CSIRO PUBLISHING

www.publish.csiro.au/journals/ajsr *Australian Journal of Soil Research*, 2006, **44**, 265–275

Availability of soil potassium and diagnostic soil tests

P. W. Moody[A,C] *and M. J. Bell*[B]

[A]Queensland Department of Natural Resources, Mines and Water, Indooroopilly, Qld 4068, Australia.
[B]Queensland Department of Primary Industries and Fisheries, Kingaroy, Qld 4610, Australia.
[C]Corresponding author. Email: Phil.Moody@nrm.qld.gov.au

Abstract. Thirty-seven surface (0–0.10 or 0–0.20 m) soils covering a wide range of soil types (16 Vertosols, 6 Ferrosols, 6 Dermosols, 4 Hydrosols, 2 Kandosols, 1 Sodosol, 1 Rudosol, and 1 Chromosol) were exhaustively cropped in 2 glasshouse experiments. The test species were *Panicum maximum* cv. Green Panic in Experiment A and *Avena sativa* cv. Barcoo in Experiment B. Successive forage harvests were taken until the plants could no longer grow in most soils because of severe potassium (K) deficiency. Soil samples were taken prior to cropping and after the final harvest in both experiments, and also after the initial harvest in Experiment B. Samples were analysed for solution K, exchangeable K (Exch K), tetraphenyl borate extractable K for extraction periods of 15 min (TBK_{15}) and 60 min (TBK_{60}), and boiling nitric acid extractable K (Nitric K).

Inter-correlations between the initial levels of the various soil K parameters indicated that the following pools were in sequential equilibrium: solution K, Exch K, fast release fixed K [estimated as ($TBK_{15} -$ Exch K)], and slow release fixed K [estimated as ($TBK_{60} - TBK_{15}$)]. Structural K [estimated as (Nitric K $- TBK_{60}$)] was not correlated with any of the other pools. However, following exhaustive drawdown of soil K by cropping, structural K became correlated with solution K, suggesting dissolution of K minerals when solution K was low.

The change in the various K pools following cropping was correlated with K uptake at Harvest 1 (Experiment B only) and cumulative K uptake (both experiments). The change in Exch K for 30 soils was linearly related to cumulative K uptake ($r = 0.98$), although on average, K uptake was 35% higher than the change in Exch K. For the remaining 7 soils, K uptake considerably exceeded the change in Exch K. However, the changes in TBK_{15} and TBK_{60} were both highly linearly correlated with K uptake across all soils ($r = 0.95$ and 0.98, respectively). The slopes of the regression lines were not significantly different from unity, and the y-axis intercepts were very small. These results indicate that the plant is removing K from the TBK pool.

Although the change in Exch K did not consistently equate with K uptake across all soils, initial Exch K was highly correlated with K uptake ($r = 0.99$) if one Vertosol was omitted. Exchangeable K is therefore a satisfactory diagnostic indicator of soil K status for the current crop. However, the change in Exch K following K uptake is soil-dependent, and many soils with large amounts of TBK relative to Exch K were able to buffer changes in Exch K. These soils tended to be Vertosols occurring on floodplains. In contrast, 5 soils (a Dermosol, a Rudosol, a Kandosol, and 2 Hydrosols) with large amounts of TBK did not buffer decreases in Exch K caused by K uptake, indicating that the TBK pool in these soils was unavailable to plants under the conditions of these experiments. It is likely that K fertiliser recommendations will need to take account of whether the soil has TBK reserves, and the availability of these reserves, when deciding rates required to raise exchangeable K status to adequate levels.

Additional keywords: K uptake, soil K tests.

Introduction

Recently the Australian National Land and Water Audit calculated 'farm gate nutrient balances' (nutrient input in fertilisers, rainfall, and irrigation water minus nutrient removed off-site in harvested product) for each Statistical Local Area of the intensive land-use zone of Australia and concluded that a negative potassium (K) budget existed across many areas and cropping systems (Australian Agriculture Assessment 2001). At a regional scale, Bell and Moody (2001) identified that the major rain-fed cropping systems used in the Burnett region of southern Queensland had negative K budgets, indicating that crop requirements were being met from soil reserves. This is supported by evidence from 'paired sites' (cropped *v.* uncropped land) showing severe depletion of subsoil K in the Ferrosols of southern Queensland (Bell *et al.* 1995).

10.1071/SR05154 0004-9573/06/030265

From the viewpoint of sustainable production, it is essential to have measures of soil K reserves so that K fertiliser inputs can be adjusted to ensure that these reserves are not being exhausted.

Soil K pools

Soil K exists in several conceptual 'pools' of differing accessibility to plant roots and therefore of differing availability. The various soil K pools comprise: K in the soil solution, exchangeable K, 'fixed' K, and 'structural' K (Fig. 1). Exchangeable K is the K adsorbed onto soil particle surfaces by electrostatic attraction to negative charges comprising the cation exchange capacity of the soil. 'Fixed' K is K held between the platelets of 'shrink–swell' clay minerals such as illites and vermiculites (Syers 1998). 'Structural' K is a component of primary minerals such as feldspars or secondary minerals such as alunite (Sparks and Huang 1985). These various K pools are in equilibrium with each other, but the rate of attainment of equilibrium varies between pools. Exchangeable K and solution K are in an extremely dynamic equilibrium because a change in one causes an instantaneous change in the other. The replenishment of exchangeable K from the 'fixed' K pool depends on the clay platelets expanding so that K held between the platelets can move into solution or onto the exchange sites that are on exterior surfaces of the clay minerals. Amongst other factors, this rate is dependent on soil water content (clay platelets expand as soil moisture content increases; Mehta *et al*. 1992) and temperature (higher temperatures favour expansion of the clay platelets; McLean and Watson 1985). The release of 'structural' K depends on the dissolution rate of the primary and secondary minerals, and is dependent on the product of the activities of K and other elements in the soil solution being lower than the solubility product of the mineral.

Characterising soil K therefore requires measurement of the following: activity of soil solution K [this is often expressed as the K activity ratio (AR_K), which is calculated as: $a_K/(a_{Ca} + a_{Mg})^{1/2}$], exchangeable K, 'fixed' K, 'structural' K, rate of K release from the 'fixed' pool, and rate of K release from the 'structural' pool. Various methods have been described in the literature to measure these different K parameters (Table 1). For exchangeable K determination, there is little difference in the amount of K extracted by the 3 commonly used displacing solutions in Table 1 (Gillman *et al*. 1982). However, whether boiling HNO_3 extractable K (Nitric K) is similar in magnitude to K extracted by sodium tetraphenylborate (TBK) needs to be determined.

