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Changes in phosphorus fractions at various soil depths following long-term P fertiliser application on a Black Vertosol from south-eastern Queensland

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Abstract. Long-term removal of grain P and soil test data suggested that the Colwell phosphorus (P) extraction from the surface 0.10 m of a Black Vertosol from south-eastern Queensland was a poor indicator of run-down of soil P pools. We proposed that plants were also accessing P from layers below 0.10 m or from surface soil P pools not extracted by the Colwell extraction. Both topsoil and subsoil samples in 1994 and 2003 were collected from nil and 20 kg P/ha per crop treatments in a long-term N × P field experiment established in 1985 for detailed P fractionation. An uncropped reference soil was also taken in 2003 from an adjacent area. The long-term effect of the field treatments on soil P fractions was evaluated by comparing the reference site, which was assumed to represent the original soil condition, to the 2003 samples.

Without addition of P fertiliser, 55%, 35%, and 10% of total P removal were from 0 to 0.10, 0.10 to 0.30, and 0.30 to 0.60 m, respectively, compared with the uncropped reference soil. Labile fractions comprising resin, bicarbonate, and hydroxide pools in the top 0.10 m decreased by approximately 60% and accounted for 15% of the total P decrease from 0 to 0.60 m depth. Acid and residual-P fractions decreased by 50% and 20%, respectively, and accounted for ~20% and 15% of the total P decrease. In contrast, P addition at 20 kg P/ha per crop over 18 crops doubled the resin and bicarbonate inorganic P ($NaHCO_3$-Pi) pools in the surface 0.10 m. Hydroxide (NaOH-Pi) and acid extracted inorganic P increased by 25% and 10%, respectively, while the residual-P pool decreased by about 15%. Below 0.10 m, very little P was removed by the first 3 extractants. Most of the P was present in the acid and residual fractions irrespective of fertiliser application. The acid and residual-P dropped by 30% and 12%, respectively, at 0.10–0.30 m and 12% and 8% at 0.30–0.60 m. When comparing the experimental soil samples in 2003 with those in 1994, similar trends were observed in the changes of each soil P fraction. In the surface 0.10 m, acid and residual-P pools decreased greatly and explained almost all of the total P decrease in the surface soil without P input. With P addition, labile pools acted as the main sink for P. The acid pool increased by 7%, while the residual-P showed a decrease in the topsoil. Total P level was elevated noticeably in this soil layer. However, at 0.10–0.30 m depth, acid and residual pools were the dominant fractions and decreased significantly irrespective of P fertiliser addition. Below 0.30 m, no significant changes were detected for each fraction and total P. The results suggest that crops had accessed significant amounts of P at 0.10–0.30 m depth irrespective of P fertiliser application, and that subsoil sampling (0.10–0.30 m) should be considered in order to improve the monitoring of soil P status. However, choice of appropriate extractants for monitoring subsoil P reserves is yet to be undertaken.

Additional keywords: Colwell P, long-term cropping effect, P balance, P fractions, P stratification, subsoil.

Introduction

Colwell soil test phosphorus (P) (sodium bicarbonate reagent) (Colwell and Esdaile 1968) is routinely used as an indicator of plant-available P in soils of northern New South Wales and southern Queensland. This method has a wider solution/soil ratio and longer extraction time compared with other soil tests such as Olsen and Bray. Colwell (1963) reported that the 100 : 1 ratio gave more reproducible results for several reasons, one being more reproducible equilibrium conditions associated with the long shaking period, hence P could equilibrate from the relatively slowly available pools, making it more closely related to the exchangeable P than P response (Holford 1997). Combined with the measurement of P buffer capacity, Colwell P provides an accurate prediction of plant-available P (Holford and Mattingly 1979; Holford 1980*b*).

However, the application of the Colwell P soil test as an indicator of P sustainability is questioned by the data from 2 long-term N × P experiments conducted on Vertosols in the northern grains region, one site in southern Queensland and the second in northern New South Wales. Lester *et al.* (2003) showed unchanged Colwell P soil test levels in the nil P treatments despite more than 200 kg P/ha being removed from the soil in grain at one of the sites. Where P fertiliser was applied, Colwell P values steadily increased, which is consistent with the findings

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of Strong *et al*. (1997) on 2 other Vertosols from southern Queensland. Although it is generally accepted that exchangeable P is the major source of plant-available P in neutral to alkaline soils (Holford and Mattingly 1976*b*), these results suggest that exchangeable P or plant-available P is being replenished from other soil P pools.

