficient  $b$ , which is the slope of fitted line, reflects the release rate or different site types from which K is released. For Moree site there was little or no difference in  $a$  and  $b$  coefficients of the simplified Elovich equations for the PS and the Non-PS samples. However in case of Pilliga site, the values for both coefficients were higher for the Non-PS sample than the PS sample in  $CaCl_2$  data and generally reverse was true for the  $NH_4Cl$  data. Similar to the Simplified Elovich equation the power function equation coefficients were also similar for the Moree samples. There was no consistent trend in the coefficients for the power function equation.



**Figure 2.** Observed (■) and predicted values (— & —), as described by simplified Elovich equation, of K released from the studied soils using 0.01 M CaCl<sub>2</sub>. (a) Moree Non-PS, (b) Moree PS, (c) Pilliga Non-PS and (d) Pilliga PS.

The coefficient  $a$  and the rate coefficient  $b$  of the simplified Elovich equation were correlated with water soluble, exchangeable and nonexchangeable forms of K. The correlations between the K forms and the two coefficients were better for the CaCl<sub>2</sub> data ( $r = 0.75-1.00$ ) than the NH<sub>4</sub>Cl data ( $r = 0.21-0.99$ ). The relationships between coefficients of the power function and K forms showed large variability. The coefficient  $a$  for the CaCl<sub>2</sub> data was highly correlated with exchangeable and nonexchangeable K, but relationships were very poor with parameter  $b$ ; and the reverse occurred in case of NH<sub>4</sub>Cl data. This variability in relationships with K forms may be due to K release from water soluble and exchangeable pools in the short time period considered here. Other soil properties such as clay, and CEC, generally showed good correlations with the coefficients of the two equations for both CaCl<sub>2</sub> and NH<sub>4</sub>Cl data.

The lack of conformity to the data was expected in the case of the zero order, first order and second order models since there was no pre-treatment undertaken for the removal of the water soluble and exchangeable K from the soils. Therefore, initially large amount of K was released rapidly due to mass action exchange of exchangeable K from the external surfaces of clay minerals. The difference in reaction time due to variable volume of solutions used in the study may also have contributed to poor fits for some of the equations. Several past studies indicate that K release may be a diffusion controlled process (Jardine and Sparks, 1984; Havlin and Westfall, 1985). However during the initial period diffusion controlled mechanism may not operate due to mass action exchange of K by Ca<sup>2+</sup> or NH<sub>4</sub><sup>+</sup> ions from external surfaces of illite and other clay minerals (Chute and Quirk; 1967). Discontinuity in plots of the Elovich equation were also observed by Havlin *et al.* (1985) for K release kinetics data of six Great

Plain soils from the USA. The authors attributed this to different mechanisms controlling K release processes in soils and similar mechanisms may be proposed for the soils used in the study.

The cumulative K released showed good correlation with the different forms of K in soils and there were significant differences between samples from the PS and the Non-PS sites. As pointed out by Havlin and Westfall, (1985) the best evidence of any equation to describe K release is the comparison of K rate and slope constants to plant growth response to applied K. Thus further research is required on these soils to predict the K release rate and potential.