The objectives of this paper are to: (*i*) investigate the relationships between the soil K pools across soils of contrasting clay contents and mineralogies; and (*ii*) determine which soil K tests are best related to short-term and long-term (exhaustive) uptake of K by forage grasses grown on these soils.

Materials and methods

Soils

Two successive glasshouse experiments were used to measure K availability to a test species. Soils in Experiment A (designated A1–A11) were surface samples (0–0.10 m) of agricultural soils of the Burnett region, south-east Queensland, Australia. A wider range of agricultural soils was used in Experiment B (designated B1–B27), collected from north to south-east Queensland. All B soils were also surface (0–0.10 or 0–0.20 m) soils. Soil classifications and some basic soil properties are presented in Table 2.

Soil analyses

Samples were air-dried (40°C) and ground <2 mm prior to analysis. The following analyses were carried out:

(*i*) Soil solution K concentration was determined on 'A' soils only by raising the soil to −10 kPa soil matric suction, incubating at 25°C for 3 days, and then extracting the soil solution by centrifugation (20 min at RCF 2000*G*).

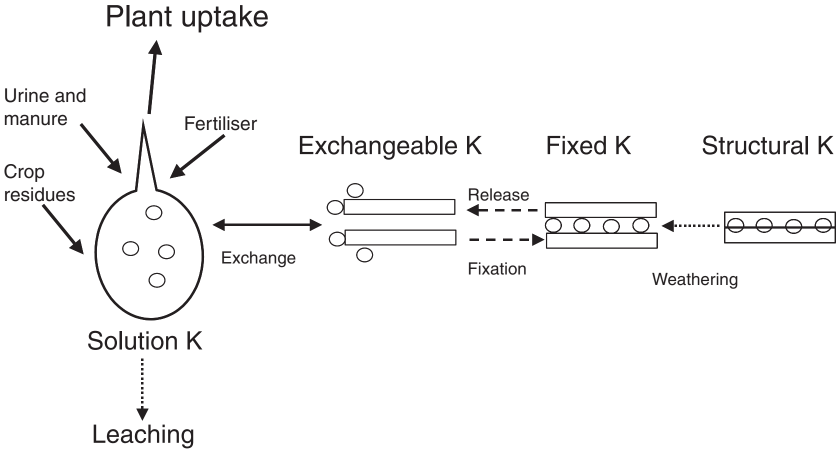

Fig. 1. The various soil K pools, and sources and loss pathways of K.

Table 1. Methods used to measure the various conceptual soil K pools

Soil K pool	Method	Reference
Soil solution K	Soil solution K	Menzies and Bell (1988)
	0.01 M $CaCl_2$ extr. K	McLean and Watson (1985)
Exchangeable K	1 M NH_4Cl	McLean and Watson (1985)
	1 M NH_4OAc	McLean and Watson (1985)
	0.1 M $BaCl_2$ + 0.1 M NH_4Cl	Gillman and Sumpter (1986)
‘Fixed’/‘structural’ K	Boiling HNO_3	Martin and Sparks (1985)
	Sodium tetraphenylborate	Cox *et al*. (1996)

(*ii*) $CaCl_2$-extractable K was determined by shaking (end-over-end) 5 g (<2 mm) soil in 25 mL 0.005 M $CaCl_2$ for 17 h, centrifuging the suspension (20 min at RCF 2000*G*), and measuring K in the supernatant.

(*iii*) Exchangeable K (Exch K) was determined by shaking (end-over-end) 4 g (<2 mm) soil in 80 mL of 1 M NH_4Cl (adjusted to pH 7 but unbuffered) for 1 h, centrifuging (20 min at RCF 2000*G*), and determining K concentration in the solution.

(*iv*) Tetraphenyl borate extractable K was determined following the procedure of Carey *et al*. (2000). Extraction times were 15 min (TBK_{15}) and 60 min (TBK_{60}).

(*v*) Boiling nitric acid extractable K (Nitric K) followed the method of Martin and Sparks (1985).

(*vi*) Soil pH was measured in water at a 1 : 5 soil : water ratio following a 30 min end-over-end shake.

Potassium was measured in all extracted solutions by atomic absorption spectrophotometry.

Table 2. Classification and some properties of the soils of Experiments A and B

Soil no.	Description	Australian Soil Classification[A]	Landscape position	pH (1 : 5 water)	EC (dS/m)	ECEC ($cmol_c$/kg)	Clay (%)
A1	G Steinhardt	Black Vertosol	Floodplain	6.7	0.06	28.3	49
A2	R Weldon	Black Vertosol	Upland	6.8	0.04	50.6	73
A3	P Ryan	Black Vertosol	Upland	8.1	0.07	35.3	48
A4	K Jorgensen	Red Ferrosol	Upland	5.7	0.09	10.9	66
A5	D Steinhardt	Brown Dermosol	Upland	6.5	0.03	10.9	35
A6	G Andersen	Red Ferrosol	Upland	6.8	0.07	16.8	51
A7	B Smith	Grey Vertosol	Floodplain	5.7	0.14	24.7	69
A8	J Thun	Brown Ferrosol	Upland	5.8	0.09	10.3	37
A9	D Scott	Black Vertosol	Upland	6.8	0.07	61.7	80
A10	Wecker B2 Dip	Black Vertosol	Upland	7.0	0.03	60.5	75
A11	Wecker B1 Hill	Black Vertosol	Upland	8.0	0.10	40.5	70
B1	Munro, Woodford Dale	Brown Dermosol	Floodplain	5.2	0.11	17.3	44
B2	Bauer-topsoil	Red Ferrosol	Upland	5.8	0.03	9.6	59
B3	Black	Grey Vertosol	Floodplain	6.1	0.14	39.7	61
B4	Larsen	Red Ferrosol	Upland	5.8	0.04	9.5	55
B5	Thompson	Black Vertosol	Floodplain	6.5	0.11	24.1	44
B6	R Weldon	Black Vertosol	Upland	6.6	0.03	43.7	66
B7	D Steinhardt	Brown Dermosol	Upland	6.9	0.04	14.1	37
B8	Wecker B2 Dip	Black Vertosol	Upland	6.5	0.03	61.5	70
B9	Scott	Black Vertosol	Upland	6.9	0.08	62.2	74
B10	Randall	Yellow Kandosol	Upland	6.2	0.03	1.7	2
B11	Smith	Grey Vertosol	Floodplain	5.7	0.15	24.8	66
B12	Krosch	Black Vertosol	Floodplain	6.9	0.17	35.0	44
B13	Biosolids site, Lowood	Black Vertosol	Floodplain	6.8	0.12	44.6	52
B14	Grey Sand, Herbert	Redoxic Hydrosol	Floodplain	5.9	0.02	1.7	2
B15	River Sand, Herbert	Rudosol	Floodplain	5.1	0.04	2.6	5
B16	Clay, Herbert	Redoxic Hydrosol	Floodplain	5.2	0.07	4.9	27
B17	Red Loam, Herbert	Red Kandosol	Floodplain	5.1	0.03	3.6	25
B18	Kelly	Brown Dermosol	Floodplain	5.2	0.03	23.6	50
B19	Sneesby	Redoxic Hydrosol	Floodplain	5.1	0.05	22.9	55
B20	Chapman, Bundaberg	Yellow Chromosol	Upland	6.1	0.08	3.9	14
B21	Harte, Bundaberg	Red Dermosol	Upland	6.6	0.04	4.5	11
B23	Santalucia	Redoxic Hydrosol	Floodplain	5.7	0.03	1.3	6
B24	Dingle	Grey Sodolsol	Floodplain	8.4	0.11	24.6	10
B25	Hubert	Red Dermosol	Upland	6.1	0.05	2.7	9
B26	Thomas	Brown Ferrosol	Upland	7.0	0.04	17.1	44
B27	Jooste	Black Vertosol	Floodplain	6.5	0.05	51.9	52