Phosphorus pools that may buffer soil test P levels have been identified for various soil types through P fractionation methods (Beck and Sanchez 1994; Sharpley 1996; Saleque *et al*. 2004). Without P addition, P fractions considered non-labile may become increasingly available to plants, although the proportion of contribution depends on soil type and other environmental conditions (Schmidt *et al*. 1996; Guo *et al*. 2000). Beck and Sanchez (1994) reported that sodium-hydroxide-extractable inorganic P (NaOH-Pi) was the dominant fraction related to plant P availability in an 18-year continuously cultivated and fertilised cropping system on an Ultisol. In contrast, acid-extractable and residual-P fractions were found to act as a major buffering pool for labile P in slightly weathered soils (Hedley *et al*. 1982; McKenzie *et al*. 1992*a*, 1992*b*). It seems that the main P buffering pools are closely associated with both soil type and the dominant P fractions. Application of P fertiliser can replenish the labile P pools and maintain or increase soil fertility. The sink of P fertiliser can be in the more labile fraction (Iyamuremye *et al*. 1996; Lilienfein *et al*. 1999; Oberson *et al*. 1999) or stable fractions such as acid-extractable or even residual pools (Linquist *et al*. 1997; Zhang and MacKenzie 1997*a*; Daroub *et al*. 2000). Investigating the source of P for plant uptake is problematic due to the confounding effect of continuous P fertiliser input.

To date, the majority of soil P research worldwide has focused on the topsoil; and little attention has been given to subsoil P pools which may act as an additional source of plant-available P. In the northern grains region of eastern Australia where stored moisture is critical to successful grain production, the contribution of subsoil P resources needs to be quantified considering that the roots of grain, fodder, and fibre crops may penetrate deeply into the soil profile, particularly later in the growing season. Norrish (2003) reported a positive correlation between grain yield and the mean concentration of Colwell P to a depth of at least 0.60 m in north-western New South Wales. Unchanged Colwell P value in the nil-P treatments at 2 long-term N × P experiment sites (Lester *et al*. 2003) demonstrated the necessity to investigate what was going on below the soil test depth of 0–0.10 m. In this present study, we hypothesised that crops could also access soil P either from subsoil layers (below 0.10 m) or from surface soil P pools which are not extracted by the Colwell method. As part of this investigation, we collected both topsoil and subsoil from one of the long-term N × P fertiliser experiments and from an uncropped reference site to study the impacts of long-term cropping with and without P fertiliser input on P fractions at various soil depths.

Materials and Methods

Experimental design

A long-term N × P fertiliser experiment was initiated in 1985 at the 'Colonsay' property in the Norwin district of the central Darling Downs, south-east Queensland. Full details of the experimental site and history are provided in Lester *et al*. (2007). Briefly, the soil at the field site is a Black Vertosol (Isbell 2002) (Table 1). The experiment consists of factorial combination of 4 N rates (0, 40, 80, or 120 kg N/ha per crop) at each of 4 P rates (0, 5, 10, or 20 kg P/ha per crop) in a randomised complete block design. The soil used in this study was collected in 1994 and 2003 from the plots receiving 80 kg N/ha with P application rates of 0 and 20 kg/ha at each of 3 blocks. Grain yield has been optimised at this N rate over the experiment's history and hence has the highest grain P removal. Nitrogen was applied as urea away from the seed, and P applied as triple superphosphate (20.7% P) in the seed furrow at sowing. From 1985 to 2003, 18 crops were sown. These included 10 crops of grain sorghum (*Sorghum bicolor*), 4 crops of barley (*Hordeum vulgare*), 3 crops of wheat (*Triticum aestivum*), and chickpea (*Cicer arietinum*) once. All the plant residues were returned to the field.

Soil sampling and phosphorus determination

Soil samples in 2003 were collected at 3 depths: 0–0.10, 0.10–0.30, and 0.30–0.60 m. In banded P fertiliser applications under minimal or zero-tillage, soil sampling is problematic due to the presence of residual P bands. To overcome variability in distribution and P residue differences due to varying row spacing configurations, soil samples were taken across the plot perpendicular to the line of application for 0–0.10 m depth from all replicates at 5 distances down a row (Stecker and Brown 2001). Samples below 0.10 m were collected using a hydraulic core sampler and 32-mm tube. An uncropped reference soil sample was taken from outside the planted area at the same depths. The experiment site was cropped for at least 44 years before establishment of the experiment. In addition, archived samples collected in 1994 from the N × P experiment were also fractionated for P determination.

Samples were dried at 40°C for 48 h, then ground to <2 mm. A subsample was further ground to ≤0.149 mm (100 mesh) for depths from 0 to 0.10 and 0.10 to 0.30 m and ≤0.5 mm for depths from 0.30 to 0.60 m. A modified version

Table 1. Soil characteristics (0–0.60 m) at Colonsay, Darling Downs, Queensland

	0–0.10 m	0.10–0.30 m	0.30–0.60 m
pH $CaCl_2$	7.7	8.1	8.1
ECse dS/m	3.5	3.5	3.7
Organic Carbon (%)[A]	1.2	0.9	–
Exchangeable Ca (cmol(+)/kg)	36	36	29
Exchangeable Mg (cmol(+)/kg)	25	25	29
Exchangeable K (cmol(+)/kg)	1.4	1.4	1.1
Exchangeable Na (cmol(+)/kg)	4.3	4.3	8.7
Bulk density (g/cm^3)	1.01	1.06	1.05

[A] 1994 site data.

of the Hedley P fractionation scheme (Guppy *et al.* 2000) was used to sequentially fractionate soil P (Fig. 1). Aliquots of the bicarbonate and hydroxide extracts were microwave digested at 120°C for 45 min using acid potassium persulfate (Turner *et al.* 2003) and analysed for total P colourimetrically. Organic P of these 2 fractions was calculated as the difference between total and inorganic P. Total soil P was analysed using concentrated $H_2SO_4 : HClO_4$ (20 : 1) acid digestion to calculate the P recovery. Inorganic phosphate in the extracts was determined colourimetrically using malachite green (Motomizu *et al.* 1983). Each P pool value expressed in mg P/kg soil was converted to kg P/ha by using the measured bulk density shown in Table 1.

