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# Pig effluent-P application can increase the risk of P transport: two case studies

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## *Abstract*

Land application of piggery effluent (containing urine, faeces, water, and wasted feed) is under close scrutiny as a potential source of water resource contamination with phosphorus (P). This paper investigates 2 case studies of the impact of long-term piggery effluent-P application to soil.

A Natrustalf (Sodosol) at P1 has received a net load of 3700 kg effluent P/ha over 19 years. The Haplustalf (Dermosol) selected (P2) has received a net load of 310 000 kg P/ha over 30 years. Total, bicarbonate-extractable, and soluble P forms were determined throughout the soil profiles for paired (irrigated and unirrigated) sites at P1 and P2, as well as P sorption and desorption characteristics.

Surface bicarbonate ($P_B$, 0–0.05 m depth) and dilute $CaCl_2$-extractable molybdate-reactive P ($P_C$) have been significantly elevated by effluent irrigation (P1: $P_B$ unirrigated 23±1, irrigated 290±6; $P_C$ unirrigated 0.03±0.00, irrigated 23.9±0.2; P2: $P_B$ unirrigated 72±48, irrigated 3950±1960; $P_C$ unirrigated 0.7±0.0, irrigated 443±287 mg P/kg; mean±s.d.). Phosphorus enrichment to 1.5 m, detected as $P_B$, was observed at P2. Elevated concentrations of $CaCl_2$-extractable organic P forms ($P_{OC}$; estimated by non-molybdate reactive P in centrifuged supernatants) were observed from the soil surface of P1 to a depth of 0.4 m. Despite the extent of effluent application at both of these sites, only P1 displayed evidence of significant accumulation of $P_{OC}$.

The increase in surface soil total P (0–0.05 m depth) due to effluent irrigation was much greater than laboratory P sorption (>25 times for P1; >57 times for P2) for a comparable range of final solution concentrations (desorption extracts range 1–5 mg P/L for P1 and 50–80 mg P/L for P2). Precipitation of sparingly soluble P phases was evidenced in the soils of the P2 effluent application area.

*Additional keywords:* run-off, leaching, phosphorus.

## Introduction

Agricultural industries are being closely scrutinised worldwide as sources of water and soil resource contamination (Sharpley 1995; Abbozzo *et al.* 1996; Burkholder *et al.* 1997). Researchers have focussed considerable attention on waste nutrients and management techniques designed to minimise environmental impacts (Abbozzo *et al.* 1996; Edwards *et al.* 1996; Gburek and Sharpley 1997), methods of measuring the mobility of agricultural waste nutrients (Sharpley *et al.* 1996), and the effects of short-term applications of wastes and accidental spills (Edwards and Daniel 1993).

This paper describes an investigation of the long-term impact of piggery effluent application on the phosphorus characteristics of soils in two case studies. Some research has been published on the longer term effects of livestock wastes on soil conditions and chemistry. Heckrath *et al.* (1995) as part of the Broadbalk Experiment at Rothamsted, investigated the impact of farmyard manure application on soil P characteristics (40 kg P/ha annually) over a period of >150 years. They observed significant concentrations of P in drainage water at a depth of 0.65 m. Between 66% and 86% of this P was in the form of dissolved molybdate-reactive P at the time of analysis. The authors concluded that leaching losses of P applied as manure can be closely related to soil bicarbonate-extractable P. King *et al.* (1990) found that applications of piggery effluent over an 11-year period resulted in

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elevation of soil test P (extracted with 0.05 M HCl + 0.05 M $H_2SO_4$) to 10 times the level above which no response to P fertilisers would be expected. This elevation resulted from the application of effluent (equivalent to 6100 kg P/ha of total application over 11 years) to ‘coastal’ bermudagrass [*Cynodon dactylon* (L.)] growing in a Paleudult.

The reaction of solution P with soil, and the resultant decrease in solution concentration through sorption processes, has been studied for many decades (e.g. Black 1942). Scientists, regulators, and consultants use P sorption determinations (for example the techniques set out in Rayment and Higginson 1992) to determine P fixation and mobility for both agricultural and environmental purposes. While these widely used laboratory techniques only allow equilibration for a relatively short period of time, longer term continued decrease in solution concentrations is well evidenced (Black 1942; Barrow and Shaw 1975). In effluent application systems, where the soil’s capacity to retain P may determine the useable life of an application area, the impact of long-term equilibration effects on appropriate management for a site may be large.