[A] Isbell (1996).

K depletion experiments

Soil was weighed into freely draining, 0.15-m-diameter pots fitted with drip trays, in a glasshouse. There were 2 treatments per soil: nil applied K and K applied as K_2SO_4 at a rate equivalent on an area basis to 70 kg K/ha. Basal nutrients were applied in solution form to all pots at the following rates (kg/ha) calculated on an area basis: N, 70; P, 50; Ca, 30; Mg, 30; S, 40; Zn, 5; Cu, 5; B, 1; and Mo, 0.2. The entire contents of each pot were allowed to dry and thoroughly mixed. The soil was then watered to −10 kPa matric suction (field capacity) and incubated for 7days. In Experiment A, seeds of *Panicum maximum* cv. Green Panic were sown in each pot and thinned to 10 plants following establishment. In Experiment B, forage oats (*Avena sativa* cv. Barcoo) were used as the test species, with 15 seeds planted per pot and thinned to 10 plants after establishment. In both experiments, pots were watered daily and any drainage returned to the soil surface. Plants were cut at a height of 2 cm following a suitable growth period, dried, weighed, ground, and analysed for Ca, Mg, and K using X-ray fluorescence. Nitrogen, and N + K in the case of the +K pots, were re-applied after each harvest at rates (kg/ha) equivalent on an area basis to 70 N and 70 K. Basal nutrients were re-applied every second harvest at the above rates.

A maximum of 9 harvests were taken in Experiment A over the period 25 September 2000 to 30 April 2001, whereas a maximum of 5 harvests were taken in Experiment B over the period 27 May 2003 to 2 October 2003. Experimentation was terminated for most soils when plants no longer re-grew after a harvest because of severe K deficiency. In both experiments, soil samples were taken before planting and after the final harvest, and also after the first harvest in Experiment B.

Results and discussion

Soils

The soils of Experiments A and B represented a wide range of soil types and basic soil properties (Table 2). Clay content ranged from 2 to 80%, ECEC ranged from 1.3 to 62.2 $cmol_c$/kg, and pH_w ranged from 5.1 to 8.4. Measured soil K parameters are presented in Table 3.

Table 3. K parameters of the soils of Experiments A and B and plant K uptake

Soil no.	$CaCl_2$-K (mg/kg)	Exch K	K satn (%)	TBK_{15}	TBK_{60} (mg/kg)	Nitric K	Total K (%)	K uptake (mg/kg) Harvest 1	Cumulative
A1	46.1	254	2.3	607	907	1013	n.d.	256	603
A2	18.7	164	0.8	188	202	399	n.d.	93.0	199
A3	17.9	125	0.9	150	173	372	n.d.	48.1	136
A4	74.4	198	5.9	209	212	426	n.d.	120	285
A5	11.6	58.7	1.4	84.6	89.1	188	n.d.	23.7	81.3
A6	74.4	223	4.0	209	240	387	n.d.	111	273
A7	172	626	6.5	832	817	1114	n.d.	285	796
A8	66.5	174	5.8	182	300	465	n.d.	116	235
A9	13.2	125	0.5	145	131	301	n.d.	79.5	170
A10	13.4	156	0.7	169	162	418	n.d.	104	164
A11	15.0	129	0.8	169	182	442	n.d.	74.1	178
B1	6.1	132	1.9	588	1017	1032	1.49	85.8	133
B2	9.8	77.0	2.1	101	97.6	164	0.12	32.4	67.5
B3	34.3	283	1.8	441	472	1134	0.91	190	319
B4	139	575	15.5	759	743	911	0.25	233	604
B5	40.2	267	2.8	903	1093	1533	1.29	203	400
B6	11.9	141	0.8	184	160	297	0.16	118	158
B7	1.8	53.9	1.0	70.1	67.7	137	0.10	29.5	41.0
B8	12.1	186	0.8	197	200	422	0.17	136	206
B9	11.3	154	0.6	167	161	301	0.10	115	162
B10	12.7	30.0	4.6	27.7	28.2	35.2	0.04	20.8	20.8
B11	152	699	7.2	985	1066	1146	0.30	368	820
B12	29.9	260	1.9	345	342	966	1.16	167	287
B13	40.0	398	2.3	765	762	1138	0.89	254	434
B14	23.3	39.7	6.1	47.8	61.0	125	0.31	30.5	30.5
B15	60.6	95.4	9.5	229	301	657	2.49	77.5	103
B16	24.7	74.6	3.9	165	268	461	2.15	63.3	77.7
B17	49.4	112	7.9	342	462	856	2.45	94.4	115
B18	32.6	187	2.0	412	483	501	0.72	156	254
B19	20.7	179	2.0	527	700	540	0.88	136	198
B20	46.6	70.8	4.6	77.4	75.5	86.0	0.04	59.3	78.3
B21	50.4	78.2	4.4	90.9	79.4	102	0.06	66.1	78.6
B23	30.2	46.2	9.3	48.3	38.9	50.8	0.04	33.5	33.5
B24	14.4	56.9	0.6	79.0	66.6	93.8	0.08	38.4	38.4
B25	72.8	109	10.4	128	117	129	0.06	84.9	109
B26	9.3	107	1.6	135	121	250	0.13	65.6	93.7
B27	41.3	337	1.7	521	527	708	0.54	251	463

n.d., Not determined.