Calculations and statistical analysis

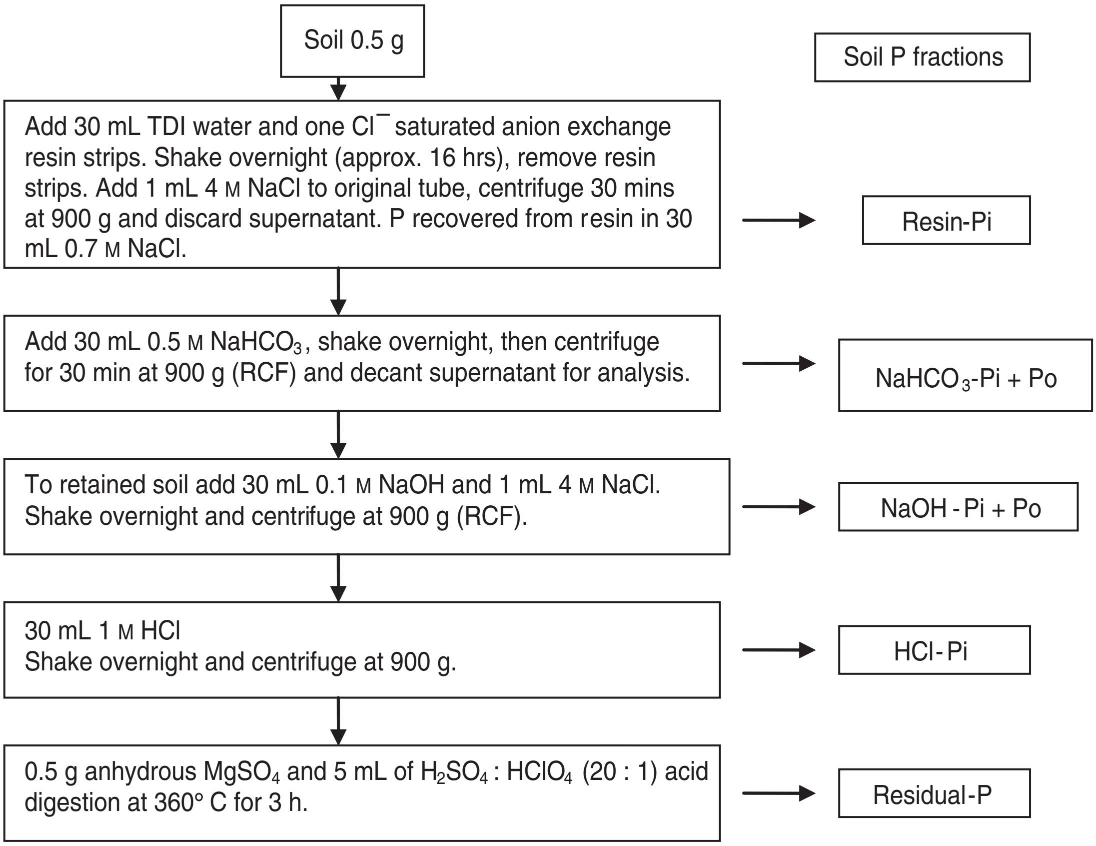
A P mass balance for the cropping system was generated using the following assumptions. Phosphorus inputs were calculated based on the application of P fertilisers. Phosphorus outputs were calculated from grain yields and, prior to 1992, estimated grain P concentration for sorghum (0.34%), and wheat and barley (0.28%). After 1992, grain P concentration in the fertilised treatments was measured as 0.37% for sorghum and 0.35% for wheat and barley, while in unfertilised plots, 0.33% for sorghum and 0.28% for wheat and barley. Net P balance was then calculated as the difference between P input from the fertiliszer and outputs in the crop grain.

Although time-consuming, the sampling method was robust and variation within rows and treatments was minimal (data not shown). Variation from subsampling within rows of each treatment was included in random error terms (i.e. 9 replicates were used for soil sampled in 2003) to increase the power of the statistical analysis. Variance within each row and the effect of P addition on distribution of P fractions along the soil depth were statistically analysed by using a 3-way analysis of variance for each fraction. The reference soil was taken at one location and 3 cores were bulked to a single sample. This limits the ability to perform statistical analysis on the differences in each fraction between reference site and experiment site. The long-term cropping effect between 1994 and 2003 were evaluated by a *t*-test between means. The statistical analyses were performed using the R software package (R 2.3.0).

