# DAQ00148: Developing diagnostic soil tests for soil phosphorus and potassium in grain cropping soils

# Final Report: Soil Processes, Science Delivery, DSITIA

## Phosphorus

### Introduction

Field experiments have demonstrated there are two phases of soil P supply to grain crops: (i) at sowing and early establishment, the seedling has a requirement for immediately available P for root development and setting of grain yield potential. The P status of the surface (0-10 cm) soil can be assessed using the Colwell soil test and critical soil test ranges have been established for determining whether or not starter P is required; (ii) following establishment, the P status of the subsoil (10-30 cm) becomes critically important for maintaining adequate P supply for maximum biomass production and realisation of the grain yield potential in rain-fed systems. Apart from requiring a soil sampling paradigm shift from surface soil sampling to a combination of surface (0-10 cm) and sub-surface (10-30 cm) sampling, the question of the usefulness of current soil P tests for assessing the longer term availability of subsoil P has been raised. Wang *et al.* (2007) found that P removed by several grain crops growing on a Vertosol was reflected in a decrease in the acid-extractable soil P and residual soil P pools while the bicarbonate (viz. Colwell-P) pool showed minimal change. These results suggest that Colwell-P may be buffered against change by replenishment from sparingly soluble (acid extractable) sources, and is therefore sensitive to the quantity of ‘reserve P’ (i.e., acid-extractable) in the soil. This raises the question of the availability of this reserve P, its importance to rainfed grain cropping, and its measurement. The variability of this reserve pool is emphasised by the huge range in Colwell-P/BSES-P (Acid-P) ratios found across northern grains region soils, even within the Vertosol soil order which covers the largest area in the region.

### Methodology

*Rationale*

Fig.1 indicates soil P pools, processes and their interactions, and this conceptual diagram underpins the experimental program of this project.

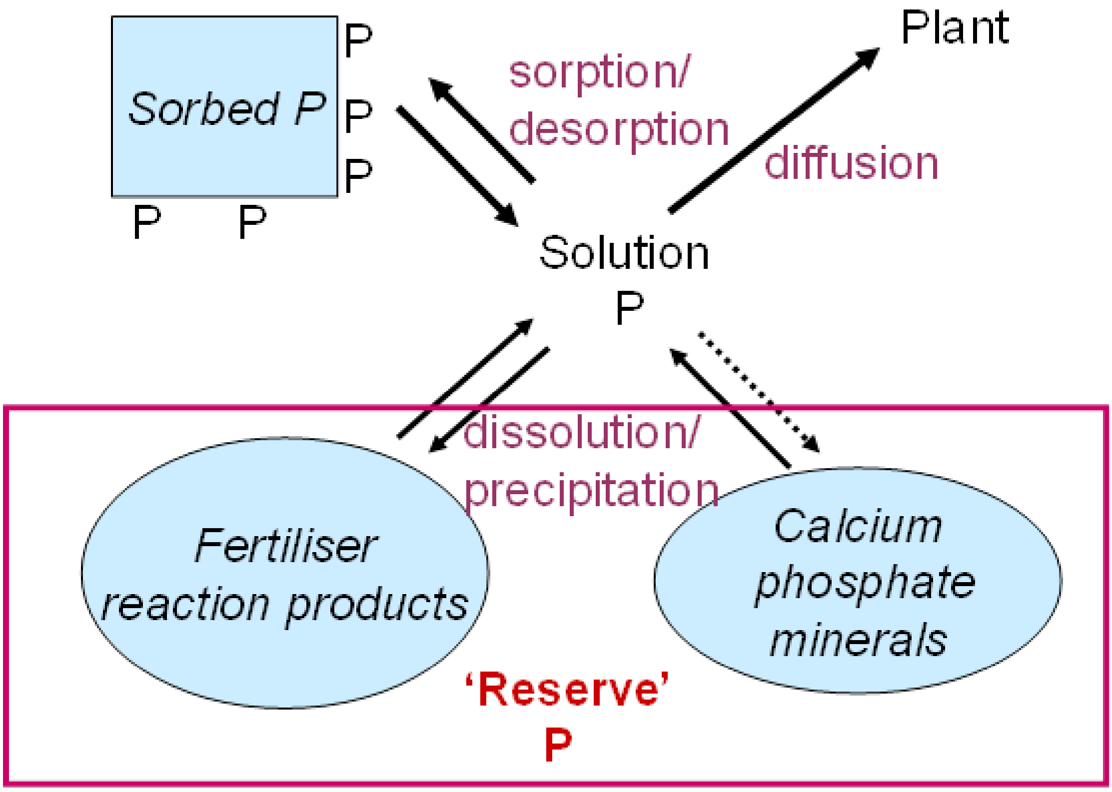


**Figure 1. Phosphorus pools and processes in soils of the northern grains region. Organic P as a P source has not been included because of the generally low organic C status of northern grains soils (<1.5% C).**

Glasshouse experiments comprising depletion of soil phosphorus (P) by exhaustive cropping have been used to determine the amount of plant available P in selected soils from the northern grains region. A wide range of P analyses have been undertaken on these soils to: (a) characterise the P pools and supply processes in these soils; (b) understand the interactions between these pools and processes in determining P supply to crops; (c) assess soil P tests for their usefulness as diagnostic indicators of soil P status; (d) determine the fate and availability of fertiliser P applied to P-depleted soils.

*Soil P characterisation*

For soil P characterisation, the following methods have been used to estimate the pools and processes in Fig. 1:

- Colwell-P (0.5 M $NaHCO_3$; 1:100 soil:extractant; 16 h extraction) estimates sorbed P plus solution P. It is recognised that Colwell-P also extracts some P from the reserve P pool (Bertrand *et al.* 2003; Six *et al*. 2012) but this is assumed to be negligible.
- BSES-P (sometimes termed 'Acid-P'; 0.005 M $H_2SO_4$; 1:200 soil: extractant; 16 h extraction) estimates sorbed P plus solution P plus reserve P.
- Soil solution P measure soil solution P concentration.
- DGT-P measures rate of diffusive P supply from the soil solution over a period of 24 h.

- FeO-P measures the rate of P released into the soil solution under diffusion non-limited conditions over a period of 17 h (2cm x 10 cm FeO strip/ g soil).
- Using successive FeO strip extractions, P can be depleted from a soil over an extended period because the FeO strip acts an infinite sink for P in solution. To determine P depletion curves, soils were shaken in 0.002 M $CaCl_2$ with FeO-P strips replaced every 17 h until the cumulative desorbed P reached a plateau.
- The P fractionation procedure (Guppy *et al.* 2000) has been used to separate soil P into the following sequential fractions: bicarbonate soluble (organic and inorganic P in 0.5 M $NaHCO_3$); hydroxide soluble (organic and inorganic P in 0.1M NaOH); and acid soluble (total P in 1M HCl). Residual soil P was not measured in this project because it was considered it would not impact on plant available P over the timeframe of the glasshouse and lab incubation experiments.

*Glasshouse experiments*

The second P depletion glasshouse trial of this project was undertaken on 18 grain cropping soils with diverse (BSES-P/Colwell-P) ratios. Treatments comprised ‘plus P’ (50 kg P/ha on an area basis; 2 reps) and ‘nil P’ treatments (4 reps). Basal nutrients were applied to all plots at the following rates (kg/ha on an area basis): N, 140; K, 140; S, 40; Ca, 30; Mg, 30; Zn, 5; Cu, 5; B, 1; Mo, 0.2. Six forage sorghum plants were established in each pot (planted: 1 Oct 2010) and dry matter cuts taken 3 times (11 Nov 2010; 22 Dec 2010; 7 Feb 2011). Soil was then removed from each pot and mixed. Visible root material was removed, the soil re-potted, and forage sorghum re-sown. Two more dry matter cuts were taken (15 April 2011; 01 Jun 2011). By this time, plants either failed to re-grow because of extreme P deficiency or were producing relative yields of less than 25% (5 soils). Plant samples from each harvest were ground and analysed for P. Crop P uptake was calculated for each harvest and summed over the five harvests to give cumulative P uptake.

Soil samples were taken from ‘nil P’ pots prior to sowing, following re-potting and after the final harvest. Analyses comprised Colwell-P, BSES-P, HCl-P, soil solution P, FeO-P and initial DGT-P. Initial and depleted soil samples were subjected to mid-infrared (MIR) analysis to determine whether there was any change in the MIR spectra caused by exhaustive depletion of soil P by the crop. Preliminary results were disappointing and this approach was not pursued any further.

*Soil P depletion curves*

P was progressively depleted from the soils by successive FeO strips until no further P could be removed by the strips (i.e., cumulative P removal had plateaued).

*Fertiliser P addition to depleted soils*

To investigate which P pool increased when fertiliser P was added to a P-depleted soil, the equivalent of 50 kg P/ha.10 cm as di-ammonium phosphate (DAP) or mono-ammonium phosphate (MAP) was added in solution to the following P-depleted soils: 1, 2, 4, 5, 6, 9, 10 and 13. The fate of this added P was tracked using the P fractionation procedure (Guppy *et el.* 2000), and Colwell-P and BSES-P extractions. Samples of depleted soil, + MAP soil and + DAP soil were maintained at field capacity and 30C for 14 days after P addition and then sampled and analysed (Time 1-

T1). Following a further 5 wetting-drying cycles, the soils were sampled again and analysed (Time 2-T2).

## Results

### *Soil P characterisation*

Some properties of the soils used in the glasshouse experiment are presented in Table 1. Soil pH (water) ranged from 7.0 to 8.9, CEC ranged from 5 to 92 cmol(+)/kg, clay content from 8 to 82%, and PBI$_{\mathrm{Colwell}}$ from 19 to 223. Colwell-P ranged from 4 to 70 mg/kg whereas BSES-P ranged from 6 to 892 mg/kg. The ratio of BSES-P/ Colwell-P ranged from 1.0 to 76.1.

### *Soil P pools and P availability*

Relative dry matter yield (nil P/+ P) at Harvest 1 and cumulative for 5 harvests is plotted against initial Colwell-P in Fig. 2.

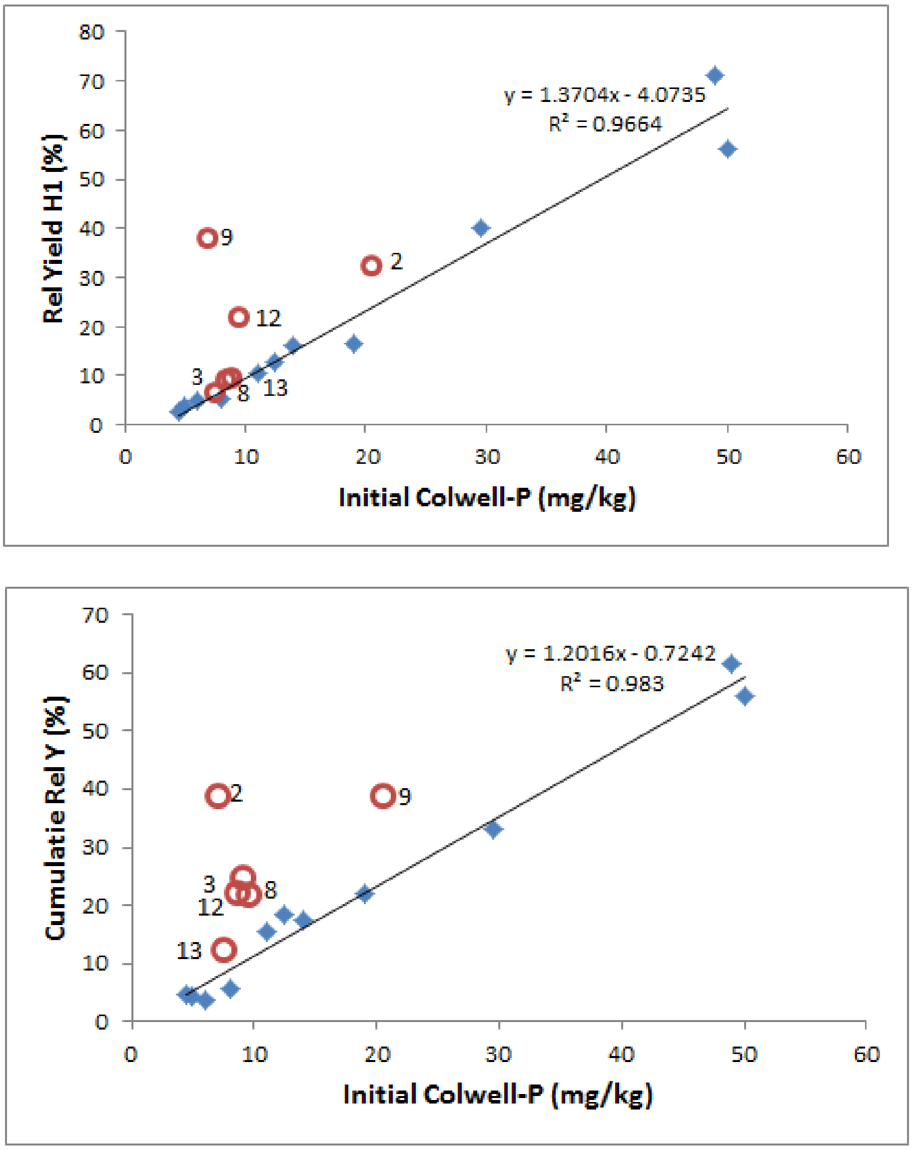


**Figure 2. Relative yield for (a) harvest 1; and (b) cumulative from 5 harvests plotted against initial Colwell-P.**

**Table 1. Some properties of the soils used in the P depletion glasshouse trial and cumulative crop P uptake. In soils with shaded BSES-Ca/BSES-P values, BSES-P would be expected to buffer Colwell-P (McLaren *et al.* (2013).**