Measurement of solution K

Soil solution K can be measured as the soil solution K concentration, or K extracted by 0.005 M $CaCl_2$. For Experiment A soils, soil solution K concentration was highly linearly correlated ($P < 0.001$) with soil solution K activity ratio, AR_K ($r = 0.99$, $n = 11$), and with $CaCl_2$-extractable K ($r = 0.98$, $n = 11$). The latter method is well suited to routine determination, and we use this method as an estimate of soil solution K concentration in this paper.

Relationship between exchangeable K and tetraphenyl borate extractable K (15 min)

In soils with little or no structural or fixed K, it could be expected that levels of Exch K and short-term (15 min) tetraphenyl borate extractable K (TBK_{15}) would be similar. This was the case for 22 soils, with the regression line (Eqn 1) having a slope not significantly ($P = 0.05$) different from unity, and a small positive intercept (Fig. 2). Units are mg K/kg soil:

$$TBK_{15} = 0.972(\pm 0.046)\ \text{Exch K} + 19.35(\pm 5.80) \quad (R^2 = 0.958,\ P < 0.001, n = 22) \qquad (1)$$

However, soils A1, A7, B1, B3, B4, B5, B11, B12, B13, B15, B16, B17, B18, B19, and B27 had more TBK_{15} than Exch K, indicating reserves of fast release fixed or structural K (Fig. 2). The increased percentage of K extracted by TBK_{15} over Exch K ranged from 27% (B12) to 342% (B1). With the exception of B4 (a Ferrosol), all these soils occurred on floodplains/terraces and comprised 8 Vertosols, 2 Hydrosols, 2 Dermosols, a Kandosol, and a Rudosol.

Relationship between tetraphenyl borate extractable K at 15 min and 60 min

In addition to the 15-min extraction period, K was also extracted by tetraphenyl borate for 60 min. Where substantial reserves of fixed and/or structural K exist, the amount of K extracted by tetraphenyl borate would be expected to increase with time of extraction. However, for 31 of the soils, the amount of K extracted in 60 min was not significantly ($P = 0.05$) different from that extracted in 15 min. Equation 2 indicates the relationship between TBK_{15} and TBK_{60} for these soils. Units are mg K/kg soil:

$$TBK_{60} = 1.025(\pm 0.029)\ TBK_{15} + 6.30(\pm 9.77) \quad (R^2 = 0.986,\ P < 0.001, n = 32) \qquad (2)$$

The following soils were outliers from this equation: A1, B1, B5, B17, and B19. For these soils, the increased percentage of TBK_{60} over TBK_{15} ranged from 21% (B5) to 75% (B1), indicating varying levels of slow release K reserves. These soils are Vertosols (A1, B5), a Dermosol (B1), a Hydrosol (B19), and a Kandosol (B17). All these soils occurred on floodplains.

Relationships between nitric acid extractable K and tetraphenyl borate extractable K at 15 min and 60 min

For combined data of the A and B soils, there was a strong linear correlation between Nitric K and TBK_{15} ($r = 0.81$, $P < 0.001$) and between Nitric K and TBK_{60} ($r = 0.81$, $P < 0.001$). The slopes of the regression lines indicated that, on average, Nitric K extracted 36% more K than TBK_{15} and 4% more than TBK_{60}. Both regression lines had significant

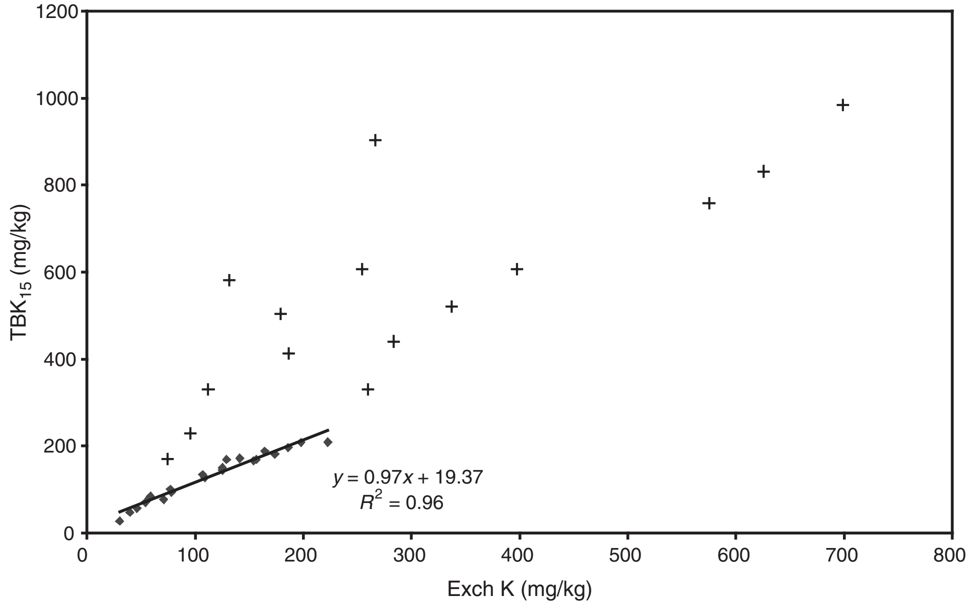

Fig. 2. Relationship between exchangeable K and tetraphenyl borate extractable K (15 min) for 37 soils. The slope of the plotted regression line for 22 soils is not significantly ($P = 0.05$) different from 1.0.

($P < 0.05$) positive *y*-axis (Nitric K) intercepts (111 and 137 mg K/kg for TBK_{15} and TBK_{60}, respectively), indicating that at zero TBK, Nitric K still extracted K, possibly by acid dissolution of soil minerals.

Estimation of soil K pools

On the basis of the above results, Table 4 presents a framework of methodologies for measuring the various soil K pools identified in Fig. 1. There is no sound empirical methodology for separating fixed from structural K, but the use of tetraphenyl borate extraction allows K pools to be differentiated on the basis of rate of release. It is assumed that K released by boiling nitric acid (Nitric K) over and above that released as TBK_{60} must be present in structural form. The availability to plants of K in the pools identified in Table 4 was assessed in the glasshouse experiments.