Results

P removal in the grain from 1985 to 2003

Compared with nil P input, 20 kg/ha of P fertiliser application significantly increased P uptake in grain in most years (Fig. 2). Reductions in crop P removal in grains were frequently associated with the poor yields in these years, e.g. 1992 and 2002, irrespective of P application (Lester *et al.* 2007). On average, 12 kg P/ha had been removed from the unfertilised soil each year. No significant decreasing pattern in P removal could be detected within each crop species from 1985 to 2003. Additionally, the



Soil 0.5 g

Add 30 mL TDI water and one Cl^- saturated anion exchange resin strips. Shake overnight (approx. 16 hrs), remove resin strips. Add 1 mL 4 M NaCl to original tube, centrifuge 30 mins at 900 g and discard supernatant. P recovered from resin in 30 mL 0.7 M NaCl.

Add 30 mL 0.5 M $NaHCO_3$, shake overnight, then centrifuge for 30 min at 900 g (RCF) and decant supernatant for analysis.

To retained soil add 30 mL 0.1 M NaOH and 1 mL 4 M NaCl. Shake overnight and centrifuge at 900 g (RCF).

30 mL 1 M HCl
Shake overnight and centrifuge at 900 g.

0.5 g anhydrous $MgSO_4$ and 5 mL of $H_2SO_4 : HClO_4$ (20 : 1) acid digestion at 360° C for 3 h.

Fig. 1. Sequential soil P fractionation procedure modified from Guppy *et al.* (2000). Pi and Po indicate the inorganic and organic fractions, respectively, within a pool.

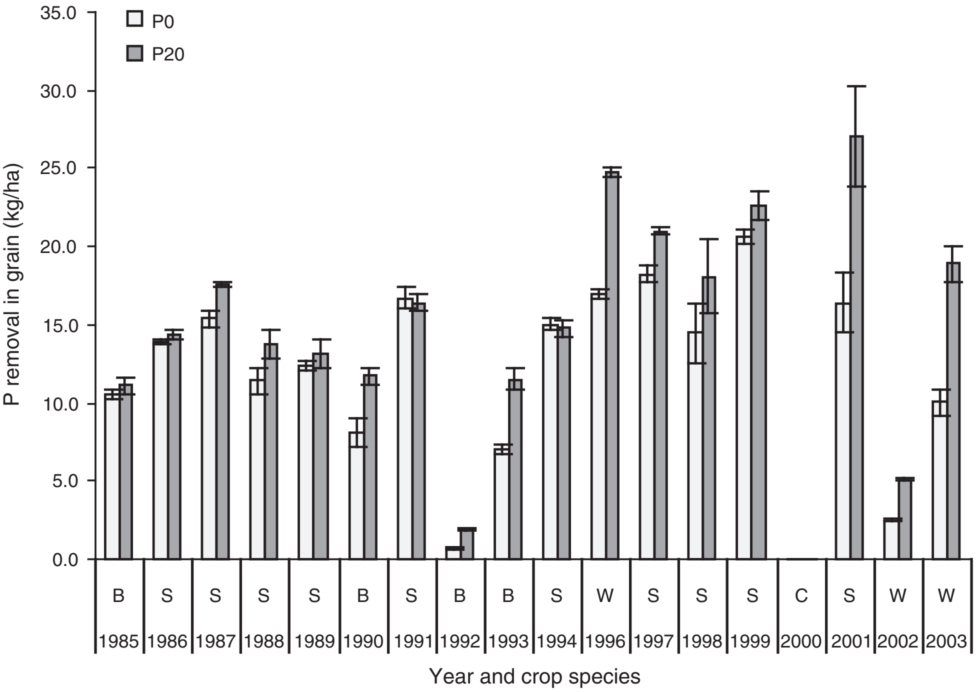


Fig. 2. P removal in response to P fertiliser application at Colonsay, Darling Downs, Queensland from 1985 to 2003. Presented data are selected from plots received 80 kg N/ha at 2 P rates: 0 and 20 kg/ha. Error bars represent standard error of means of 6 replicates. B, Barley; S, sorghum; W, wheat; C, chickpea.

extent of P removal in response to P addition varied between crop species over 18 years. With 20 kg/ha of P input, the averaged P uptake increased by 19% for sorghum and 55% for wheat and barley. Differential P response could be related to many factors, particularly variation in rainfall distribution and crop water use, or arbuscular mycorrhizae infection (Thompson 1987; Lester *et al*. 2007).

Effect of fertiliser P addition on the distribution of P fractions along the soil depth

The fractionation scheme used in this study extracted >90% of the total P from the soil (Table 2). Acid-extractable P and residual-P were the dominant fractions and collectively constituted at least 75% of the sum of all fractions. Less than 30% of the total P, irrespective of soil depth or treatment, was extracted from labile (ΣResin + $NaHCO_3$ + NaOH) fractions (Table 2). Both total P and labile P pools decreased with depth, an effect more noticeable in the fertilised treatments (Table 2). In the surface 0–0.10 m, the ratio of labile P to total P increased from approximately 5% without P application to 20% with P application (Table 2). The proportion of NaOH-extracted inorganic P (NaOH-Pi) had also been raised from 4 to 8% ($P < 0.05$) with P application. Minimal influence of P fertilisation on soil P fractions was observed below 0.10 m (Table 2). Only small increases in resin-P and NaOH-Pi ($P < 0.05$) at 0.10–0.30 m depth were observed. There were no differences in any pools within the 0.30–0.60 m layer.