| Soil | Depth | Soil Order | pH(w) | EC (dS/m) | Colwell-P (mg/kg) | BSES-P (mg/kg) | BSES-Ca/P | BSES-P/ Colwell-P | HCl-P (mg/kg) | PBI | DGT-P (ug/L) | CEC (cmol(+)/kg) | Total org.C (%) | Clay (%) | Field capacity (%) | Crop P uptake (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil 1 | 0-10 | Vertosol | 8.2 | 0.10 | 49 | 117 | 57 | 2.1 | 209 | 112 | 58 | 50 | 1.25 | 63 | 43.0 | 44.9* |
| Soil 2 | 10-30 | Vertosol | 8.6 | 0.15 | 20 | 86 | 106 | 4.2 | 167 | 107 | 13 | 46 | 1.01 | 66 | 43.4 | 17.7* |
| Soil 3 | 10-30 | Vertosol | 8 | 0.05 | 8.5 | 90 | 117 | 9.9 | 137 | 153 | 4 | 83 | 0.93 | 79 | 64.7 | 12.0* |
| Soil 4 | 0-10 | Dermosol | 8.5 | 0.19 | 50 | 84 | 238 | 2.9 | 529 | 223 | 31 | 64 | 2.74 | 70 | 55.0 | 45.6* |
| Soil 5 | 10-30 | Dermosol | 8.9 | 0.17 | 19 | 75 | 324 | 5.5 | 413 | 207 | 15 | 63 | 2.60 | 73 | 64.5 | 14.4 |
| Soil 6 | 0-10 | Vertosol | 7.7 | 0.04 | 12 | 13 | 610 | 1.0 | 17 | 120 | 4 | 74 | 1.03 | 78 | 59.0 | 12.0 |
| Soil 7 | 10-30 | Vertosol | 7.5 | 0.04 | 5 | 8 | 1007 | 1.5 | 5 | 142 | 2 | 76 | 0.85 | 78 | 58.7 | 1.7 |
| Soil 8 | 10-30 | Vertosol | 8.3 | 0.08 | 9 | 374 | 43 | 35.9 | 446 | 191 | 16 | 92 | 1.14 | 82 | 67.0 | 14.9 |
| Soil 9 | 10-30 | Vertosol | 8.5 | 0.11 | 7 | 440 | 59 | 67.2 | 609 | 176 | 11 | 92 | 1.60 | 82 | 73.1 | 11.1 |
| Soil 10 | 10-30 | Vertosol | 8.4 | 0.06 | 11 | 11 | 394 | 1.1 | 107 | 94 | 7 | 36 | 1.39 | 46 | 39.5 | 6.1 |
| Soil 11 | 0-10 | Dermosol | 7 | 0.02 | 6 | 6 | 112 | 1.0 | 10 | 19 | 4 | 5 | 0.68 | 8 | 11.6 | 0.8 |
| Soil 12 | 10-30 | Vertosol | 8.9 | 0.23 | 9 | 802 | 15 | 76.1 | 969 | 194 | 9 | 69 | 1.05 | 75 | 64.0 | 4.7 |
| Soil 13 | 10-30 | Dermosol | 8.6 | 0.18 | 7 | 14 | 388 | 1.3 | 17 | 61 | 4 | 27 | 0.94 | 41 | 31.7 | 11.3 |
| Soil 14 | 0-10 | Vertosol | 7.2 | 0.05 | 29 | 27 | 101 | 1.0 | 61 | 61 | 36 | 43 | 0.99 | 51 | 39.7 | 25.1 |
| Soil 15 | 10-30 | Vertosol | 7.5 | 0.05 | 8 | 8 | 215 | 1.8 | 18 | 77 | 4 | 41 | 0.76 | 53 | 40.9 | 1.6 |
| Soil 16 | 0-10 | Vertosol | 8.7 | 0.13 | 14 | 28 | 209 | 2.5 | 42 | 89 | 18 | 33 | 0.66 | 55 | 36.1 | 6.0 |
| Soil 17 | 10-30 | Vertosol | 8.6 | 0.32 | 4 | 13 | 978 | 2.3 | 15 | 89 | 2 | 34 | 0.54 | 55 | 41.8 | 0.7 |
| Soil 18 | 0-10 | Vertosol | 7.8 | 0.20 | 70 | 892 |  |  | 1122 | 144 | 85 | 61 | 1.67 | 65 | 59.7 | 18.2* |

*Relative dry matter yield (nil P/plus P) >25% at final harvest

Soils 2, 9 and 12 produced higher relative yields at Harvest 1 than would be expected from their Colwell-P values, and after prolonged cropping, Soils 3 and 8 also joined this group of soils. Colwell-P is therefore under-estimating available P initially in 3 soils, and then in 5 soils after prolonged cropping. These results indicate that sorbed P (estimated by Colwell-P) is not the sole source of available P in these soils.

To assess the contribution of reserve P to available P, cumulative relative yield was plotted against initial BSES-P (Fig. 3). Soils 2, 3 and 13 lie on the same response line as the other soils, but Soils 8, 9 and 12 are outliers, producing much lower relative yields than would be expected from their high BSES-P values.

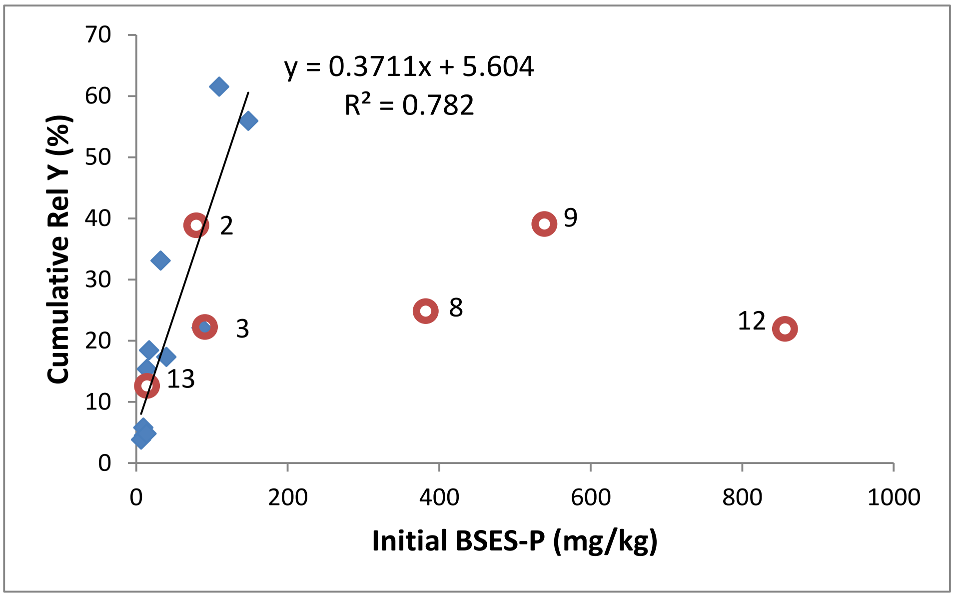


**Figure 3. Cumulative relative yield from 5 harvests plotted against initial BSES-P.**

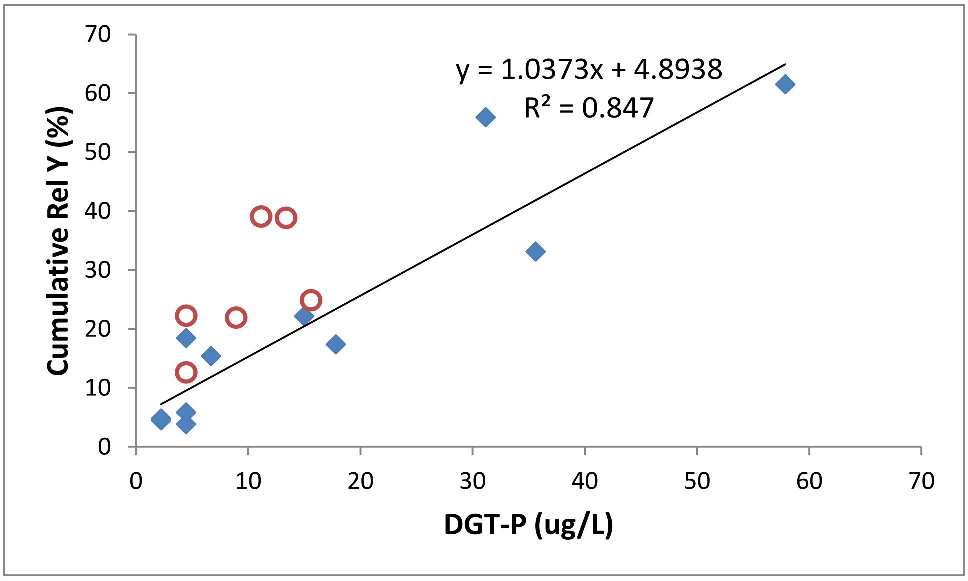


**Figure 4. Cumulative relative yield from 5 harvests plotted against initial DGT-P.**

When cumulative relative yield was plotted against initial DGT-P (Fig.4), Soils 2 and 9 tended to be outliers although they were not as far removed from the overall response curve as occurred with Colwell-P.

When cumulative P uptake was plotted against initial soil P test values, Soils 3, 8, 9 and 13 were outliers for Colwell-P (Fig. 5), whereas Soils 8, 9 and 12 were outliers for BSES-P (Fig. 6). These results indicate that BSES-P is a better indicator of available P in Soil 3 whereas Colwell-P is a better indicator in Soil 12. BSES P in Soils 8 and 9 is only partially available. It is apparent that the availability of BSES-P is variable and some means of discriminating this availability is necessary to enable the diagnostic interpretation of BSES-P.