Inter-correlations between soil K pools

In Experiment B, all soil K parameters were measured prior to cropping and again at the end of the experiment following exhaustive K removal by the crop. This allowed investigation of the effects of K removal on the equilibrium between the K pools. Table 5 indicates that prior to cropping (‘Initial’) there is a strong correlation between $CaCl_2$-K (i.e. soil solution K) and (Exch K − $CaCl_2$-K). There is also a positive correlation between (Exch K − $CaCl_2$-K) and the additional K released by tetraphenyl borate over 15 min, and between this K and the extra K released to tetraphenyl borate over 60 min. The structural K pool (Nitric K − TBK_{60}) was not correlated with any of the other pools. It can therefore be inferred that the soil solution, exchangeable, and fast and slow release fixed K pools are interlinked, but the structural K pool is independent of the others. The lack of correlation between soil solution K ($CaCl_2$-K) and fast release fixed K (TBK_{15} − Exch K) suggests that these 2 pools are linked through the exchangeable K pool. These results indicate that the ‘series’ representation of the K pools in Fig. 1 requires alteration such that the structural pool is represented as being independent of the other pools (Fig. 3).

Table 4. Framework for measuring conceptual soil K pools

Soil K pool	Measure
Soil solution K	$CaCl_2$-extractable K
Exchangeable K	(Exch K − $CaCl_2$-K)
Fast release fixed K	(TBK_{15} − Exch K)
Slow release fixed/structural K	(TBK_{60} − TBK_{15})
Structural K	(Nitric K − TBK_{60})

Table 5. Correlation coefficients (*r*) between the soil K pools for the 26 B soils prior to planting (initial) and following exhaustive K removal by the crop (postharvest)

Soil K pool	Exch K − $CaCl_2$-K	TBK_{15} − Exch K	TBK_{60} − TBK_{15}	Nitric K − TBK_{60}
		Initial		
$CaCl_2$-K	0.647***	0.232	−0.100	0.102
Exch K − $CaCl_2$-K		0.465***	0.142	0.290
TBK_{15} − Exch K			0.716***	0.104
TBK_{60} − TBK_{15}				−0.169
		Postharvest		
$CaCl_2$-K	0.812***	0.372*	0.014	0.617***
Exch K − $CaCl_2$-K		0.361*	0.134	0.586***
TBK_{15} − Exch K			0.811***	−0.027
TBK_{60} − TBK_{15}				−0.294

*$P < 0.05$; ***$P < 0.001$.

However, post-harvest, there was a significant correlation between $CaCl_2$-K and (Nitric K − TBK_{60}). This correlation was also significant after Harvest 1 ($r = 0.406$, $P < 0.05$, data not shown). These results provide circumstantial evidence that the structural pool contributes K to the soil solution following exhaustive K removal. This is in contrast to the situation when little or no K removal has occurred (viz. ‘Initial’ samples) and the structural K pool is not correlated with the soil solution (or any other) pool. These results suggest that there might be a threshold soil solution concentration below which the structural K pool begins to provide soluble K through dissolution.

Diagnostic soil tests for K

For a soil test to be useful diagnostically, there must be a high correlation between the soil test taken prior to planting and subsequent K uptake by the crop. To assess the diagnostic usefulness of the measured soil K parameters, the initial value of each parameter was correlated with Harvest 1 K uptakes and cumulative K uptakes for the combined data of both experiments (Table 6). No attempt was made to calculate the various K pools as was done in the previous section. Consequently, Exch K includes solution K; TBK_{15} and TBK_{60} include Exch K; Nitric K probably includes TBK.

Plant K uptakes were highly correlated with the initial values of all the measured soil K parameters except K saturation (Table 6). However, Exch K and TBK_{15} were both consistently better correlated with K uptake than any

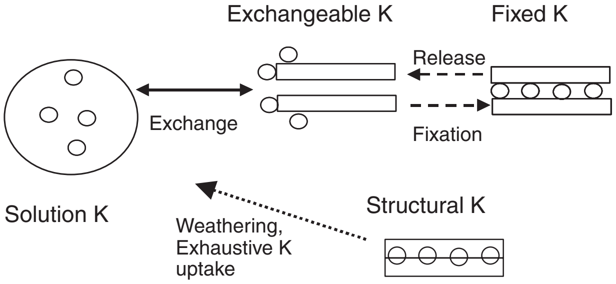

Fig. 3. Interactions between the various soil K pools.

Table 6. Correlation coefficients (*r*) between K uptake and soil K parameters
All coefficients are significant at $P < 0.001$ except those labelled n.s. (not significant at $P = 0.05$)

Experiment/harvest	$CaCl_2$-K	Exch K	K satn	TBK_{15}	TBK_{60}	Nitric K
A, Harvest 1	0.759	0.864	0.304n.s.	0.961	0.957	0.973
A, Cumulative	0.825	0.919	0.149n.s.	0.990	0.950	0.970
B, Harvest 1	0.656	0.951	0.007n.s.	0.889	0.773	0.777
B, Cumulative	0.746	0.988	0.042n.s.	0.890	0.768	0.742

of the other parameters except for Nitric K for Harvest 1 in Experiment A. Figure 4 indicates the relationship between cumulative K uptake and initial Exch K. Soil A1 is an obvious outlier with a much higher cumulative K uptake than would be expected from the level of Exch K in this soil. When Soil A1 is omitted from the regression between cumulative K uptake and initial Exch K, the slope of the linear equation of best fit is 1.21, indicating that, on average, 21% more K is taken up from soil than is present as Exch K. Fixed and/or structural K reserves are therefore being exploited by the plant.

To further investigate this finding, cumulative K uptake was related to the change (initial level minus level after final harvest) in the various K parameters. Soil K data were only available for B soils at Harvest 1, but for both A and B soils at the end of the experiments.

Availability of K from different soil K pools

Six soils (B3, B5, B12, B13, B18, B27) were outliers in the relationship between the change in Exch K and K uptake at Harvest 1 of Experiment B (Fig. 5), with an additional soil (A1) being an outlier when cumulative K uptake by all A and B soils was considered (Fig. 6). The regression equations are presented:

$$\text{K Uptake Harvest 1} = 1.097(\pm 0.033)\Delta\text{Exch K} + 8.9(\pm 3.4) \quad (R^2 = 0.982,\ P < 0.001,\ n = 20) \tag{3}$$

$$\text{K Uptake Cumulative} = 1.353(\pm 0.041)\Delta\text{Exch K} + 12.93(\pm 11.4) \quad (R^2 = 0.987,\ P < 0.001,\ n = 30) \tag{4}$$

The change in Exch K per unit of K uptake by the plant tops was not significantly ($P = 0.05$) different from unity at Harvest 1 for 20 of the 26 soils (Eqn 3), but an average of 35% more K was removed by cumulative K uptake than was reflected in a change in Exch K in 30 of the 37 soils (Eqn 4). This indicates that Exch K was being replenished from other pools as it was exhaustively removed by plant uptake. This was particularly the case with the outlying soils, where cumulative K uptake was up to 300% higher than the change in Exch K (Fig. 6).