Bicarbonate-extracted organic P ($NaHCO_3$-Po) is negligible (<1%) while hydroxide-extractable organic P (NaOH-Po) accounted for >8% of the total extracted P at top soil (Table 2). Both of these organic pools decreased with soil depth as expected, since under no-till systems, crop residues remained at the surface.

Cropping effects on soil P

The effect of conversion to cropping on soil P fractions was evaluated by comparing the reference site, which was assumed to represent the original soil condition, to the 2003 samples (Table 3). Without P fertilisation, there was a total P loss of 264 kg/ha from the soil profile, 55% of which came from the surface 0.10 m, with 35% and 10% from 0.10 to 0.30 m and 0.30 to 0.60 m, respectively. Resin-P + $NaHCO_3$-Pi in the top 0.10 m decreased by 70%, and accounted for 8% of the total P decrease. The NaOH-Pi pool declined by 60% and accounted for 5% of total P decrease. Acid and residual P, theoretically the most stable pools, dropped by 50 and 20%, respectively, and accounted for about 19% and 15% of the total P decrease. Below 0.10 m, very little P was removed by the first 3 extractants. Most of the P was present in the acid and residual fractions (Table 2). The acid and residual P dropped by 30% and 12%, respectively, at 0.10–0.30 m and 12% and 8% at 0.30–0.60 m.

By comparison with the reference soil, long-term application of P fertiliser caused the soil to accumulate P preferentially in the labile fractions (Resin/$NaHCO_3$/NaOH) in the surface 0.10 m (Table 3). Resin-P and $NaHCO_3$-Pi doubled. NaOH-Pi and acid pool increased by 25% and 10%, respectively, while residual P decreased by 14%. Below 0.10 m, acid and residual pools were the dominant fractions and their reduction was equivalent to that of unfertilised soil.

Table 2. Distribution of different soil P fractions (mg/kg) at soil depths of 0–0.10, 0.10–0.30, and 0.30–0.60 m on a Black Vertosol collected from a long-term experiment site at Colonsay, Darling Downs, Queensland in 1994 and 2003

Reference represents a site which remained uncropped since the start of trial and was included for comparison. Standard errors are shown in parentheses

P addition (kg/ha)	Soil depth (m)	Resin-P	$NaHCO_3$		NaOH (mg/kg)		HCl-P	Residual-P	Sum	Total P	Recovery (%)
			Pi	Po	Pi	Po					
					2003						
0	0–0.10	5.5 (0.5)	5.0 (0.2)	1.8 (0.2)	10.7 (0.3)	21.4 (0.9)	61 (2)	154 (1)	259 (3)	270 (4)	96
	0.10–0.30	0.8 (0.2)	2.2 (0.1)	0.5 (0.1)	5.1 (0.4)	9.9 (1.0)	57 (3)	139 (3)	214 (3)	223 (2)	95
	0.30–0.60	1.1 (0.1)	1.6 (0.1)	0.5 (0.1)	5.7 (0.4)	5.8 (1.2)	68 (6)	129 (3)	212 (5)	223 (3)	95
20	0–0.10	33.7 (1.4)	34.1 (1.4)	2.9 (0.6)	34.1 (1.1)	17.2 (1.6)	130 (4)	170 (1)	407 (4)	450 (5)	93
	0.10–0.30	2.5 (0.6)	2.7 (0.5)	0.3 (0.0)	7.3 (0.6)	7.8 (0.8)	59 (2)	139 (3)	218 (5)	228 (5)	96
	0.30–0.60	1.1 (0.1)	1.4 (0.1)	0.5 (0.1)	5.6 (0.2)	4.8 (0.3)	69 (6)	130 (3)	212 (6)	221 (3)	96
Reference	0–0.10	16.7	16.8	3.3	27.1	32.1	117	198	411	410	95
	0.10–0.30	1.7	3.0	1.0	9.0	13.7	82	157	267	267	100
	0.30–0.60	1.3	1.7	0.3	5.8	7.7	72	136	240	232	104
					1994						
0	0–0.10	7.8 (0.6)	5.0 (0.4)	2.1 (0.1)	11.9 (0.9)	22.8 (0.4)	80 (4)	179 (4)	309 (4)	316 (5)	97
	0.10–0.30	1.3 (0.4)	1.5 (0.7)	1.4 (0.0)	5.6 (1.2)	9.0 (0.7)	65 (4)	148 (4)	234 (6)	238 (4)	98
	0.30–0.60	1.6 (0.4)	2.0 (0.2)	0.4 (0.1)	5.4 (0.4)	5.4 (1.1)	70 (7)	132 (5)	218 (7)	226 (9)	94
20	0–0.10	28.9 (4.0)	20.1 (2.7)	3.0 (0.3)	23.5 (0.9)	16.5 (2.0)	121 (4)	180 (6)	386 (7)	419 (8)	94
	0.10–0.30	2.0 (0.9)	1.7 (0.8)	1.4 (0.3)	6.6 (1.5)	8.3 (0.5)	69 (6)	147 (4)	230 (5)	240 (6)	96
	0.30–0.60	1.6 (0.3)	2.0 (0.2)	0.1 (0.1)	5.2 (0.5)	4.2 (1.5)	70 (10)	132 (3)	219 (4)	226 (7)	97