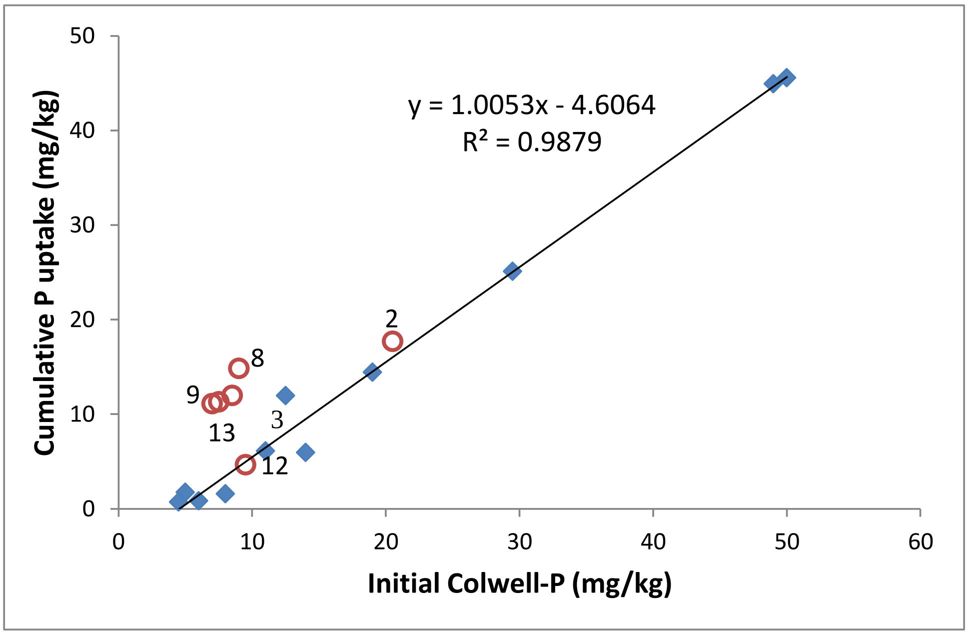


**Figure 5. Cumulative P uptake from 5 harvests plotted against initial Colwell-P.**

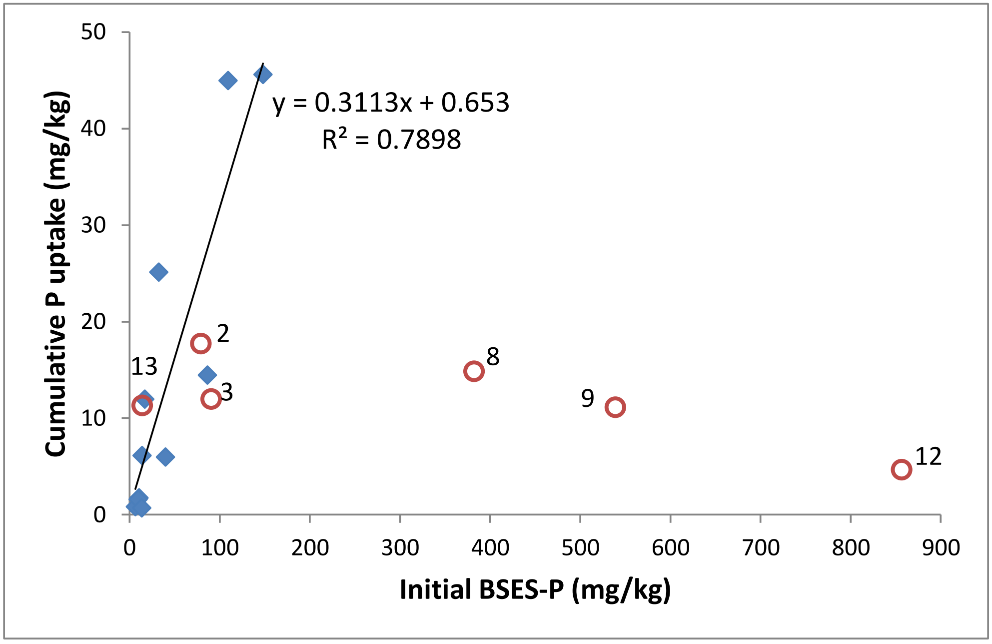


**Figure 6. Cumulative P uptake from 5 harvests plotted against initial BSES-P.**

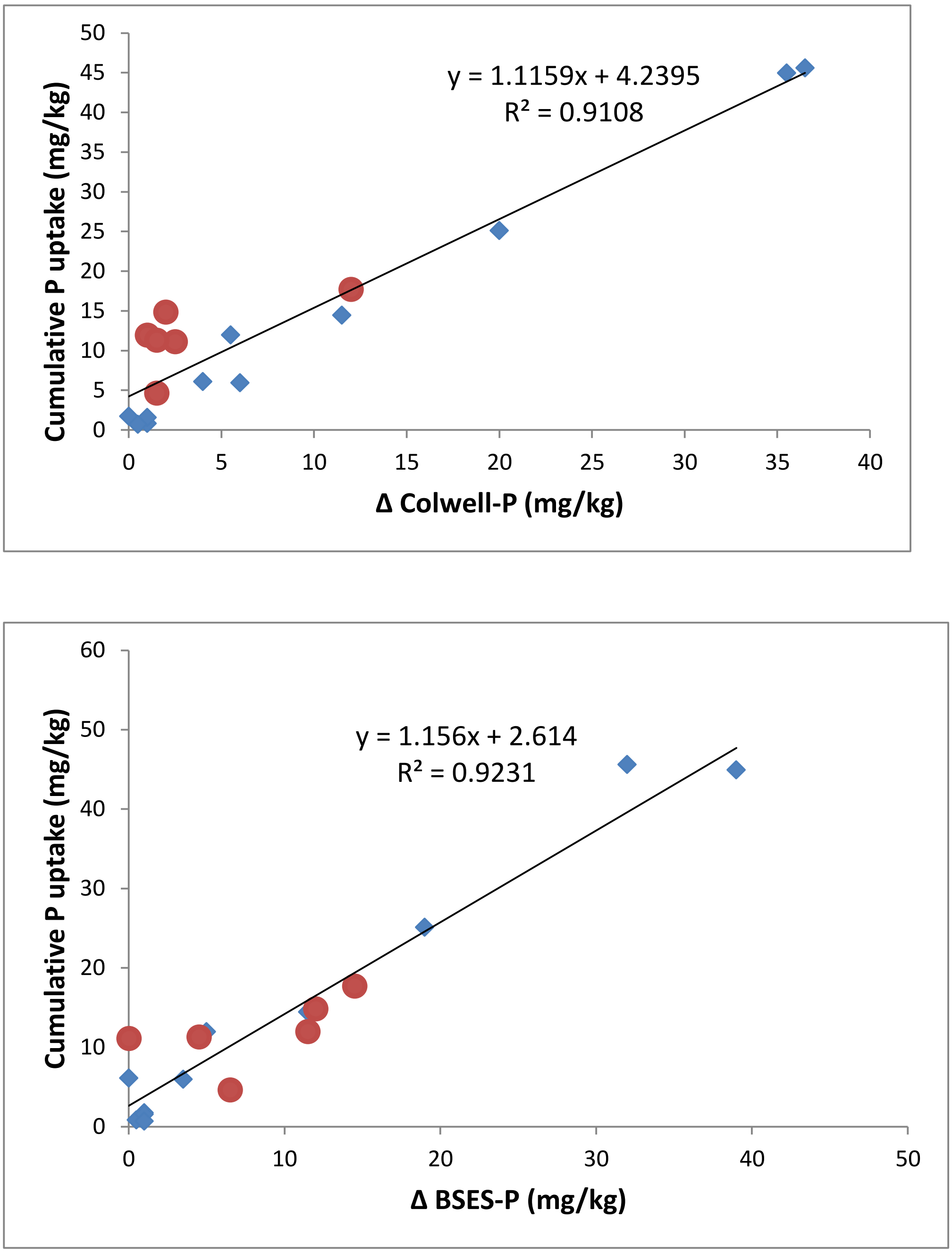


**Figure 7. Cumulative P uptake versus (a) change in Colwell-P and (b) change in BSES-P. Open circles are Soils 2, 3, 8, 9 and 12 and are not included in the regression line.**

To verify these findings, the changes in Colwell-P and BSES-P (initial value – post harvest value) as a result of soil P depletion through crop uptake are plotted in Fig. 7. The change in BSES-P is closely and quantitatively related to P uptake in all soils, while it is apparent that the change in Colwell-P in Soils 3, 8, 9 and 13 is less than crop P uptake as a consequence of the buffering effect of ‘reserve P’ (i.e., BSES-P) on sorbed P (i.e., Colwell-P) (see Fig. 1). These results support the findings of McLaren *et al.* (2013) that BSES-P can buffer decreases in Colwell-P. For a suite of Vertosols from the Liverpool Plains, NSW, they found this buffering effect occurred when BSES-P > 61 mg/kg and BSES-Ca/BSES-P < 74. Soils 8 and 9 in the current study fit these criteria, although Soil 3 has a higher BSES-P/Ca ratio (117) suggesting that the cut-off value suggested by McLaren *et al.* (2013) might be higher when a larger suite of soils is examined. Despite Soils 3, 8 and 9 having this buffering effect, their BSES-P values do not reflect P availability because together with Soil 12, they are outliers when plotted against cumulative P uptake (Fig. 6).

These results provide evidence that:

- The primary source of plant available P in these soils is ‘sorbed P’ (Colwell-P).
- However, in soils containing appreciable amounts of ‘reserve P’ (estimated by BSES-P/ Colwell-P >2), a variable proportion of this reserve P is available to plants through the dissolution of sparingly soluble P compounds. These compounds may have originated from the parent material of the soil (e.g., apatites – Soils 2, 3, 5, 8, 9, and 12) or occur as reaction products from the application of P fertilisers to the soils (Soils 1, 4 and 18).
- As well as being a source of plant available P, the dissolution of these compounds in some soils buffers sorbed P and solution P so the decline in these latter P pools is smaller than that required for quantitative equivalence with crop P uptake.

*Characterising reserve P*

To investigate the dissolution rate of reserve P, and to assess why the large amounts of BSES-P in Soils 8, 9 and 12 were mainly unavailable, sequential extraction of soil was undertaken by FeO strips. Dissolution curves are presented for Soil 4 and Soil 14 in Fig. 8. Soil 14 had similar levels of Colwell-P and BSES-P (25 and 34 mg/kg, respectively) and a cumulative crop P uptake of 25 mg P/kg. In contrast, Soil 4 had higher BSES-P (123 mg/kg) than Colwell-P (50 mg/kg) and a crop P uptake of 46 mg P/kg. Soil 14 did not contain appreciable amounts of reserve P (BSES-P and Colwell-P values are similar) and the P depletion curve has uniform slope, suggesting only one form of desorbable P. In contrast, soil 4 has much higher BSES-P than Colwell-P (BSES-P/Colwell-P = 2.5) which is indicative of the presence of apatites. The depletion curve shows a series of ‘break points’ where slope changes, suggesting the existence of several phases with different dissolution characteristics. Soil 9 had 440 mg/kg BSES-P, but this was predominantly unavailable (Fig. 6). The FeO depletion curve (Fig. 9) shows that not all of this BSES-P was extractable by the strips. This is in contrast to Soil 4 (Fig. 8a), for example, where all BSES-P was extractable. Note that the FeO depletion curve for Soil 9 plateaus from strip number 6 to strip 12 before releasing more P at varying rates and demonstrating several breakpoints. These results are explicable if the various P compounds are distributed in successive layers that are not susceptible to dissolution until outer layers of lower solubility are first removed by dissolution.

It is interesting to note that the relatively high BSES-P values in Soils 1 and 4 are plant-available in contrast to the high values in subsurface soils such as 2, 8, 9 and 12. The origin of the high levels in the former surface soils is probably fertiliser residues, whereas the origin of the subsoil P compounds is likely to be from the soils’ parent materials. The use of a BSES-P availability discriminator based on the origin of this P (fertiliser residue/parent material) may be useful for inferring the availability of the BSES-P when it greatly exceeds Colwell-P.

For all soils, the plateau for cumulative P removal by FeO strips was less than HCl-P indicating that varying proportions of this latter P pool are insoluble when the extraction pH is the same as the soil solution pH (as it is under the experimental conditions of the FeO depletion curve).  However, it is plausible that if the extracting solution was acidic, then more of this HCl-P would be solubilised. The effect of solution pH on P dissolution suggests that rhizosphere pH has a significant effect on P availability from sparingly soluble sources.