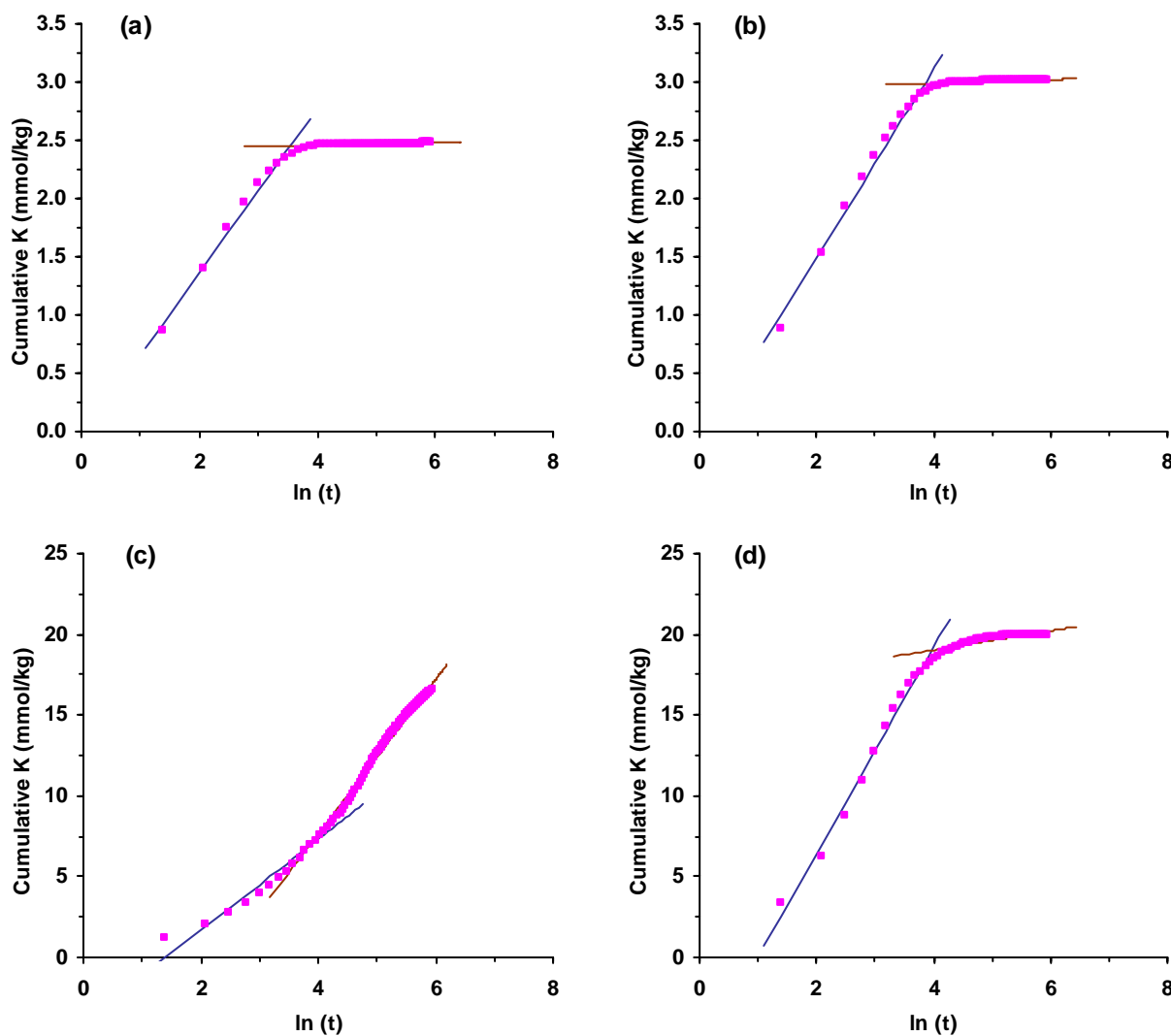


Figure 3. Observed (■) and Predicted values (— & —), as described by Simplified Elovich equation, of K released from the studied soils using 0.01 M NH<sub>4</sub>Cl. (a) Moree Non-PS, (b) Moree PS, (c) Pilliga Non-PS and (d) Pilliga PS.

### Conclusions

Except for Pilliga PS sample, K release in the soils was closely related to their exchangeable K contents. In Pilliga PS sample significant amount of K was released from non-exchangeable K pool. NH<sub>4</sub>Cl released more K than CaCl<sub>2</sub> in all the soils, which was due to release of K from the sites which are easily accessible to smaller NH<sub>4</sub><sup>+</sup> ions than hydrated Ca<sup>2+</sup> ions.

Elovich and power function equations described K release data well but there are clear breaks in the equations which may indicate K release from different sites. Initial rapid release of K was due to mass action exchange from external planner sites whereas slow releases at later stages indicate release of K from internal sites which is diffusion controlled. Kinetics parameters were generally well related to exchangeable and nonexchangeable forms of K in soils but further research is required to study the relationship between K parameters with plant response and uptake of K.

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