Effluent constituents can have an influence on P sorption behaviour of soils. Holford *et al.* (1997) indicated that in some of the soils in their study areas, P-adsorbing constituents of dairy, pig, and sewage effluents (such as C and Fe) may have partially counteracted the exhaustion of adsorption capacity with continued effluent application. Iron and aluminium hydrous oxides and organic complexes often have very large surface areas and can be important P adsorbers, while Fe phosphates can be important precipitated phases in acid soils (Holford 1997).

Unfortunately, the study described in Holford *et al.* (1997) was unable to quantify P additions, other than those in the form of superphosphate, making comparisons between treatments difficult.

The quantity of organic matter dissolved in effluents may also influence P sorption and transport. In a column leaching experiment, Chardon *et al.* (1997) found that leached P was dominated by dissolved organic forms. Holford and Mattingly (1975) indicated the possibility that organic anions may lower the strength of sorption of P through interaction with sorbing P anions.

The purpose of this paper is to describe the impact of prolonged application of piggery effluent-P in two different management systems. These two case studies have allowed conclusions to be drawn with direct relevance to natural resource protection in the pork industry, since P application rates for these two systems can be accurately estimated and management practices have been consistent with the industry standards of past decades. The study also seeks to compare the relationship between P accumulation in long-term piggery effluent irrigation systems to the sorption behaviour predicted by laboratory isotherms. Since some literature has indicated the potential for mobility of soluble organic P forms (e.g. Chardon *et al.* 1997), the current paper also examines organic P forms in the soil profiles of the two case studies.

## Materials and methods

### *Site descriptions and sampling*

Two Australian piggery effluent application areas were selected for the case studies. The first (P1) was from a southern Queensland piggery that has been operating since 1979, with anaerobic lagoon effluent (inputs into the anaerobic ponds include feed wastage, urine, faeces, and flushing water from the pig housing) and separated manure solids (effluent is screened before entry into ponds, reducing the total solids loading of the ponds by approximately 20%, Payne 1990) being applied to an area of land used for horticultural crop production. This piggery is currently operating with 1200 sows. The climate in the area is dominated by summer rainfall (701 mm mean annual rainfall), with an annual pan evaporation of 1700 mm (Queensland

Department of Natural Resources 1998). The soil of P1 is a Natrustalf (Soil Survey Staff 1998), and is classified as a Eutrophic Mesonatric Grey Sodosol (Thick, Non Gravelly, Sandy, Clay Loamy, Deep) in the Australian Soil Classification (Isbell 1996). This soil has a sand-textured B1 horizon, under-lain by a highly sodic, dispersive clay loam B2 horizon.

The second effluent irrigated area (P2) has been used for effluent irrigation on a disposal basis for 30 years, with occasional *in situ* grazing. Piggery P2 now operates with 800 sows. This piggery is located in central Queensland, in a summer rainfall dominated area, with average annual precipitation of 910 mm and annual pan evaporation of 1800 mm (Queensland Department of Natural Resources 1998). Piggery P2 has operated without use of anaerobic lagoons, effluent (urine, faeces, wasted feed, and flushing water) being collected in earthen sumps then immediately flood-irrigated onto the disposal area. The soil of P2 is a Haplustalf (Soil Survey Staff 1998), and is classified as a Haplic Eutrophic Red Dermosol (Medium, Non Gravelly, Clayey, Clayey, Deep) in the Australian Soil Classification (Isbell 1996). This soil grades from light–medium clay at the surface to medium clays at the base of the profile (1.2–1.5 m).

The principles described in Kruger *et al.* (1995, pp. 37–40) were used to estimate piggery waste production. The model described by Casey (1995) was used to estimate the partitioning of P between anaerobic lagoon effluent and sludge. Casey (1995) assumes that 90% of influent P partitions into the effluent pond sludge, with the remainder being available for land application. This assumption was based on reviewed publications and has recently been confirmed by a survey of 15 effluent ponds in North Carolina (Bicudo *et al.* 1999).

During the 19-year period of waste re-use at P1, 3700 kg P/ha in excess of crop requirements has been applied to the effluent application area. Mass balance calculations under the *in situ* grazing regime of P2 indicated negligible removal of nutrients. During the 30-year period of operation at P2, a total of approximately 310 000 kg P/ha has been applied.

Soil coring for the purposes of soil classification and sample collection was carried out using a vehicle-mounted hydraulic push-tube soil-sampling rig. This rig was used to collect samples from the maximum depth of penetration (P1, 1.5–1.6 m; P2, 1.2 m). Paired sites for replicated composite sample collection were selected at both P1 and P2. These paired sites represented the irrigated and unirrigated soil (the unirrigated soils had not been used for crop production), and were in close proximity. Once selected, 10 whole profile cores were collected at random from within a 10-m-radius circle at each sample site. These cores were sectioned into 0.10-m depth intervals. Composite samples were created for each of these depth intervals by mixing like-depth sections together. Second and third replicates of 10 profile cores were then collected, sectioned identically, and composited. This provided a total of 30 complete cores of the sample profile, mixed to create 3 composite samples for each depth interval. Five composite surface samples (0–0.05 m) were also collected from each 10-m-radius area. Each of these composite surface samples was made by bulking together 18 randomly located cores collected with a manual push tube sampler. The soil samples were air-dried at 40°C within 12 h of collection.