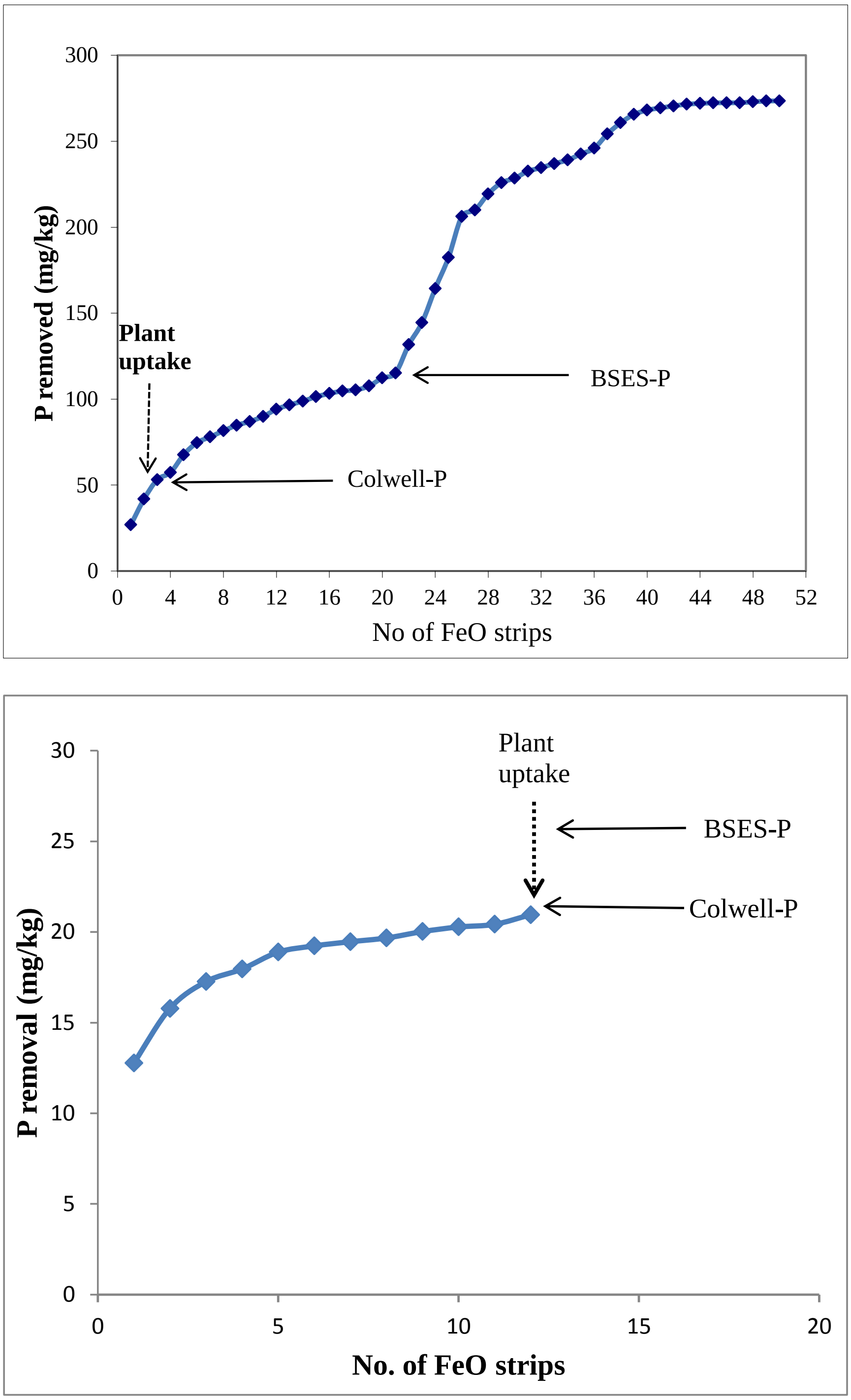


**Figure 8. Soil P depletion by successive FeO-impregnated strips: (a) Soil 4; (b) Soil 14.**

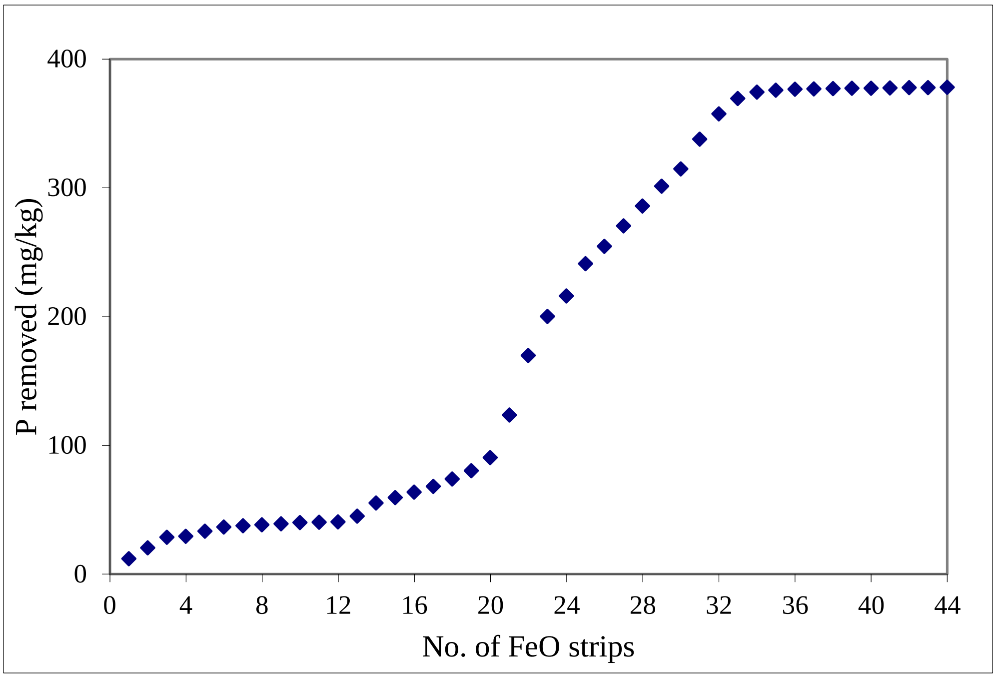


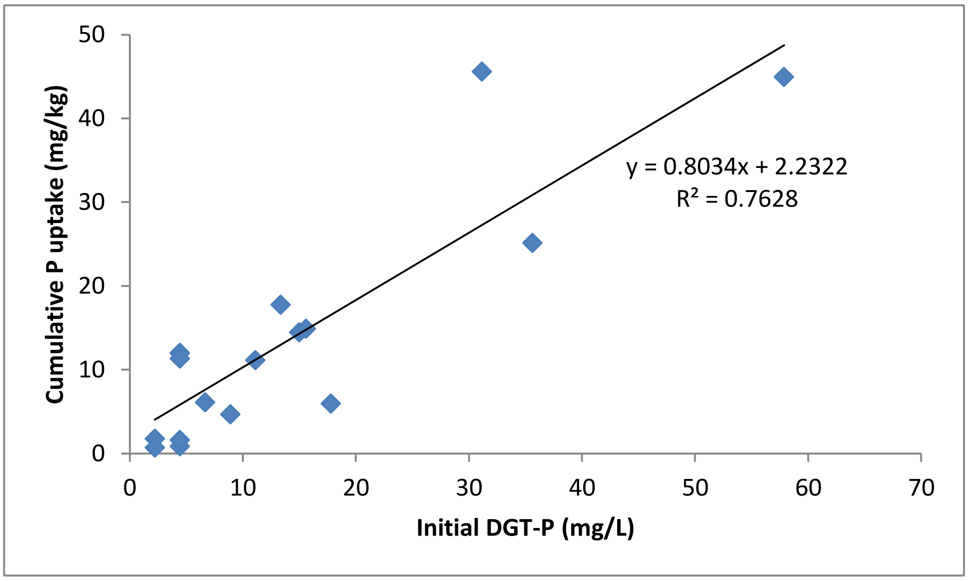
**Figure 9. Soil P depletion by successive FeO-impregnated strips for Soil 9.**

Soil solution P concentrations at field capacity were measured before and after P depletion by cropping (Table 2). While there is a wide range in initial concentrations, following exhaustive P removal the solution concentrations are uniformly low at about 0.006-0.010 ug P/L. At these low solution P concentrations, the crop is unable to take up much P, but the FeO depletion curves indicate that in many soils, considerable amounts of sparingly soluble reserve P are still present.

**Table 2. Soil solution P concentrations before and after exhaustive crop P uptake. $^{A}$Crop still growing.**

| Soil | Rel Y Final harvest (%) | Initial conc. (ug P/L) | Final conc. (ug P/L) |
|---|---|---|---|
| Soil 01 | 32 | 0.147 | 0.009$^{A}$ |
| Soil 02 | 29 | 0.042 | 0.008$^{A}$ |
| Soil 03 | 35 | 0.010 | 0.010$^{A}$ |
| Soil 04 | 66 | 0.085 | 0.001$^{A}$ |
| Soil 05 | 13 | 0.032 | 0.010$^{A}$ |
| Soil 06 | 18 | 0.014 | 0.007$^{A}$ |
| Soil 07 | 0 | 0.008 | 0.006 |
| Soil 08 | 24 | 0.016 | 0.006$^{A}$ |
| Soil 09 | 0 | 0.012 | 0.005 |
| Soil 10 | 0 | 0.023 | 0.006 |
| Soil 11 | 0 | 0.014 | 0.010 |
| Soil 12 | 0 | 0.018 | 0.011 |
| Soil 13 | 0 | 0.015 | 0.011 |
| Soil 14 | 14 | 0.037 | 0.010$^{A}$ |
| Soil 15 | 0 | 0.012 | 0.006 |
| Soil 16 | 0 | 0.045 | 0.009 |
| Soil 17 | 0 | 0.011 | 0.007 |
| Soil 18 | 73 | 0.288 | 0.060$^{A}$ |

These soil solution P results provide insight into discriminating that part of the reserve P that is available- it is the reserve P that is able to dissolve sufficiently rapidly at solution P concentrations that are above the threshold concentration for crop P uptake. Both initial FeO-P and DGT-P are essentially measuring rate of P supply over 17-24 h (the time of equilibration with the soil, respectively, of the two methods) rather than the quantity of available P. FeO-P measures the rate of P dissolution under diffusion non-limiting conditions whereas DGT-P measures this rate of dissolution as well as taking account of soil properties that affect diffusive supply of P. The effect of rate of P supply on P availability was assessed by plotting cumulative P uptake against initial FeO-P and DGT-P for all soils (Fig. 10).



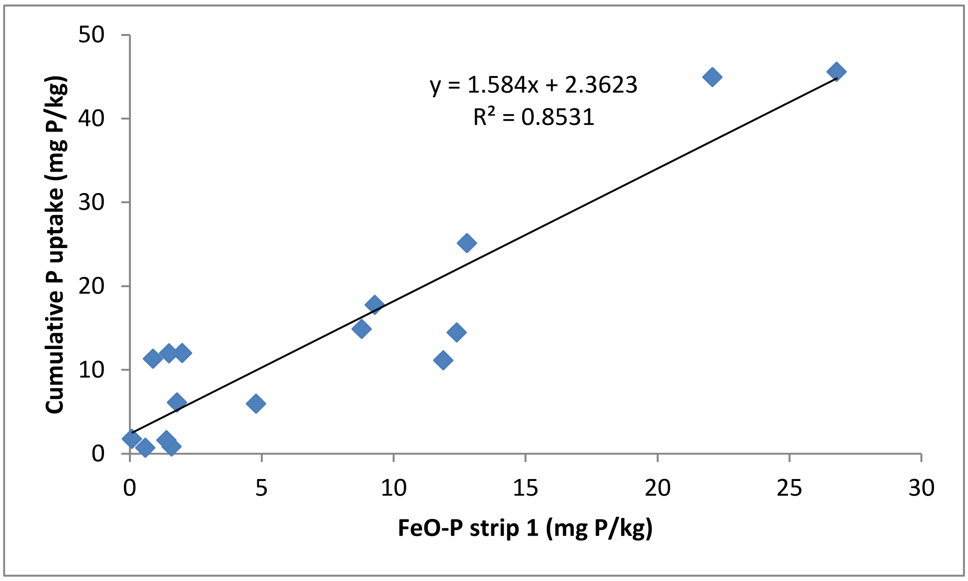


**Figure 10. Cumulative P uptake versus (a) initial DGT-P and (b) initial FeO-P strip.**

It is apparent that the rate of P supply from the dissolution of reserve P (assessed by FeO-P) is highly correlated with cumulative P uptake across all soils, including those soils that are outliers when initial BSES-P is plotted against P uptake (Fig. 6). However, the correlation coefficient is not as high as that obtained with initial Colwell-P (Fig. 5) when soils with proportionally high levels of reserve P (i.e., BSES-P/Colwell-P>2) are not considered. This finding supports the earlier conclusion that the quantity of sorbed P in these soils is the primary determinant of P availability in those soils with low reserve P. Although DGT-P is also highly correlated with cumulative P uptake when all soils are considered (Fig. 10), the correlation coefficient is not as high as for FeO-P indicating that it is the dissolution process rather than the diffusive supply that is the major factor affecting P supply.

From a diagnostic viewpoint, the issue still remains of finding a method that allows scaling of the variable contribution that reserve P makes to P availability. When BSES-P in soils with proportionally high levels of reserve P (i.e., BSES-P/Colwell-P>2) is plotted against initial FeO-P, two distinct trends are apparent. BSES-P in Soils 3, 8, 9, and 12 (solid square symbols) is only 2% as available as FeO-P, whereas BSES-P in the other soils has an availability of 17% relative to FeO-P (Fig. 11).