Table 3. Changes in different P fractions (kg P/ha) at depth 0–0.10, 0.10–0.30, and 0.30–0.60 m due to long-term effects of continuous cropping with and without P fertiliser application from a Black Vertosol at Colonsay, Darling Downs, Queensland

Data in parentheses are in per cent of total soil P decrease at 0–0.60 m depth

Treatment depth		Change in P fractions and total P (kg P/ha) Resin-P+ $NaHCO_3$-P	NaOH-Pi	NaOH-Po	HCl-P	Residual-P	Total-P
				1. Reference–2003[A]			
P0	0–0.10 m	−24.7 (8)	−16.6 (5)	−10.9 (4)	−56.6 (19)	−44.8 (15)	−144.3 (55)
	0.10–0.30 m	−4.7 (2)	−8.4 (3)	−8.1 (3)	−52.6 (17)	−38.4 (13)	−94.0 (35)
	0.30–0.60 m	−0.5 (0)	−0.3 (0)	−6.1 (2)	−11.0 (4)	−22.1 (7)	−26.0 (10)
P20	0–0.10 m	+34.3	+7.1	−15.1	+11.8	−29.1	+40.0
	0.10–0.30 m	−0.6	−3.7	−12.5	−48.9	−37.9	−84.0
	0.30–0.60 m	−0.5	−0.6	−9.3	−9.8	−18.9	−33.6
				2. 1994–2003[B]			
P0	0–0.10 m	−2.6	−1.2	−1.4	−20.2	−25.6	−46.5 (53)
	0.10–0.30 m	−1.5	−1.1	+1.9	−17.0	−19.1	−31.8 (36)
	0.30–0.60 m	−3.1	+0.9	+1.3	−6.3	−9.5	−9.5 (11)
P20	0–0.10 m	+19.0	+10.7	+0.7	+9.1	−10.1	+31.3
	0.10–0.30 m	+0.7	+1.5	−1.1	−21.2	−16.9	−25.4
	0.30–0.60 m	−2.2	+1.3	+1.9	−3.2	−6.3	−9.5

[A] Difference in P fractions between soil samples in 2003 and the reference soil (uncropped since start of trial in 1985).

[B] Difference in P fractions between soil samples in 2003 and those in 1994.

Change in $NaHCO_3$-Po was undetectable due to its minimal proportion of total P (Table 3). However, NaOH-Po pools from 0 to 0.60 m decreased by about 30% regardless of P application. In the unfertilised soil, decrease of this pool accounted for nearly 10% of total P decrease from 0 to 0.60 m.

Changes were also seen in soil P fractions from 1994 to 2003 (Table 3). In the nil P treatment there was a decline in profile total P of 88 kg/ha, with the proportions lost from each depth being remarkably similar to those for the comparison based on the reference soil (Table 3). Labile P pools in the surface soil (0–0.10 m) remained relatively unchanged during these 10 years of continuous cropping without P input. However, acid and residual P pools decreased greatly and explained almost all of the total P decrease in the surface soil. With P addition, labile pools acted as the main sink for P. The acid pool increased by 7%, while the residual P showed an obvious decrease at the topsoil. At depth 0.10–0.30 m, acid and residual pools were the dominant fractions and significantly decreased irrespective of fertiliser addition. Below 0.30 m, no significant changes were detected for each fractions and total P. Unlike that based on the reference soil, NaOH-Po pools did not contribute significantly to the plant uptake during these 10 years of continuous cropping with and without P input. Therefore, it is possible that the reference soil had increased this fraction over 18 years by deep grass roots pumping P up from below 0.60 m.

P balance

Grain P removal by the crops during these 18 years was estimated as 210 ± 11 and 280 ± 10 kg/ha for unfertilised and fertilised soil, respectively. By comparison with the reference site, an estimated 260 kg P/ha had been removed from the top 0.60 m of the unfertilised soil, which is slightly higher than the grain export in these 18 years (Fig. 3). Where P fertiliser was applied at 20 kg P/ha per crop, it was expected that approximately 80 kg P/ha should have accumulated in the soil (difference between the P input and grain removal) (Fig. 3). Although increases in labile and NaOH-Pi fractions in the top 0.10 m can explain 55% of this balance, concomitant decreases in the residual fraction and subsoil pools resulted in a decrease in total soil P level (Fig. 3). When compared with the soil sample in 1994, total P decrease in the unfertilised soil in 2003 only contributed to about 80% of crop uptake from 1994 to 2003, suggesting that crops had exploited additional P sources outside the surface 0.60 m. In comparison, with the P input (20 kg/ha/crop), ~30 kg/ha P was missing from the top 60 cm profile over 10 years.