### *Laboratory methods*

The following analytical techniques as set out in Rayment and Higginson (1992) were applied to the soil samples collected: pH in 1:5 soil:water suspension (Method 4A1, detection limit 0.1); organic carbon (OC) content by the method attributed to Walkley and Black (1934; Method 6A1; detection limit 0.01%); oxalate extractable Fe and Al (method 13A1; detection limit 0.001%); total P by X-ray fluorescence (9A1; detection limit 0.001%); 1:100 soil:0.5 M Bicarbonate extractable P (Colwell 1963; detection limit 1 mg P/kg) with automated colorimetry ($P_B$; method 9B2). Some bicarbonate extract solutions were also analysed by inductively coupled plasma techniques (ICP) to determine total P in the extracts ($P_{TB}$; detection limit 1 mg/kg; using a Thermo Jarrell Ash Iris/HR Duo). Bicarbonate-extractable P is related to the quantity of labile P (Dalal and Hallsworth 1977; Holford 1980), and was used in this study as an estimate of labile P. Particle size analysis of the soil samples was carried out using the pipette method described in Gee and Bauder (1986), including sample pre-treatment for removal of soluble salts and organic matter (where necessary).

The methods applied to determine phosphate sorption curves and single-point phosphate sorption indexes of soils are also described in Rayment and Higginson (1992). Method 9J2 for P sorption curves specifies a 1:10 soil to solution ratio (0.01 M $CaCl_2$ matrix) and a 17-h contact time. In this study, initial solution concentrations were 1–40 mg P/L for P1 and 0.14–240 mg P/L for P2. The method used to determine the P sorption index (9J1) equilibrates a solution of 7.5 mg P/L in a matrix of 0.02 M KCl (1:20 soil to solution ratio) for 17 h. The sorption index is expressed as $X/\log_{10}C$, where X represents mg P sorbed/kg of soil, and C is µg P/L of the final supernatant solution.

A dilute, unbuffered salt solution extraction of P was also carried out, using a 1:5 soil : 0.005 M $CaCl_2$ ratio (method 9F2). Extracts were centrifuged and analysed both colorimetricaly for orthophosphate ($P_C$; detection limit 0.01 mg P/kg; analysis using Murphy and Riley 1962), and by ICP to determine total P in the extracts ($P_{TC}$; detection limit 0.05 mg P/kg). The non-molybdate reactive P forms in the extractant ($P_{OC}$) were estimated by subtraction of $P_C$ from $P_{TC}$. The quantity calculated in this manner is used here as an estimate of the dissolved organic P in the extract solutions that is not readily hydrolysed by the acid Murphy and Riley (1962) colour reagent. Other authors (e.g. Chardon *et al.* 1997) have previously applied similar calculations. This estimation assumes that any P in the $CaCl_2$ extracts following centrifuging is in solution. Such an assumption is based on the $CaCl_2$ extractant's effect in reducing soil dispersion, and the employment of centrifuging appropriate to settle particles of >0.2 µm (Stokes law, as described in Gee and Bauder 1986; extractants centrifuged for 20 min at 2100 g, assuming a particle density of 2600 $kg/m^3$). Analyses of $P_C$ by Moody *et al.* (1988) indicated that this measurement was a reasonable estimate of phosphorus intensity, as it was found to be highly correlated with soil solution P (10 kPa matric suction).

Replicated 3-point desorption curves were determined for each treatment of the 2 soils. A 3.5-g sample of air-dry soil (<2 mm) was transferred to a 50 mL centrifuge tube. A 0.5-mL aliquot of chloroform was added to each tube to inhibit microbial activity. This sample was then extracted with 35 mL of 0.005 M KCl solution. The suspension was agitated end-over-end for 17 h, centrifuged, and the supernatant retained for analysis. Three of these extractions were carried out sequentially on the same soil sample, allowing the determination of 3 points on a curve of successive desorption. After centrifuging the supernatant solutions were analysed by ICP for total P.

Total effluent P was determined by persulfate digest (Greenberg *et al.* 1992; method 4500-P B). Filtered (0.45 µm) samples of effluent were analysed by ICP for total P (Varian Liberty 200; detection limit 1.0 mg P/L). The Murphy and Riley (1962) technique was applied to determine the molybdate reactive P concentration (detection limit 0.01 mg P/kg).