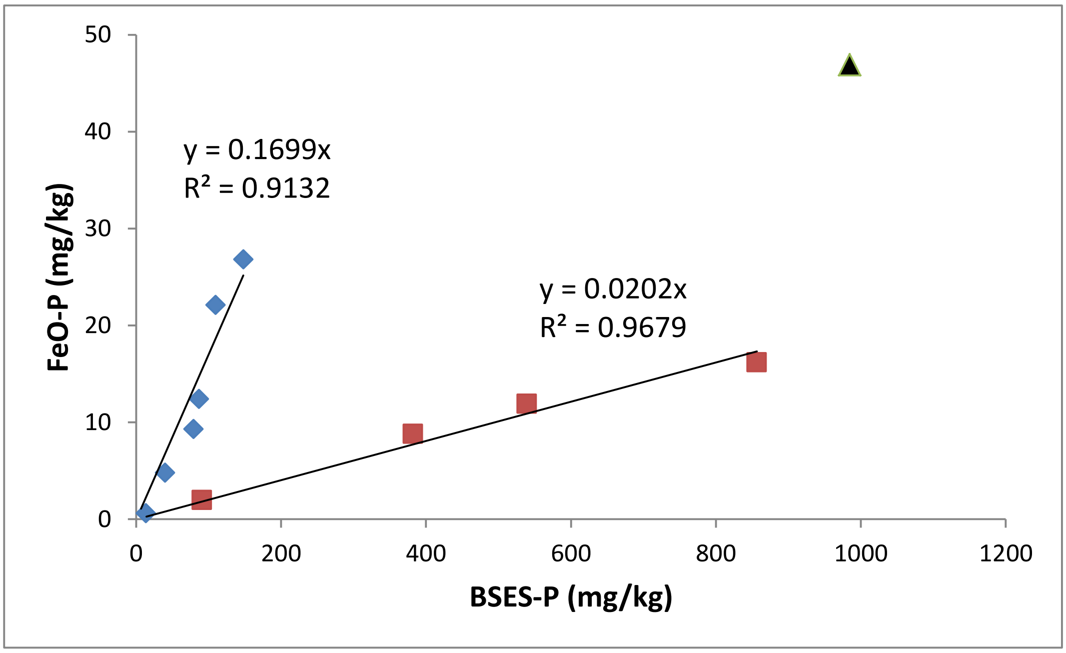


**Figure 11. Relationship between BSES-P and FeO-P for soils with BSES-P/Colwell-P>2.**

When data from the same soils are plotted against DGT-P (as an alternative measure of rate of P supply), the relationships are much poorer (Fig. 12). However, DGT-P is commercially available as a soil P test whereas FeO-P is not, so further work is needed to develop the diagnostic application of DGT-P for this purpose.

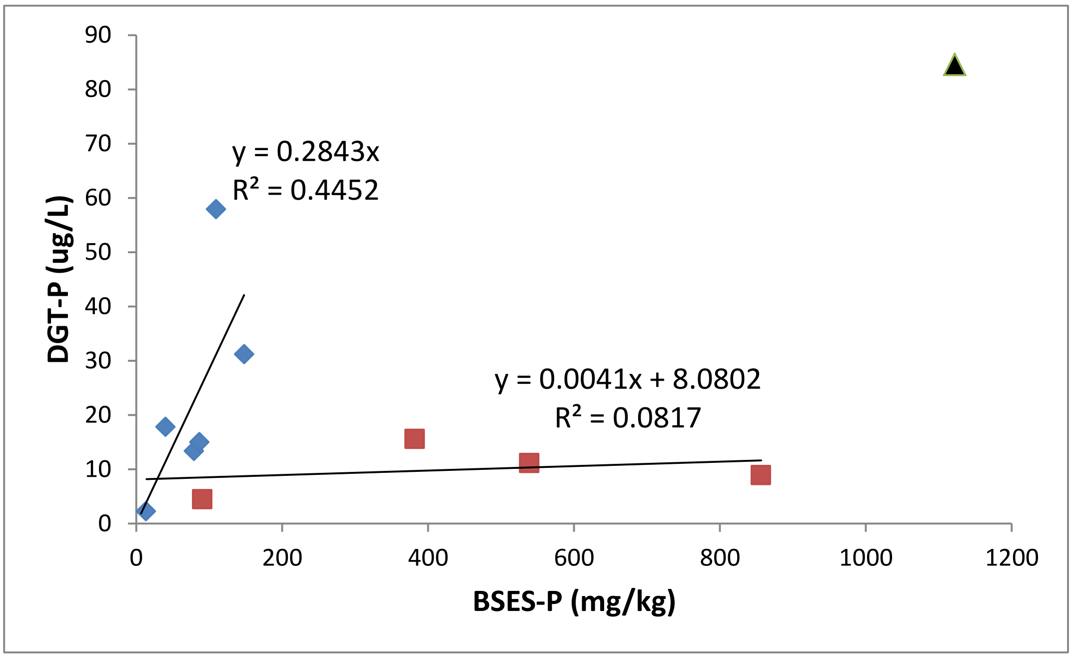


**Figure 12. Relationship between BSES-P and DGT-P for soils with BSES-P/Colwell-P>2.**

Note that in both plots Soil 18 is an outlier indicating different dynamics between rate of P release and reserve P occur in this soil.

*Fate of fertiliser P applied to P-depleted soils*
The recovery of added MAP and DAP by the P fractionation procedure was 103±6% at T1 (14 days after addition) and 102±7% at T2 (additional wetting-drying cycles), indicating there was no movement of added P into P pools that were not extractable by the bicarbonate-hydroxide-acid sequence.

Colwell-P extractability of the added P averaged 58±7% and 73±14% at T1 and T2, respectively, except for DAP in Soil 2 and MAP in Soil 9 (Fig. 13). There were no significant ($P<0.10$) changes in Colwell-P extractability between T1 and T2. BSES-P extractability was higher than Colwell-P extractability in Soils 1, 2 and 9, indicating movement of added P into the reserve pool in these soils. In the other soils, added P remained in the sorbed P pool (Colwell-P). From 10% (Soils 2 and 9) to 50% (Soil 6) of the added P could not be recovered by BSES-P but was recovered in the P fractionation procedure. There were no significant ($P<0.10$) differences between DAP and MAP in BSES-P extractability, but the Colwell-P extractability of DAP in Soil 2 was less than MAP.

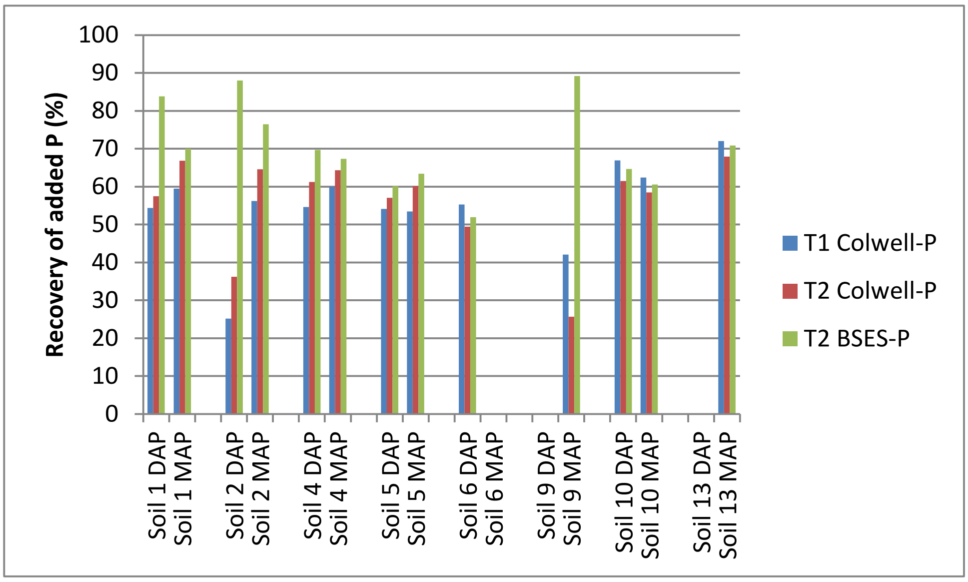


**Figure 13. Recovery of P added as DAP or MAP by Colwell-P at two times (T1 and T2) and BSES-P at T2.**

These results indicate that at least half of the water soluble P added to P-depleted soils is retained in the sorbed form (Colwell-P extractable) after incubation and several wetting-drying cycles. With MAP as the P source, there was no movement of added P into the reserve pool (BSES-P minus Colwell-P) except in Soil 9. However, when DAP was the P source in two soils, a large amount of the added P entered the reserve pool. In summary, the added P remains in sorbed and/or reserve pools that would be expected to be available, but it is apparent that the relative distribution of the added P between these pools is P-form and soil-type dependent.

## Discussion

### *Soil P pools and P availability*

The results of the glasshouse trial, the FeO depletion curves, soil P test data and the soil solution P concentration data have been synthesised into a conceptual diagram of P supply and availability that is applicable to soils containing appreciable amounts of reserve P (i.e., BSES-P/Colwell-P >2) (Fig. 15). As soil solution P concentration is lowered by plant P uptake in the rhizosphere, it is buffered by dissolution of reserve P at rates dependent on the composition of the reserve P compounds. Once the soil solution P concentration reaches the threshold concentration below which roots can no longer absorb P, the dissolution process ceases and the remaining reserve P is essentially unavailable. However, if the soil solution P concentration is lowered further, then more of the reserve P can dissolve in accord with the solubility products of the reserve P compounds.

When water soluble P forms such as DAP and MAP are added to P-depleted soils, soil solution P concentration increases and the added P is distributed between the sorbed P and reserve P pools, depending on soil type and P source (Fig. 16).

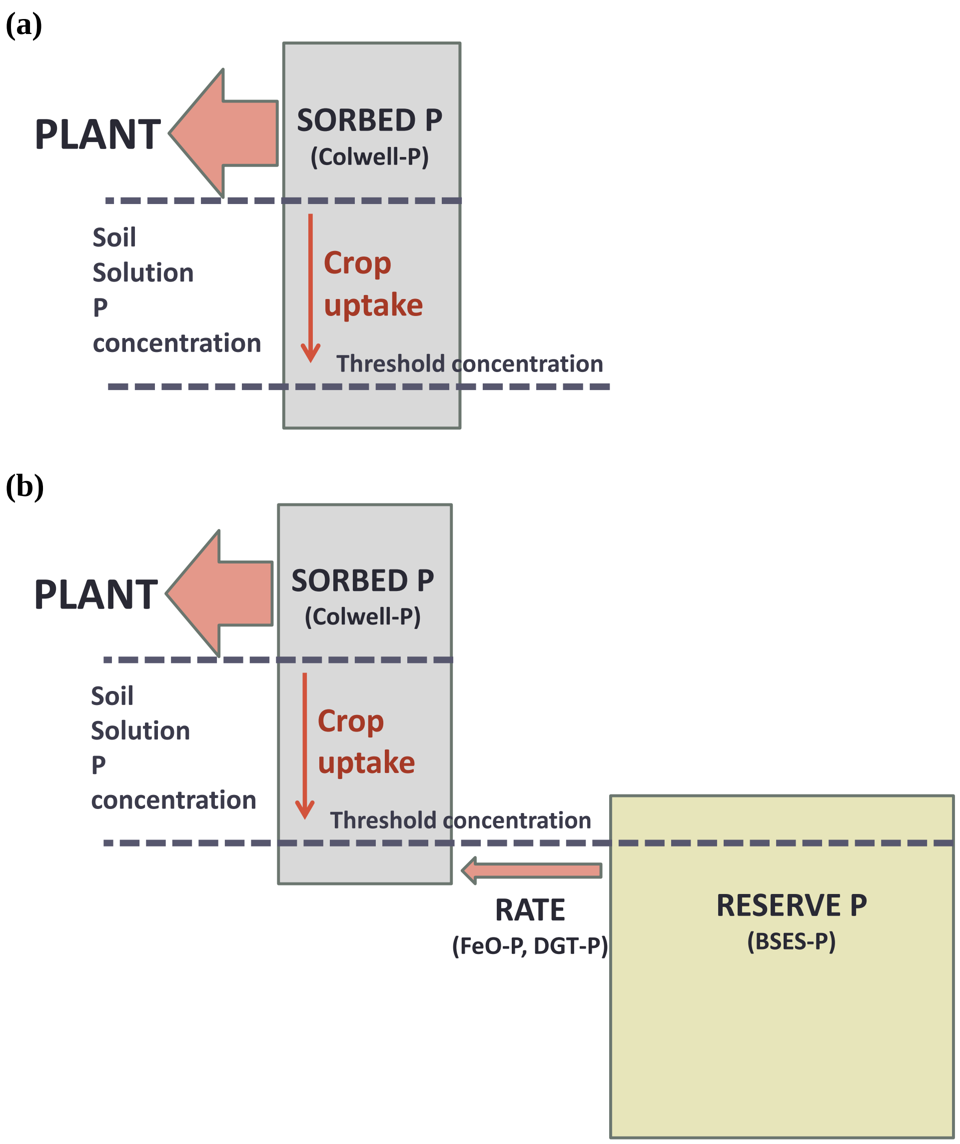


**Figure 15. Conceptual diagram of changes in soil P pools as crop P uptake occurs in Vertosols containing (a) little reserve P (i.e., BSES-P/Colwell-P < 2), and (b) appreciable amounts of reserve P (i.e., BSES-P/Colwell-P > 2).**