Changes in TBK_{15} per unit of K uptake by plant tops at Harvest 1 were not significantly ($P = 0.05$) different from a 1 : 1 relationship (Eqn 5), but changes in TBK_{60} over-

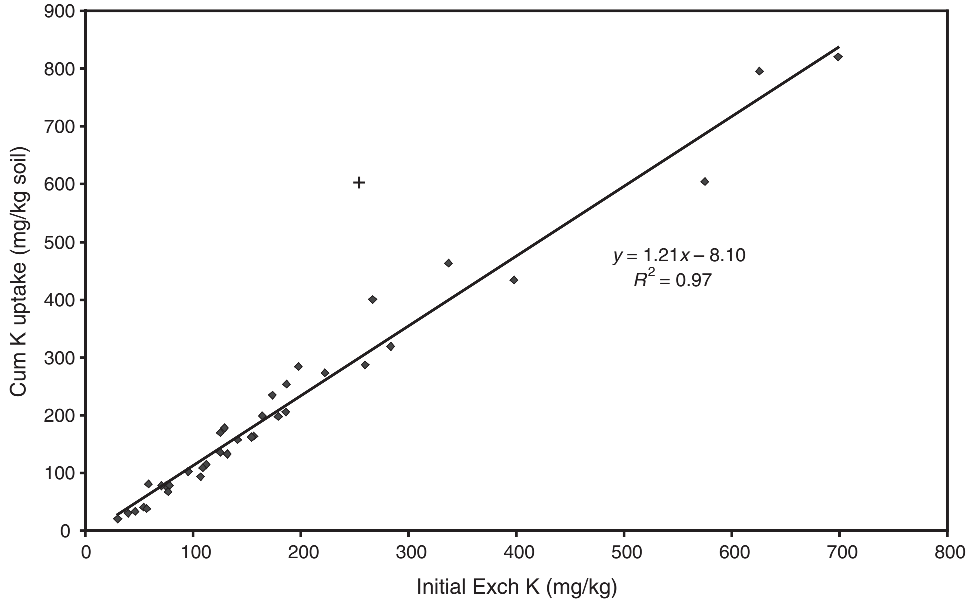

Fig. 4. Relationship between initial exchangeable K and cumulative K uptake for 37 soils. The regression line is for 36 soils, omitting soil A1 (+).

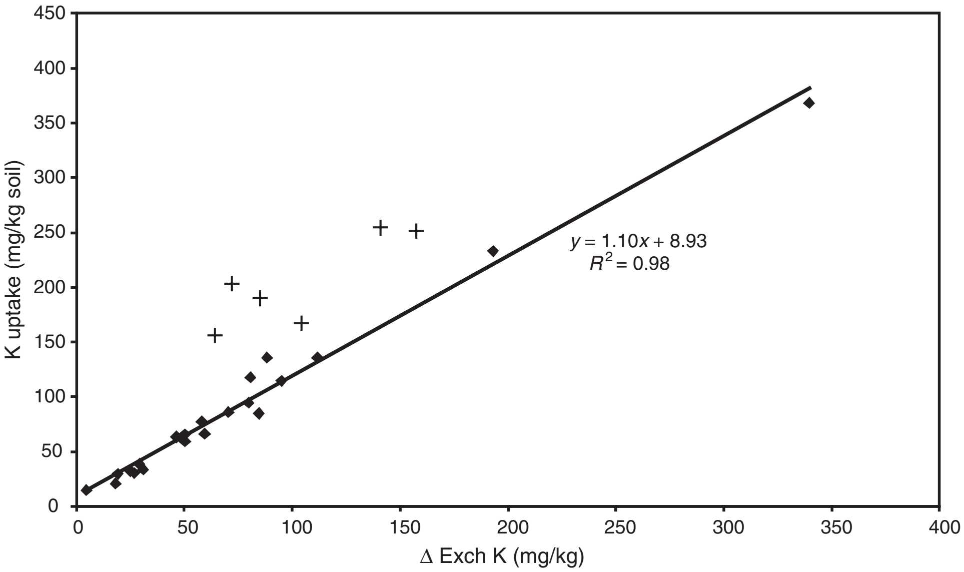

Fig. 5. Relationship between Δ exchangeable K and K uptake at Harvest 1 for the 26 soils of Experiment B. The regression equation for 20 soils is presented as Eqn 3 above.

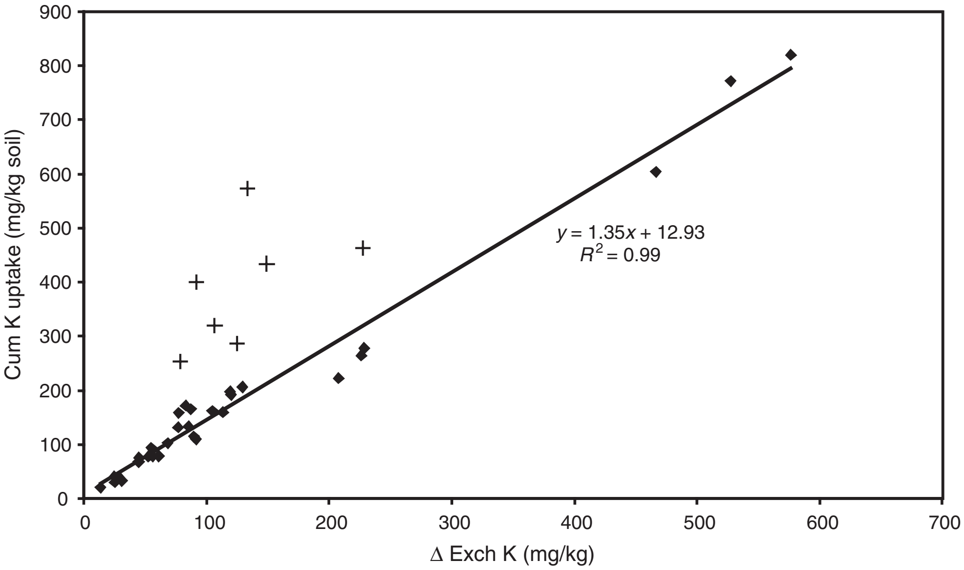

Fig. 6. Relationship between Δ exchangeable K and cumulative K uptake for the 37 soils of Experiments A and B. The regression equation for 30 soils is presented as Eqn 4 above.

estimated K uptake (Eqn 6). Correlation coefficients for both extraction periods were lower than those observed between Harvest 1 K uptake and change in Exch K (Eqn 3):

$$\text{K Uptake Harvest 1} = 0.877(\pm 0.077)\Delta\text{TBK}_{15} + 15.00(\pm 11.29) \quad (R^2 = 0.837, n = 26) \tag{5}$$

$$\text{K Uptake Harvest 1} = 0.762(\pm 0.062)\Delta\text{TBK}_{60} + 29.23(\pm 9.64) \quad (R^2 = 0.856, n = 26) \tag{6}$$

However, when the changes in TBK_{15} or TBK_{60} were related to cumulative K uptake across all soils, the relationships had high correlation coefficients and the slopes of the regression equations were not significantly ($P = 0.05$) different from unity, with very small intercepts:

$$\text{K Uptake Cumulative} = 1.117(\pm 0.073)\Delta\text{TBK}_{15} + 52.0(\pm 15.4) \quad (R^2 = 0.899, n = 37) \tag{7}$$

$$\text{K Uptake Cumulative} = 0.994(\pm 0.041)\Delta\text{TBK}_{60} + 48.4(\pm 15.5) \quad (R^2 = 0.970, n = 37) \tag{8}$$

These results indicate that available K is quantitatively captured by the TBK parameters.