### *Statistical methods*

Comparisons of soil profile chemical data were carried out using the analysis of repeated measures techniques. Single depth interval soil data was compared using *t*-tests. Both of these statistical procedures were applied using the GENSTAT software package (Lawes Agricultural Trust 1996).

## Results and discussion

### *Piggery waste management ethos*

Concentrations of constituents in Australian piggery effluents vary greatly. Kruger *et al.* (1995), however, have published some indicative average concentrations that may help establish the context of the following discussion. An average land applied piggery effluent contains: 44 mg/L of total P; 29 mg/L of orthophosphate P; 384 mg/L of total N; and 249 mg/L of ammonia-N. This effluent would have a pH of approximately 8, and an electrical conductivity of approximately 10 dS/m.

The total quantity of P retained by an effluent receiving soil and whether P is in forms subject to desorption are both important considerations in the management of piggery effluent application to land. Piggery effluent is not usually a balanced fertiliser (Kruger *et al*. 1995), and for this reason, and other pressures related to a lack of area available for effluent application, effluent-P is often applied at a rate greater than plant or crop requirements.

To allow interpretation of the observations collected from the soil profiles of the two effluent application areas, it is necessary to understand the ethos of waste management employed at both sites. Practices at P2 have been directed only at disposing of the effluent, largely without consideration of its resource value, and without an understanding of the consequences. It should be stressed that while this approach may have been common in Australian piggeries several decades ago, few piggeries practice in this manner today. The management of the effluent application areas at P2 has resulted in considerable elevation of the soil OC content (Table 1). An accumulation of organic matter resistant to pre-treatment

**Table 1. Properties of the surface 0.05 m of soil for the unirrigated and effluent irrigated areas at the P1 and P2 piggery sites, including oxalate extractable Fe and Al**

Values for organic C, Fe, and Al are mean±s.d.; All units are %, except for pH

| Soil | pH | Organic C | Sand | Silt | Clay | Al | Fe |
|---|---|---|---|---|---|---|---|
| P1, Unirrigated | 5.9 | 0.93±0.11 | 91 | 4 | 5 | 0.014±0.003 | 0.061±0.000 |
| P1, Irrigated | 6.8 | 0.98±0.04 | 89 | 6 | 5 | 0.018±0.003 | 0.075±0.007 |
| P2, Unirrigated | 6.1 | 3.43±0.88 | 41±1 | 23±1 | 36±0 | 0.166±0.001 | 0.827±0.091 |
| P2, Irrigated | 6.2 | 10.85±0.14 | 53±1 | 25±1 | 22±1 | 0.096±0.001 | 0.859±0.045 |

with $H_2O_2$ (Gee and Bauder 1986) during 30 years of effluent irrigation may have prevented full dispersion of the soil during particle size analysis. This would explain the increased proportion of sand size particles (Table 1) relative to the unirrigated soil for P2. Some gleying was also apparent in the irrigated soil that was not evident in the unirrigated soil.

The management at P1 has recognised piggery waste as a resource. Perceptions of the value of the effluent have, however, changed over the past 2 decades as more information has been made available to piggery managers. Initially, the effluent was merely considered a supplemental source of low quality irrigation water for the horticultural production on site. During the past 5 years the manager's perceptions changed to considering the effluent and screened manure solids as sources of nutrients and as soil conditioners in addition to the water value of the effluent. Piggery wastes, however, do not normally constitute a fertiliser with an agronomically balanced ratio of nutrients (Kruger *et al.* 1995), and the approach of applying effluent at the rate necessary to satisfy the range of crop macronutrient requirements may have resulted in over-application of some nutrients. In the years following the introduction of environmental legislation in Australia (e.g. Anon. 1996), extension activities related to agricultural waste re-use have focused more on developing sustainable approaches to waste management. This is reflected in recently adopted practices that are designed to restrict effluent re-use according to the most environmentally limiting constituent. The observed chemical characteristics of P1's effluent irrigated soil profile probably represents the influence of all but this final stage in the development of effluent management. Crop production and effluent application to the irrigated soil have resulted in decreased soil acidity (0–0.05 m; soil characteristics summarised in Table 1).