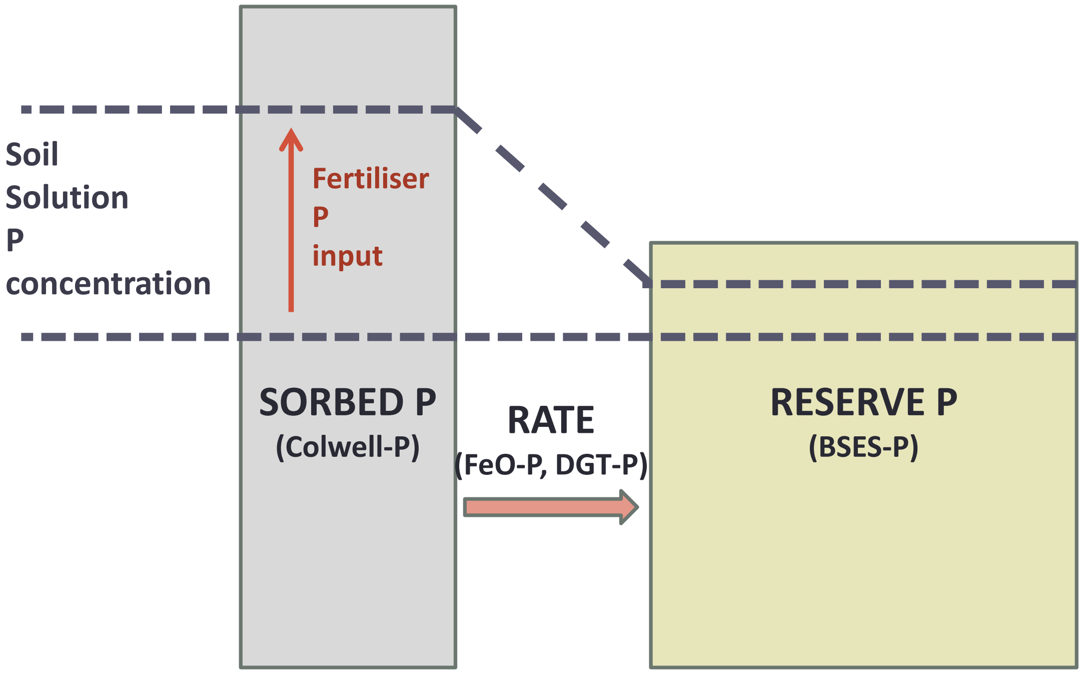


**Figure 16. Conceptual diagram of changes in soil P pools as fertiliser P is added to P-depleted soils containing appreciable amounts of reserve P (i.e., BSES-P > Colwell-P).**

These concepts allow the development of a diagnostic methodology for using soil P tests to assess the need for P fertiliser application. Based on the experimental results, the following decision trail is suggested:

- Use Colwell-P value of the 0-10 cm sample to decide whether starter P is required.
- Determine Colwell-P and BSES-P on the 10-30 cm sample.
- If BSES-P/Colwell-P<2, use Colwell-P as the indicator of the need for deep P placement. If Colwell P>10 mg/kg, deep P responses will be unlikely
- If BSES-P/Colwell-P>2, determine FeO-P (research lab) or DGT-P (commercial lab) noting that the latter test requires further refinement/development to improve its diagnostic usefulness in this situation.
- If FeO-P is less than 10% of BSES-P, then BSES-P is unlikely to contribute to available P unless some of the strategies suggested below for unlocking this reserve P are implemented. Assuming Colwell P is less than 10 mg/kg, deep fertiliser P placement will be necessary.
- If FeO-P is greater than 10% of BSES-P, then it is likely that BSES-P will contribute to available P. Test strips of deep placed P should be applied in the field and crop response monitored.
- FeO-P (or DGT-P) will only need to be measured once for each soil type because they are characterising an intrinsic soil P property.
- Where subsoil BSES-P/Colwell-P>2, monitor subsoil Colwell-P and BSES-P by sampling prior to the start of a crop cycle (say every 5-6 years). It is likely that Colwell-P will not decrease as much as BSES-P, but the decline in BSES-P will be an indication of the rate of soil P removal by the crops, and provide an early warning of the need for deep placement of P.

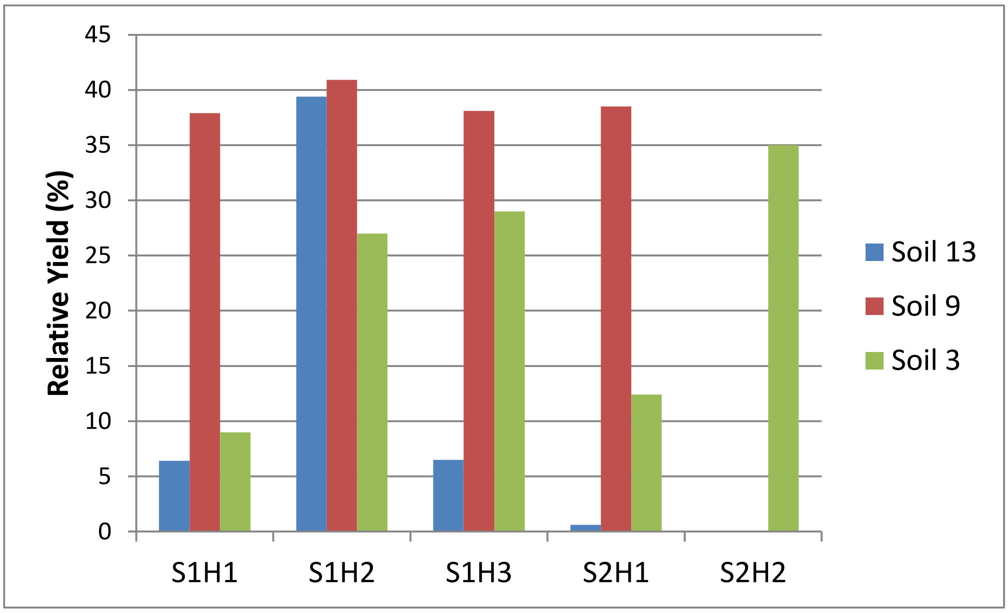
To test this methodology it was applied to Soils 13, 9 and 3. Key soil P test values of these soils are indicated in Table 3.

**Table 3. Key diagnostic soil P indicators for three soils of the northern grains region.**

| | Soil 13 | Soil 9 | Soil 3 |
|---|---|---|---|
| Colwell-P (mg/kg) | 8 | 7 | 9 |
| BSES-P (mg/kg) | 14 | 539 | 91 |
| BSES-P/Colwell-P | 1.8 | 77 | 10 |
| FeO-P (mg/kg) | 0.9 | 11.9 | 2.0 |
| FeO-P/BSES-P (%) | 6 | 2 | 2 |

The Colwell-P levels in these soils are uniformly low (8, 7 and 9 mg/kg, respectively) indicating the soils should be responsive to P fertiliser addition. However their BSES-P (and therefore reserve P) levels are vastly different, being 14, 539 and 91 mg/kg, respectively. Soil 13 has limited sorbed and reserve P pools and would require immediate fertiliser P application. Although Soils 3 and 9 have much higher BSES-P than Colwell-P (BSES-P/Colwell-P>2), the FeO-P/BSES-P ratio indicates that this P is of low availability in both soils (FeO-P/BSES-P ratio <10%). Reserve P may partially buffer declines in Colwell-P caused by crop P removal and therefore these soils may be expected to be less P deficient than Soil 13, although P fertiliser application will still be required.

The P-depletion glasshouse experiment allowed these conclusions to be compared with the progressive relative yields and P uptakes of these soils over 5 successive harvests (Fig. 17). Soil 13 quickly experienced soil P exhaustion and plants did not grow after three harvests. In contrast, although the reserve P in Soils 3 and 9 was assayed as being of low availability, plants were able to continue suboptimal growth until the fourth or fifth harvest. The diagnostic interpretation of the soil P tests is therefore in agreement with the observed plant responses.



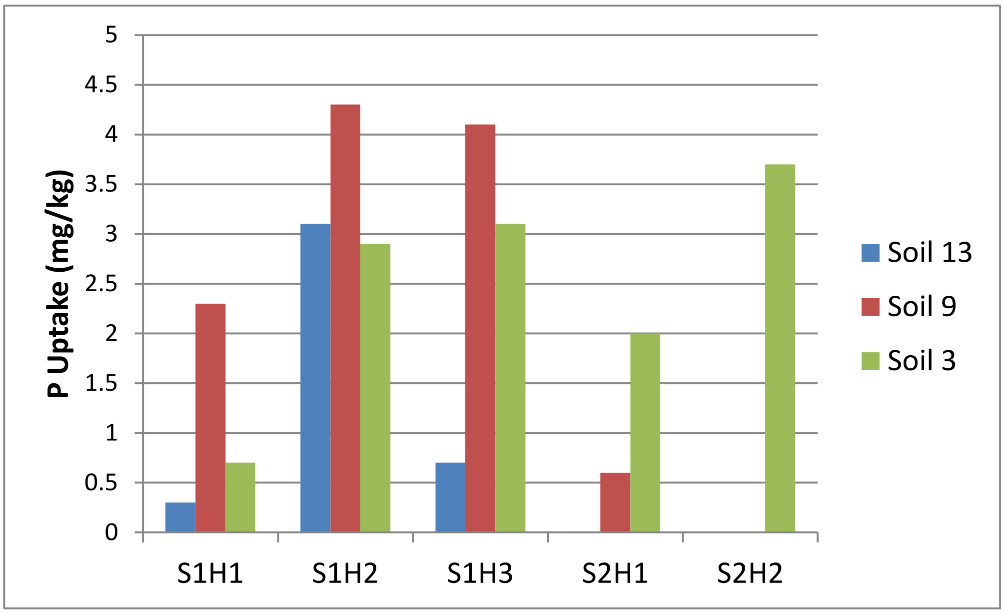


**Figure 17. Progressive relative yields and P uptakes over 5 harvests for Soils 13, 9 and 3. Soils were re-potted and re-planted after the third harvest in season 1 (S1), after which a further two harvests were conducted in season 2 (S2).**

## Summary of soil P studies

For the Vertosols and Dermosols in the study of the northern grains region soils:

- Crop P uptake lowers soil solution P concentration to a threshold value below which plants can no longer take up P (0.005-0.010 mg P/L). In this P-depleted condition, soils with BSES-P/Colwell-P ratios>2 may still contain appreciable amounts of reserve P that can be solubilised if the soil solution P concentration is lowered further.
- ‘Sorbed P’ and ‘solution P’ (both estimated by Colwell-P) are generally the primary sources of plant available P;
- However, in soils containing proportionally large amounts of ‘reserve P’ (i.e., BSES-P/Colwell-P>2), a variable proportion of this reserve P is also available to plants through the dissolution of sparingly soluble P compounds. These compounds may originate from the parent material of the soil (e.g., apatites) or occur as reaction products from the application of P fertilisers to the soils.
- The availability of reserve P can be assessed by measuring the initial rate of P supply using FeO-P (17 h equilibration time), or much less effectively, DGT-P.
- As well as being a source of plant available P, the dissolution of these compounds buffers sorbed P and solution P so the decline in these P pools is smaller than that required for quantitative equivalence with crop P uptake.
- When water-soluble P fertiliser (e.g., DAP, MAP) is added to P-depleted soils, most enters the Colwell-P fraction and remains available. Smaller, variable amounts enter the acid (BSES-P) fraction, depending on P source and soil type. Fertiliser P will have a high residual value in these soils.
- A diagnostic framework for assessing the availability of soil P reserves and the necessity for fertiliser application has been developed using currently available soil P tests.

## Implications for further work

- Many soils of the northern grains region have reserve P of varying availability. Circumstantial evidence suggests the availability of this P may relate to its origin and a rapid scan of the archived soils data of projects DAQ00084 and DAQ 00148 will be undertaken to discriminate between surface and subsurface BSES-P reserves and between subsoils with colluvial or base rock parent material.
- Further validation of the use of a one-off measurement of FeO-P (and DGT-P) to scale the availability of reserve P will be undertaken in UQ00063.

- ‘Unlocking’ the reserve P could potentially result in productivity and profitability benefits. Although variable proportions of this reserve P have been shown to be unavailable to test crops in glasshouse trials, chemical assays indicate that conditions can be manipulated to change this situation. ‘Unlocking’ this P source can potentially be achieved by:
  (a) increasing the ability of crops to take up P from very low soil solution P concentrations (i.e., lowering the ‘threshold’ solution P concentration for crop P uptake). This might be achieved by increasing the mycorrhizal infectivity of mycorrhizally-dependent crop species and/or growing these types of species more frequently in crop rotations;
  (b) causing dissolution of the soil P reserves by acidifying the rhizosphere. This could be achieved by including crops in the cropping system that are known to emit acids from their root systems (e.g., citric acid), and/ or promoting ammonium-N dominant N supply to crops through fertiliser management (nitrification inhibitors, slow-release ammonium-N fertilisers, split ammonium-N fertiliser applications in accord with crop N demand). Roots secrete protons (acid) when ammonium-N is taken up, thus acidifying the rhizosphere. This contrasts with the alkaline rhizosphere produced by nitrate-N uptake.