While the changes in Nitric K in the soils of Experiment B were highly correlated with K uptakes at Harvest 1 and cumulative uptakes, on average 17 and 19% more K was taken up by the plants than was reflected by changes in Nitric K (Eqns 9 and 10):

$$\text{K Uptake Harvest 1} = 1.168(\pm 0.071)\Delta\text{Nitric K} + 13.6(\pm 8.0) \quad (R^2 = 0.912, n = 26) \tag{9}$$

$$\text{K Uptake Cumulative} = 1.188(\pm 0.073)\Delta\text{Nitric K} + 28.3(\pm 15.4) \quad (R^2 = 0.911, n = 26) \tag{10}$$

The ratio of TBK$_{15}$ to Exch K was >2 in 8 soils (A1, B1, B5, B15, B16, B17, B18, and B19), suggesting substantial K reserves in these soils. If these K reserves were, in fact, plant-available, then K uptake per unit change in Exch K would increase as the ratio increased. An exponential relationship was observed between these 2 parameters for 32 soils (Fig. 7), but soils B1, B15, B16, B17, and B19 were outliers. Although the TBK$_{15}$: Exch K ratios in these latter soils exceeded 2, there was no evidence that K extracted by tetraphenyl borate over and above that in the exchangeable form was plant available. This was particularly evident for soil B1 which had a very high content of TBK$_{15}$ compared with Exch K (588 and 132 mg/kg, respectively), but a low cumulative K uptake (133 mg/kg). It is noteworthy that the Exch K level at final harvest in this soil was 0.12 cmol$_c$/kg, and plants were extremely K-deficient. In contrast, in soils A1, B5, and B18 (whose TBK$_{15}$: Exch K ratios also exceeded 2), Exch K concentrations at final harvest ranged from 0.28 cmol$_c$/kg (B18) to 0.45 cmol$_c$/kg (B5) and there were no symptoms of K deficiency on the plants when the glasshouse experiments were terminated. These results are explicable if the TBK reserves in soils A1, B5, and B18 are buffering Exch K, whereas the TBK reserves in soils B1, B15, B16, B17, and B19 are not being solubilised as a result of plant K uptake. Soil pH declined in all soils from the initial value to the value measured after the final harvest (data not presented), but the final pH values in the former group of soils (pH 4.90–5.41) were higher than those of the latter group (pH 4.35–4.49). This indicates that acid solubilisation of the TBK reserves is not an explanation for the observed differences in the availability of these reserves. A plausible explanation for the situations where TBK reserves are not available is that solution K concentration is reduced by the tetraphenyl borate extractant to lower levels than the threshold concentration required for plants to take up K sufficiently quickly to meet growth requirements. The TBK reserves are therefore solubilised by the extractant, and their availability is over-estimated.

The observation that TBK acts as an available K reserve in some soils but not in others can be illustrated by plotting cumulative K uptake against Exch K for soil B8 (an upland Vertosol) (Exch K, 0.48 cmol$_c$/kg; TBK$_{15}$, 0.50 cmol$_c$/kg), soil B18 (a Dermosol) (Exch K, 0.48 cmol$_c$/kg; TBK$_{15}$, 1.06 cmol$_c$/kg) and soil B19 (a Hydrosol) (Exch K, 0.46 cmol$_c$/kg; TBK$_{15}$, 1.29 cmol$_c$/kg) (Fig. 8). Soil B8 has negligible TBK reserves (TBK$_{15}$ = Exch K), and Exch K declines sharply as K uptake occurs. For soil B18, Exch K does not decline as quickly with cumulative K uptake. The decline in Exch K is buffered by the substantial TBK reserves in this soil. However, soil B19, which has larger TBK reserves than soil B18, behaves similarly to B8, indicating that these reserves are not buffering the decline in Exch K. These

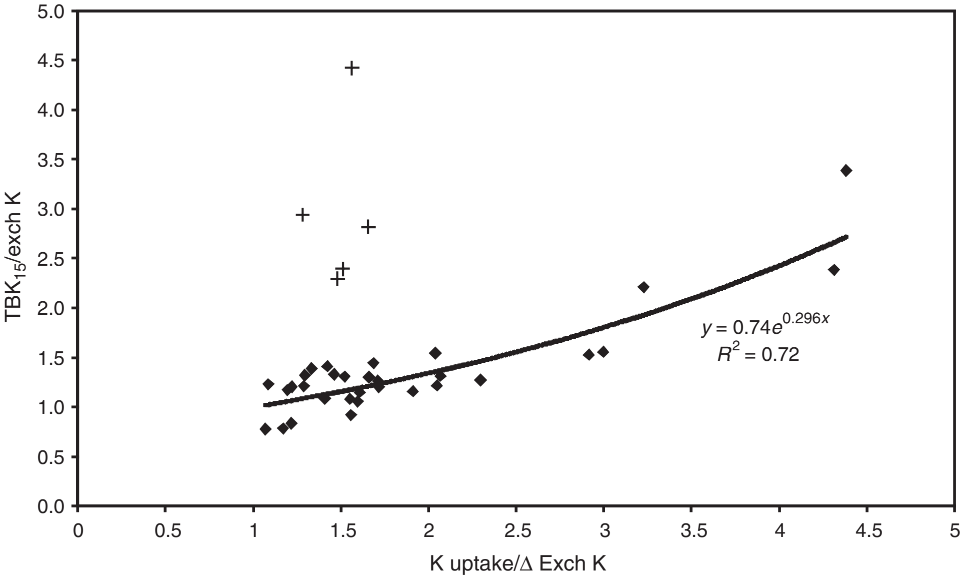

Fig. 7. Relationship between K uptake per unit change in exchangeable K and the ratio of TBK$_{15}$ to exchangeable K. The regression equation is for 32 soils.