Discussion

P balance

In the literature, unaccounted P balances have been frequently reported (Blake *et al*. 2003; Spears *et al*. 2003; Goel and Noguera 2006). The magnitude of discrepancies depends on many factors (e.g. rainfall, soil properties, root distribution, etc.) that influenced the input and output balance of a certain soil system, or on the sampling method, estimation of P concentration in the grain and laboratory analysis, although the latter is relatively less significant (<30 kg P/ha in our study). Blake *et al*. (2003) suggested a loss of P from surface soil, when more than 150 kg P/ha was missing during 20 years of continuously cultivation with and without P input on a Chromic Luvisol and Eutric Gleysol. The P loss by surface runoff is less likely at our site, since the whole experiment area is quite flat. Since larger errors in P balance were observed between the reference site and the 2003 data than that between the 1994 and 2003 data, we suggest that grass growing at the reference site could have redistributed P from between depths, which may subsequently raise the total P level from 0 to 0.60 m depth at the reference site. Further reference sampling at the site and in the surrounding areas may allow better definition of the 'native' soil P fractions.

This also raises issues regarding the ongoing management of long-term agronomic experiments. The loss of soil samples collected at the commencement of this experiment inhibits the ability to elucidate changes in soil P pools since the start of the experiment. Communications to staff members within operating organisations regarding the value of archived samples and the potential opportunities that may exist in the future for investigation are key ingredients in successful sample retention (Martin and Grace 1998).

Accumulation of applied fertiliser P on the surface

Nearly all the applied P was retained within the surface 0.10 m and minimal vertical movement was observed (Table 2). Under the no-till system, P was expected to accumulate in the soil surface due to minimal mixing of surface-applied fertiliser (banded with seed) with soil, and cycling of P from deep soil layers to surface layer by crop residue return (Eckert 1991; Robbins and Voss 1991). Similar results were obtained by Saleque *et al*. (2004) and Han *et al*. (2005), who reported that P addition did not influence the concentration of any fraction below the plow layer. In addition, our results revealed that this

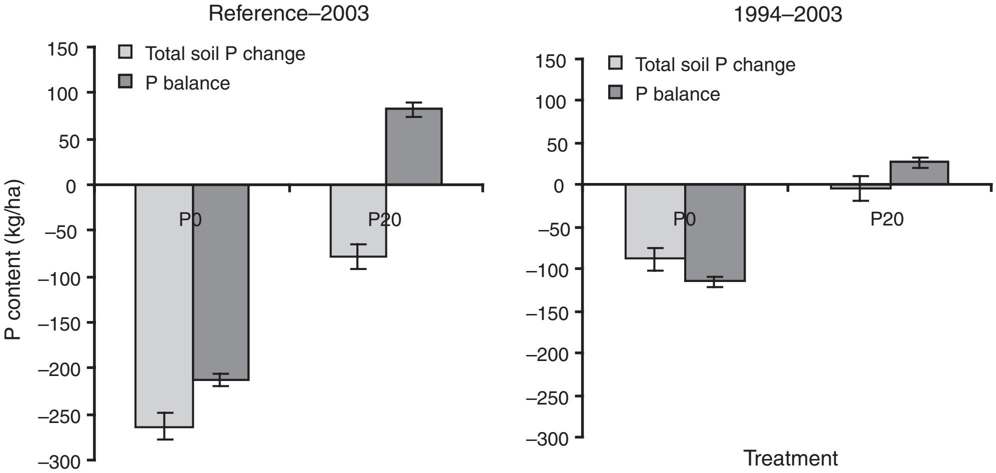


Fig. 3. Total soil P change and P balance from 1994 to 2003 and from 1985 (represented by the reference site) to 2003. Total P balance was calculated as the difference between P input from the fertilizer and outputs in the crop grain. Total soil P changed was the difference between the measured total soil P content (kg/ha) at depth 0–0.60 m in 1985, 1994, and that in 2003. Error bars represent the standard error of means of 6 replicates.

retained fertiliser residual P in the surface soil was preferentially accumulated in the labile inorganic P and moderately labile P pools. Strong *et al.* (1997) also found an increase in P availability with successive P application at any rate of 4, 8, 12, and 25 kg/ha in wheat-growing soils of the Western Downs, Queensland. Transformation of P into the acid pool was evident and most likely associated with the high Ca content in this soil. This is consistent with the findings of McKenzie *et al.* (1992*b*) and Song *et al.* (2007), who reported that acid P increased due to fertiliser P during long-term crop production. However, Ca-P originating from liming and fertiliser P could be among the least stable P compounds in specified soil types and can be readily re-mobilised back into the labile pools (O'Halloran *et al.* 1987).

Depletion of residual-P pools

It was evident that acid and residual-P pools were depleted due to grain P removal without P addition; hence, they appear to act as the main buffering pools replenishing plant-available P in the unfertilised soil. This is consistent with the dominance of these fractions in the soil. The dynamics of the residual pool is more complex than those of labile pools due to its unknown nature. This pool is routinely considered as the least plant-available fraction. However, despite application of P, the residual pool depletion in our study implies either buffering of the labile fractions for plant uptake, or direct removal from this fraction by the crop.