- Differences were observed between P sources (e.g., MAP, DAP) in the distribution of added P between sorbed P and reserve P pools depending on soil type. These results suggest that fertiliser reaction products may have different short term availabilities and could be manipulated to maximise residual availability based on soil-specific fertiliser management.

# Potassium

## Introduction

The supply of soil potassium (K) to grain crops has many similarities to that of P; the K status of the surface (0-10 cm) soil can be assessed using exchangeable K, but following establishment, the K status of the subsoil (10-30 cm) becomes critically important for maintaining adequate K supply for maximum biomass production and realisation of the grain yield potential in rain-fed systems. Similar to P, a soil sampling paradigm shift from surface soil sampling to a combination of surface (0-10 cm) and sub-surface (10-30 cm) sampling will be required and the question of the usefulness of current soil K tests for assessing the longer term availability of subsoil K has been raised. Given the large range in cation exchange capacities (CECs) of the soils of the northern grains region and the occurrence of sodic/magnesic subsoils, the effects of CEC and K saturation of the CEC on K availability require investigation. Furthermore, like P, K supply can be buffered by the dissolution of K minerals such as feldspars, vermiculites and micas, and so the quantity of ‘reserve K’ and its availability need to be characterised. This requires the development of new soil tests and methodologies not currently used.

## Methodology

*Rationale*

Fig.18 indicates soil K pools, processes and their interactions, and this conceptual diagram underpins the experimental program of this project.

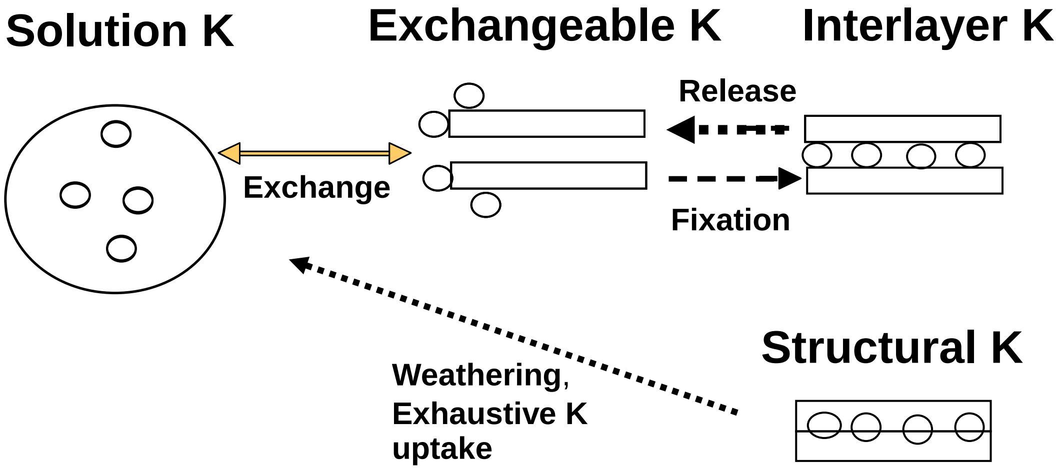


**Figure 18. Potassium pools and processes in soils of the northern grains region.**

Glasshouse experiments comprising depletion of soil potassium (K) by exhaustive cropping have been used to determine the amount of plant available K in selected soils from the northern grains region. Several K analyses have been undertaken on these soils to: (a) characterise the K pools and supply processes; (b) understand the interactions between these pools and processes in determining K supply to crops; (c) assess soil K tests for their usefulness as diagnostic indicators of soil K status; (d) determine the fate and availability of fertiliser K applied to K-depleted soils.

**Table 4. Some properties of the soils used in the K depletion glasshouse trial and cumulative crop K uptake in the first two harvests.**

| Soil | Soil Type | Depth (cm) | pH(w) | EC (dS/m) | Exch K (cmol/kg) | TB-K (cmol/kg) | CEC (cmol(+)/kg) | Total C (g/kg) | Clay (%) | Crop K uptake (cmol/kgsoil) |
|---|---|---|---|---|---|---|---|---|---|---|
| Soil 01 | Ferrosol | 0-10 | 5.4 | 54 | 0.13 | 0.25 | 8.3 | 14.6 | 51 | 0.13 |
| Soil 02 | Vertosol | 10-30 | 7.1 | 45.5 | 0.24 | 0.37 | 25.9 | 12.5 | 54 | 0.23 |
| Soil 03 | Vertosol | 0-10 | 6.7 | 75.5 | 0.53 | 0.68 | 45.4 | 17.7 | 62 | 0.62 |
| Soil 04 | Vertosol | 10-30 | 7.4 | 37.7 | 0.08 | 0.09 | 43.2 | 5.7 | 67 | 0.05 |
| Soil 05 | Vertosol | 10-30 | 8.1 | 39.5 | 0.19 | 0.26 | 68.1 | 8.3 | 73 | 0.15 |
| Soil 06 | Vertosol | 0-10 | 5.4 | 160.2 | 1.05 | 1.65 | 37.4 | 24.3 | 59 | 1.05 |
| Soil 07 | Vertosol | 10-30 | 5.9 | 70.2 | 0.45 | 0.61 | 36.5 | 18.1 | 61 | 0.46 |
| Soil 08 | Vertosol | 0-10 | 7.4 | 96.1 | 0.87 | 1.41 | 48.0 | 18.3 | 59 | 0.61 |
| Soil 09 | Vertosol | 0-10 | 7.1 | 59.2 | 0.47 | 0.84 | 34.7 | 9.1 | 53 | 0.4 |
| Soil 10 | Vertosol | 10-30 | 7.8 | 52.5 | 0.25 | 0.39 | 37.0 | 7.1 | 56 | 0.2 |
| Soil 11 | Vertosol | 0-10 | 6.4 | 117.3 | 0.69 | 2.82 | 24.9 | 16.9 | 47 | 1.33 |
| Soil 12 | Vertosol | 0-10 | 8.4 | 114.6 | 0.40 | 0.61 | 39.5 | 10 | 50 | 0.51 |
| Soil 13 | Vertosol | 0-10 | 8.1 | 201 | 1.09 | 2.67 | 45.1 | 17.5 | 45 | 0.38 |
| Soil 14 | Vertosol | 0-10 | 8.2 | 45.5 | 0.21 | 0.43 | 23.5 | 6.6 | 39 | 0.32 |
| Soil 15 | Vertosol | 0-10 | 7.4 | 52.1 | 0.47 | 0.87 | 28.8 | 10.5 | 49 | 0.92 |
| Soil 16 | Vertosol | 0-10 | 8.3 | 95.7 | 0.93 | 3.14 | 44.0 | 11.4 | 64 | 0.75 |
| Soil 17 | Vertosol | 10-30 | 8.7 | 160 | 0.67 | 2.50 | 45.4 | 9 | 66 | 0.58 |
| Soil 18 | Ferrosol | 0-10 | 8.3 | 174.5 | 1.45 | 2.39 | 74.8 | 24.9 | 73 | 1.27 |
| Soil 19 | Ferrosol | 0-10 | 8 | 46.5 | 1.20 | 1.63 | 68.4 | 9.6 | 80 | 1.04 |
| Soil 20 | Ferrosol | 10-30 | 7.9 | 38.3 | 0.48 | 0.66 | 68.7 | 8.1 | 81 | 0.4 |
| Soil 21 | Ferrosol | 10-30 | 8.3 | 73.1 | 0.95 | 1.46 | 89.7 | 11.2 | 83 | 1.14 |
| Soil 22 | Vertosol | 10-30 | 8.5 | 62.4 | 0.31 | 1.72 | 34.8 | 12.8 | 49 | 0.42 |
| Soil 23 | Podosol | 0-10 | 6.6 | 22.9 | 0.29 | 0.56 | 3.2 | 6.9 | 7 | 0.4 |
| Soil 24 | Vertosol | 0-10 | 8.8 | 148.1 | 1.57 | 2.86 | 39.3 | 5.8 | 58 | 0.85 |

*Soil K characterisation*

For soil K characterisation, the following methods have been used to estimate the pools and processes in Fig. 18:

- Exchangeable K (Exch K) (0.5 M $NH_4Cl$, pH 7) measures solution plus exchangeable K;
- Tetraphenyl borate extractable K (TB-K) (1 g soil, 0.2 g Na-tetraphenyl borate, 1 h shake) estimates exchangeable K plus solution K plus reserve K.
- K depletion curves using graded amounts of tetraphenyl borate to partially deplete the soil K reserves, followed by 24 h equilibration of the depleted soil with DI water, and measurement of K concentration in solution. K removed by tetraphenyl borate (*y* axis) plotted against equilibrium solution K concentration (*x* axis) is used to assess the rate of release of reserve K.

*Glasshouse experiments*

Two K depletion glasshouse experiments have been undertaken- the first comprised 27 soils of the northern grains region, and the second was undertaken on a further 24 grain cropping soils with an emphasis on selecting soils of diverse (TB-K/ Exch K) ratios (Table 4). The second glasshouse trial is continuing. In both experiments, treatments comprise ‘plus K’ (140 kg K/ha on an area basis; 2 reps) and ‘nil K’ treatments (4 reps). Basal nutrients were applied to all plots at the following rates (kg/ha on an area basis): N, 140; S,40; Ca, 30; Mg, 30; Zn, 5; Cu, 5; B, 1; Mo, 0.2. The first experiment comprised 3 harvests of forage oats, re-potting, 2 harvests of millet, re-potting, and 6 harvests of forage sorghum. In the second experiment, six forage sorghum plants were established in each pot (planted: 21/03/2012) and two dry matter cuts taken (18/05/2012; 14/09/2012). Soil was then removed from each pot and mixed. Visible root material was removed, the soil re-potted, and forage sorghum re-sown (21/09/2012). Two more dry matter cuts have been taken (23/11/2012; 21/12/2012). Currently, plants have failed to re-grow because of extreme K deficiency in all except 5 soils. Plant samples from each harvest have been ground and analysed for K. Crop K uptake has been was calculated for each of the first two harvests and summed to give cumulative K uptake.

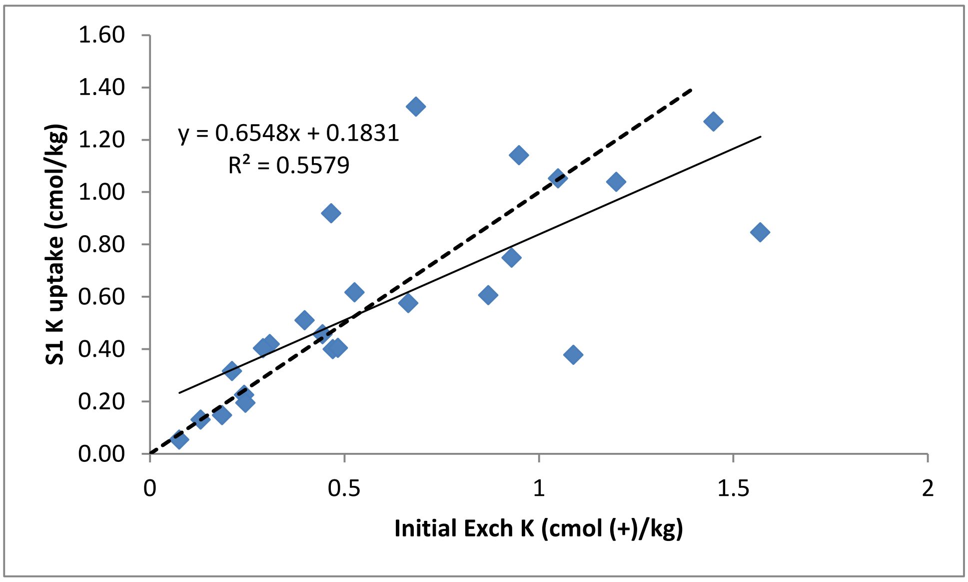
*Fertiliser K addition to depleted soils*

Soluble K was added to several K-depleted soils from the first glasshouse experiment and they were incubated at field capacity for 7 days (Time 1:T1) prior to determination of exchangeable K (Exch K) and $TB\text{-}K_{1h}$. A separate set of soil samples were taken through the same incubation procedure and then subjected to 5 wetting/drying cycles (Time 2:T2) before extracting Exch K and $TB\text{-}K_{1h}$.

## Results

*Glasshouse experiment 2*

Cumulative K uptake from the two harvests of Season 1 is plotted against initial exchangeable K and $TB\text{-}K_{1h}$ in Fig. 19. While soils with less than about 0.5 cmol(+)/kg exchangeable K lie on the 1:1 line, the line of best fit for all soils indicates that cumulative K uptake is about 65% of exchangeable K. Similarly for TB-K, soils with less than about 0.7 cmol/kg $TB\text{-}K_{1h}$ lie on the 1:1 line, but overall, K uptake is approximately 25% of TB-K.