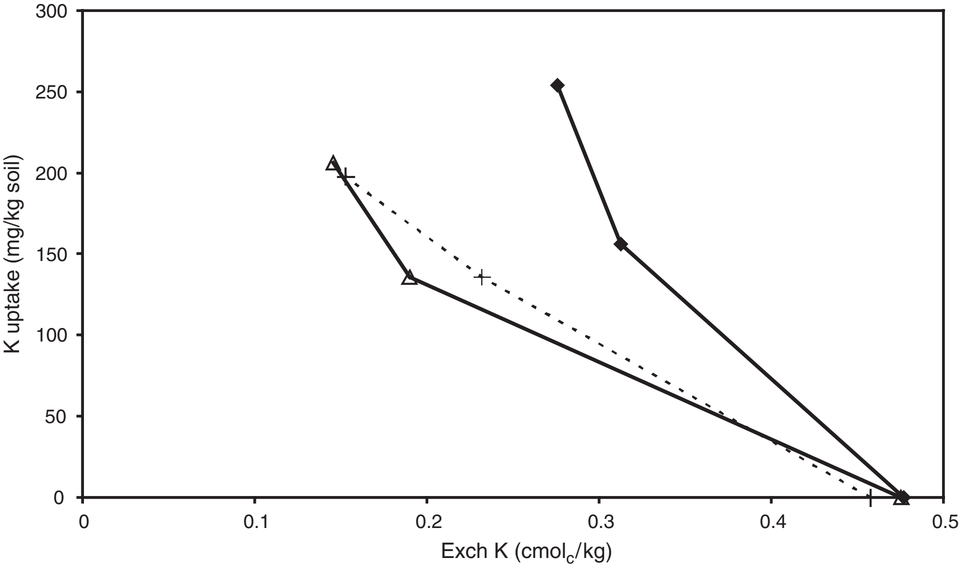

Fig. 8. Cumulative K uptake as a function of initial exchangeable K in 3 soils. ◆, B18; +, B19; △, B8.

differences in the availability of TBK may be related to soils of different mineralogy having different sources of tetraphenyl borate extractable K. Elucidation of this point awaits mineralogical analysis of selected soils.

Conclusions

It is apparent that whereas Exch K is very useful as a diagnostic soil test for the current crop (Fig. 4), the changes in Exch K following plant K uptake are soil dependent, with some soils able to buffer changes in Exch K (e.g. floodplain Vertosols, Dermosols, Hydrosols, and Rudosols) but others (most Ferrosols and upland Vertosols) having no K reserves beyond Exch K. These differences mean that it is not possible to predict what level of Exch K will occur in the soil after a crop. Similarly, soil samples taken shortly after the harvest of a current crop may well be a poor indicator of Exch K status for the next crop due to replenishment of Exch K (which includes solution K) during the fallow. This makes it extremely difficult to make accurate K fertiliser recommendations unless it has been determined whether or not the soil has TBK reserves. A soil with no TBK reserves will presumably require less K fertiliser to raise its Exch K status to an adequate level than a soil whose TBK reserves have been run down and where added K moves into the fixed and/or structural pools. How quickly added fertiliser K moves into these pools and replenishes them is not known and is the focus of current work.

It appears that some forms of K extractable by tetraphenyl borate can provide K for plant uptake, but other TBK forms are not available because they are only extracted when the solution K concentration is lower than the threshold concentration at which roots can take up K fast enough to meet plant demands.

Acknowledgments

This work would not have been possible without funding from Canpotex and the Grains Research and Development Corporation. We gratefully acknowledge the technical assistance of Bruce Compton, Sioy Ay Yo, Pat Victor, and Gary Harch.

References

Australian Agriculture Assessment (2001) Nutrient management in Australian agriculture. In 'Australian agriculture assessment'. Vol. 1. (National Land and Water Audit: Canberra, ACT)

Bell MJ, Harch GR, Bridge BJ (1995) Effects of continuous cultivation on Ferrosols in subtropical southeast Queensland. I. Site characterization, crop yields and soil chemical status. *Australian Journal of Agricultural Research* **46**, 237–253. doi: 10.1071/AR9950237

Bell MJ, Moody PW (2001) Nitrogen, potassium, calcium and magnesium balances for dryland cropping systems (Burnett region, Queensland). In 'Australian agriculture assessment'. Vol. 1. (National Land and Water Audit: Canberra, ACT)

Carey PL, Metherell AK, Huen CG, Almond C (2000) Using an improved tetra-phenyl boron K method to measure Westland soil K reserves. In 'Soil research: A knowledge industry for land-based exporters'. Occasional Report No. 13. (Eds LD Currie, P Loganathan) pp. 247–257. (Fertilizer and Lime Research Centre, Massey University: Palmerston North, New Zealand)

Cox AE, Joern BC, Roth CB (1996) Nonexchangeable ammonium and potassium determination in soils with a modified sodium tetraphenylboron method. *Soil Science Society of America Journal* **60**, 114–120.

Gillman GP, Sumpter EA (1986) Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Australian Journal of Soil Research* **24**, 61–66. doi: 10.1071/SR9860061

Gillman GP, Skjemstad JO, Bruce RC (1982) A comparison of methods used in Queensland for determining cation exchange properties. Division of Soils Technical Paper No. 44, CSIRO Australia.

Isbell RF (1996) 'The Australian Soil Classification.' (CSIRO Publishing: Melbourne, Vic.)

Martin HW, Sparks DL (1985) On the behaviour of nonexchangeable potassium in soils. *Communications in Soil Science and Plant Analysis* **16**, 133–162.

McLean EO, Watson ME (1985) Soil measurements of plant-available potassium. In 'Potassium in agriculture'. (Ed. RD Munson) pp. 277–308. (ASA, CSSA, SSSA: Madison, WI)

Mehta SC, Singh N, Singh M (1992) Effect of wetting and drying on the dynamics of potassium in some soils of Haryana. *Journal of Potassium Research* **8**, 290–294.

Menzies NW, Bell LC (1988) Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Australian Journal of Soil Research* **26**, 451–464. doi: 10.1071/SR9880451

Sparks DL, Huang PM (1985) Physical chemistry of soil potassium. In 'Potassium in agriculture.' (Ed. RD Munson) pp. 201–276. (ASA, CSSA, SSSA: Madison, WI)

Syers JK (1998) 'Soil and plant potassium in agriculture.' (The Fertiliser Society: Newcastle-upon-Tyne: UK)

Manuscript received 30 September 2005, accepted 16 February 2006