In the literature, changes in residual-P under cropping systems showed 2 contrasting patterns. Residual-P declined in slightly weathered soils (Hedley *et al.* 1982; McKenzie *et al.* 1992*a*, 1992*b*; Agbenin and Goladi 1998), but seemed to build up gradually in highly weathered soils (Guo *et al.* 2000). These suggest that the residual pool separated by the same sequential fractionation method was not of equal availability to plants in different soils. The nature of the residual pool could differ greatly among soil types. Tiessen *et al.* (1992) reported a high positive correlation between $NaHCO_3$-Po and residual-P in Ultisols and suggested that the contribution of the residual fraction may come from its organic portion. However, Guo *et al.* (2000) demonstrated a faster decline of residual-P in the Lualualei soil with higher calcite content and postulated that some plant-available P in the residual fraction in that soil was Ca-P. Dalal and Mayer (1986) reported that for Waco-type soils (black earths) organic P is a property moderately affected by cultivation. Therefore, we consider that the residual-P pool in the black Vertosol at Colonsay may be one of the important sources of replenishment, and its contribution was mostly lying in its organic portion. Further research is needed to identify the nature of this 'labile' residual pool since the total organic P pool was not determined in our soil.

An alternative hypothesis for the depletion of residual pools may be related to the P acquisition strategies of plants. Some crop species are capable of taking up P from stable pools, due to its specialised root morphology and physiology. A well-known example is white lupin which forms cluster roots and exudes large quantities of organic acids (Shen *et al.* 2003), and accesses up to 6 times more P from bound P fractions than a range of crop plants (Braum and Helmke 1995; Watt and Evans 2003). Sorghum may also possess some strategies to mobilise P from stable (acid and residual) pools down the whole soil profile. It has already been reported that sorghum could acidify the rhizosphere at low soil P status and caused an obvious P depletion zone (Ortas *et al.* 1996). Mycorrhizal infection could also be associated with the efficiency of P uptake in sorghum (Osonubi 1994; Ortas *et al.* 1996). Further opportunities in research exist to establish which hypothesis is the mechanism for the decline in the residual-P pool.

Depletion of subsoil (0.10–0.30 m) P pool

In comparison to the reference soil, total P at 0.10–0.30 m depth decreased greatly due to long-term cultivation with and without P input. Few published data are available on the quantitative measurement of subsoil P resource contribution. Subsoil P supply could substantially contribute to P uptake by sorghum–sudangrass in pot culture when surface P was low (Pothuluri *et al.* 1986). In a long-term field experiment, Richards *et al.* (1995) described an unaccounted P input in 0–0.20 m after 10 years of continuous cultivation without P application and implied the possibility of contribution from subsoil P pools. In addition, Kuhlmann and Baumgartel (1991) described a method which allowed the quantification of the potential uptake of P from the subsoil (>0.30 m) by spring wheat. Their results showed that P uptake from the subsoil increased from 37 to 85% of total P uptake, with decreasing P supply in the topsoil.

These above studies suggest that low P in the surface soil results in subsoil exploitation. However, the data from our study imply that subsoil utilisation occurred even when the surface soils remain relatively P fertile (Table 2). Part of the explanation for utilisation of subsoil P is uptake of P from where moisture is also present. The Colonsay site is located in the northern cereal-belt in southern Queensland, which has a summer-dominant rainfall pattern. The self-mulching nature of Vertosols can create conditions where unsaturated hydraulic conductivity is negligible at the surface. Moreover, no-tillage operations and surface-banded fertiliser P tend to accumulate P in the top few centimetres of the soil profile. A relative accumulation of P near the soil surface may decrease nutrient availability to plants because of the increased likelihood of dry conditions in this zone. Therefore, the subsoil P acquisition in our experiment possibly resulted from the water stress-induced P deficiency in the surface soil. When the topsoil dries out during the growing season, P in this enriched zone would become unavailable and immobilised. Plants had to explore deeper for both water and nutrients. Crop root length density and distribution were considered to decrease exponentially with the soil depth (Gregory 2006). However, under water-limiting conditions, this growth pattern could be reversed (Merrill and Rawlins 1979; Merrill *et al.* 2002). Moroke *et al.* (2005) reported that the root length density of tropical species, such as sorghum, tended to decrease at the soil surface while increasing at deep depths throughout the growing season. In addition, Pan and Hopkins (1991) showed a water stress-induced P deficiency in an eroded top-sequence and demonstrated an apparent P deficiency during grain filling of the crop even when P was band-applied at recommended rates during planting. Considering the decreased P availability and root distribution on the dry topsoil, surface replenishment of P will make the P acquisition by crops more difficult. This may help explain the lack of P response during some years.

From a resource sustainability viewpoint, Colwell P appears a poor indicator of overall P status. With no P input, acid and residual fractions declined steadily and acted as the main source pools in the top 0.10 m. In the subsoil (0.10–0.30 m), these 2 pools also tended to be depleted regardless of P application. It is apparent that the alkaline reagent $NaHCO_3$ used in the Colwell P method did not result in the mobilisation of some potentially plant-available P present in the acid and residual P pools. The build-up of P in labile pools from fertiliser inputs accounts for the continued increase in Colwell P, despite a negative P balance. The extents to which the acid and residual pools can be depleted with regard to the long-term sustainability and productivity of grain production are questions for further research. Further subsoil sampling and fractionation of cropping soils across the northern grains region is recommended to provide further information for soil P status, and will allow further examination of appropriate extractants for estimation of subsoil P reserves.

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