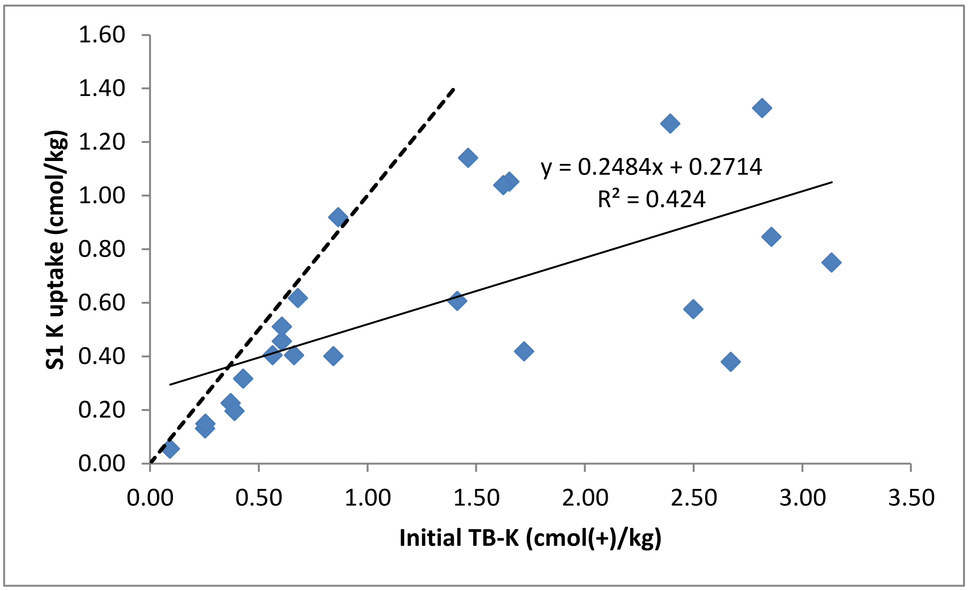


**Figure 19. Cumulative Season 1 crop K uptake plotted against (a) initial exchangeable K, and (b) initial TB-$K_{1h}$. Dashed lines are 1:1 relationship.**

When the change in exchangeable K and TB-$K_{1h}$ between planting and the final Season 1 sampling is plotted against cumulative K uptake, TB-K quantitatively accounts for K uptake whereas exchangeable K only accounts for about 60% of the cumulative uptake (Fig. 19). These results indicate that TB-K buffers changes in exchangeable K, but not all TB-K is plant available (cf. Fig 19 and Fig 20).

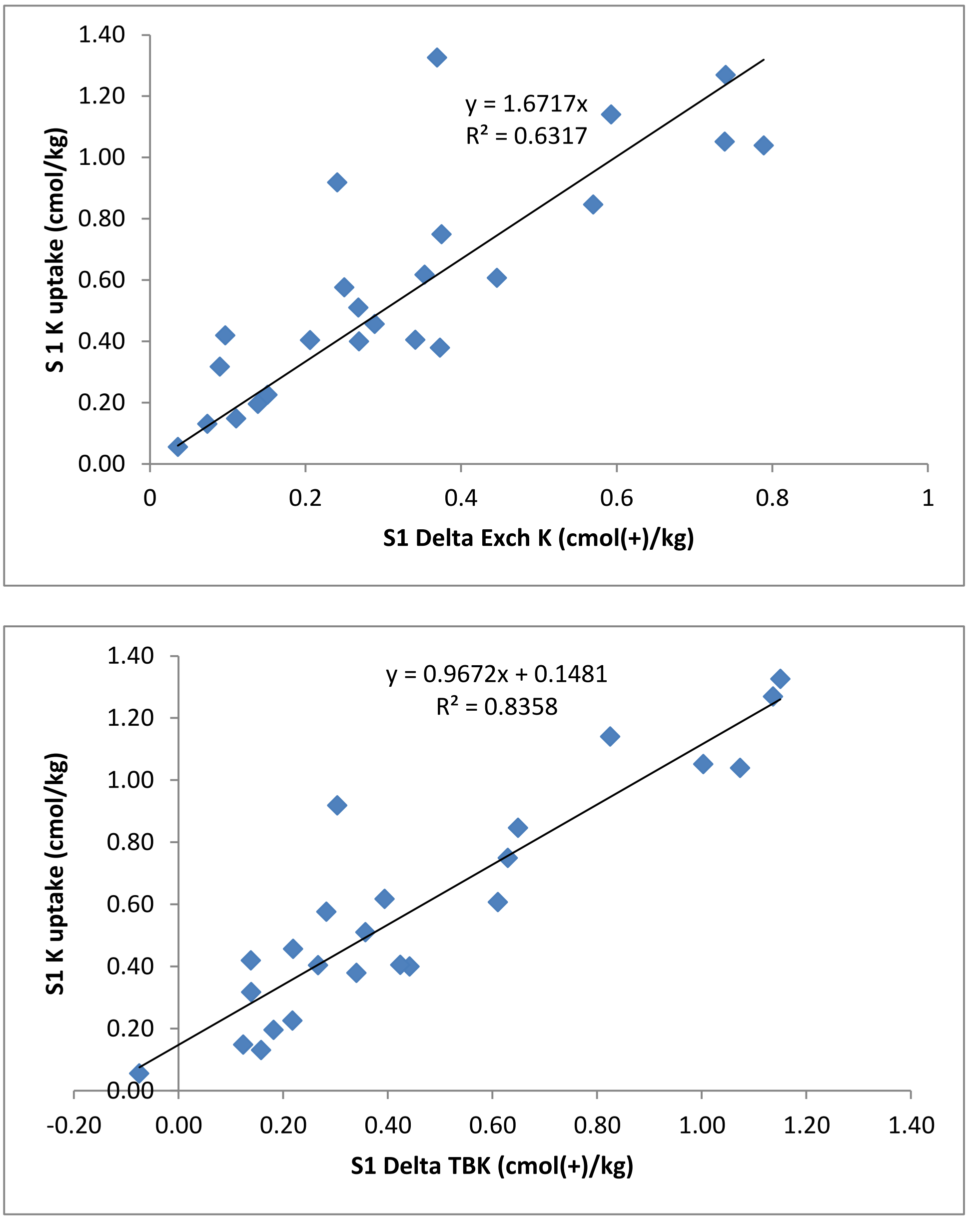


**Figure 20. Cumulative Season 1 crop K uptake plotted against change in (a) exchangeable K, and (b) TB-$K_{1h}$.**

*K desorption curves*

To discriminate between available and unavailable TB-K, K desorption curves were carried out on selected soils from the first glasshouse experiment to establish whether a single point K desorption index could be developed to describe the rate of release of TB-K. Typical desorption curves are shown in Fig. 21. Although a single linear regression equation best fits the data for two of the soils, the other soil exhibits a breakpoint and then a much higher rate of release at a soil solution K concentration of less than 0.05 cmol K/L. The slopes of the curves are correlated with TB-$K_{1h}$ (r=0.75; $P$<0.001) and exchangeable K (r=0.53; $P$<0.01). Therefore, by measuring the solution K concentration after TB-$K_{1h}$ extraction plus the solution K concentration after an addition of tetraphenylborate equivalent to the exchangeable K, it should be possible to use these two points to estimate the rate of K release. This approach will be trialled on all soils used in the second glasshouse trial because they cover a much wider range of TB-K/Exch K ratios than the soils used in the first experiment.

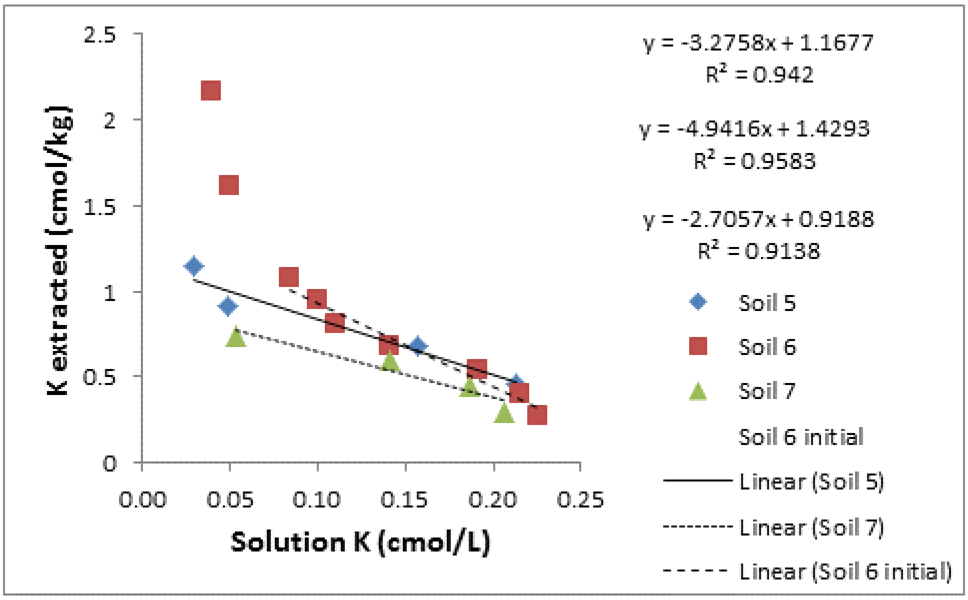


**Figure 21. K desorption curves for 3 soils.**

*Fertiliser K addition to depleted soils*

Table 5 shows the initial K status of the soils, the amount of K added in the incubation experiment and the soil K status after incubation at field capacity (T1) and then following a series of wetting-drying cycles (T2). In all soils, at least 68% of added K was present as exchangeable K after initial incubation at field capacity. In Soils 15, 16 and 17, all remaining added K was extracted as TB-K, but in Soil 12, TB-K did not extract all added K and about 20% was unaccounted for. Following 5 wetting/drying cycles, the proportion of added K present as exchangeable K decreased in Soils 12 and 15, and was recovered as TB-K, but there was no movement of K from the TB fraction into un-extracted forms. The high variability in the TB-K in some soils after wetting/drying (e.g., Soil 17) suggests the variable nature of the sorption-fixation reactions occurring.

**Table 5. Initial K status, K added and percentage of added K extracted at two times (T1, T2) after K addition. SE mean is presented in brackets.**

| *Soil No.* | *Initial Exch K* (cmol/kg) | *Initial TB-K (1 h)* (cmol/kg) | *K added* (cmol/pot) | **T1** | | **T2** | |
|---|---|---|---|---|---|---|---|
| | | | | **Exch K** | **TB-K(1h)** | **Exch K** | **TBK (1 h)** |
| 12 | 0.11 | 0.40 | 1.5 | 80 (±2) | 78 (±5) | 64 (±2) | 76 (±7) |
| 13 | 0.06 | 0.06 | 1.1 | 93 (±3) | 92 (±5) | 85 (±1) | 90 (±2) |
| 15 | 0.12 | 2.2 | 0.8 | 80 (±3) | 119 (±6) | 68 (±2) | 95 (±27) |
| 16 | 0.25 | 3.0 | 1.3 | 68 (±1) | 105 (±14) | 60 (±2) | 102 (±8) |
| **17** | 0.14 | 4.2 | 0.9 | 76 (±4) | 111 (±17) | 69 (±2) | 99 (±26) |

### Summary of soil K studies

- Vertosols of the northern grains region often have high contents of reserve K in comparison to exchangeable K.
- Cumulative K uptake is quantitatively related to change in soil tetraphenyl borate extractable K (TB-K), although the proportion of this reserve K that is available is variable. The source of this available reserve K is interlayer K and/or soil mineral K.
- As well as being a source of plant available K, the reserve K buffers exchangeable K so the decline in this K pool is smaller than that required for quantitative equivalence with crop K uptake.
- When K fertiliser is added to K-depleted soils, most enters the exchangeable K fraction and remains available. Smaller, variable amounts enter the TB-K pool, depending on soil type, but will remain available. Therefore, K fertiliser will have a high residual value in these soils

### Implications for further work

- On completion of the current K depletion experiment, further assessment of the usefulness of exchangeable K and TB-K as diagnostic indicators of soil K status will be undertaken. However, it is apparent that changes in TB-K quantitatively reflect plant available K.
- The overall availability of TB-K needs definition, and to achieve this, the two-point K desorption index developed in the current project will be validated using the results of the completed glasshouse trials. This index will require one further TB-K analysis in addition to the diagnostic TB-$K_{1h}$, but will only need to be measured once on a soil type because it characterises an intrinsic soil chemical property.

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