### *Vadose zone*

The profiles of both the P1 and P2 irrigation areas indicate significant downward transport of P. This is particularly evident in the $P_B$ profiles (Fig. 1). Similar increases in total P concentrations for the effluent-irrigated profiles were also observed, though the lower sensitivity of the method applied did not allow clear statistical differentiation. Significant elevation of $P_B$ relative to the control was observed in the P1 irrigation area from the surface to a depth of 0.70 m. According to the interpretation of $P_B$ data published by Solis and Torrent (1989), this represents a significant increase in the labile P pool for this interval. In the P2 irrigation area this elevation extended from the surface to the deepest sample depth (1.2 m, $P < 0.05$), which is close to the base of the soil profile, despite the relatively high capacity of this soil to sorb P. It appears likely that effluent P is exiting the base of the soil profile at P2.

Leaching of P at P1 appears to have occurred within the coarse-textured upper 0.5 m of the profile, but has been curtailed by the underlying dispersive clay loam (a significant increase in $P_B$, $P < 0.05$, was observed to a depth of approximately 0.70 m, Fig. 1). In this horizon, infiltration (other than macropore flow) would be expected to be very slow, and the P sorption index is much higher than in the coarse-textured shallower horizons (Fig. 2). It is likely that P storage in the P1 profile can be safely increased without significant leaching from the base of the soil profile, since the soil extends to a depth >1.6 m and the current depth of transport of P is within the observed root-zone of the crops being grown (>1 m depth). If macropore flow is an important process in this soil, however, significant leaching of P may have occurred without being detected by soil coring and analysis. Subsurface lateral flow of leachate along the dispersive B2 horizon may be an additional concern since the effluent application area is within 200 m of a surface water body.

In their short-term examination of leaching of several soils after piggery slurry application, Chardon *et al.* (1997) found that the majority of leached phosphorus was in the form of dissolved organic P (DOP), and that DOP dominated solution P forms at depth in soils. Chardon *et al.* (1997) also observed significant concentrations of non-molybdate-

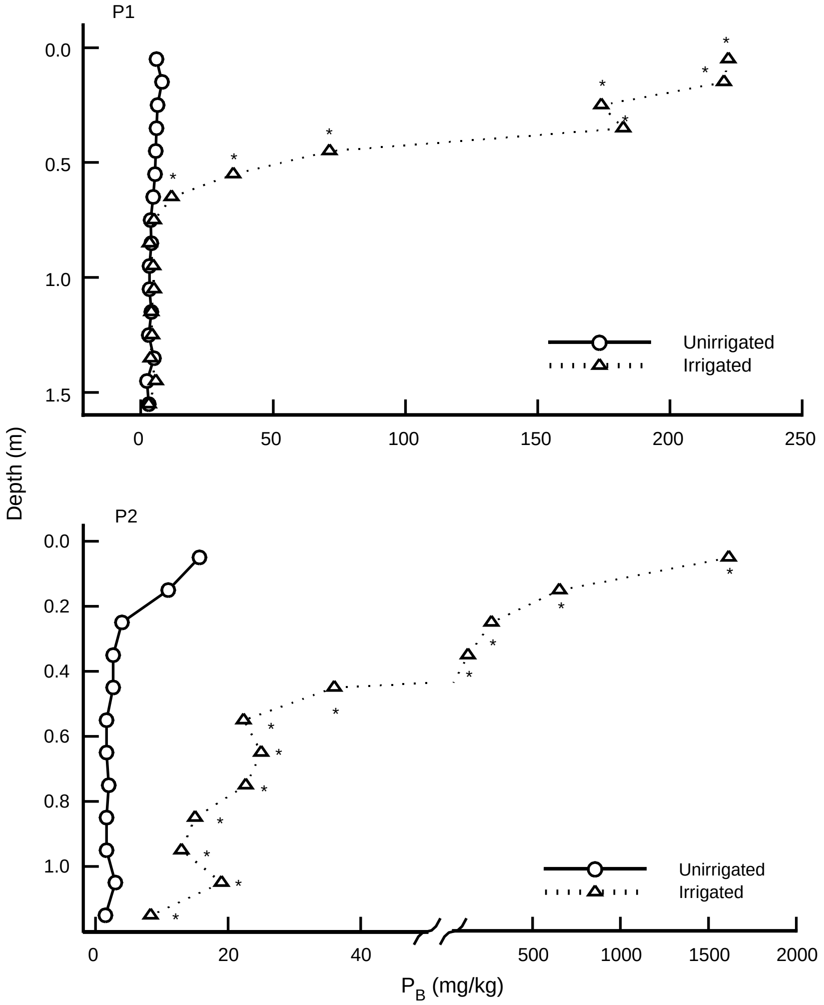

**Fig. 1.** Soil profile bicarbonate extractable P ($P_B$) for the effluent irrigated and unirrigated P1 and P2 soils. Where present, '*' indicates that the effluent irrigated treatment is significantly different from the unirrigated ($P < 0.05$).

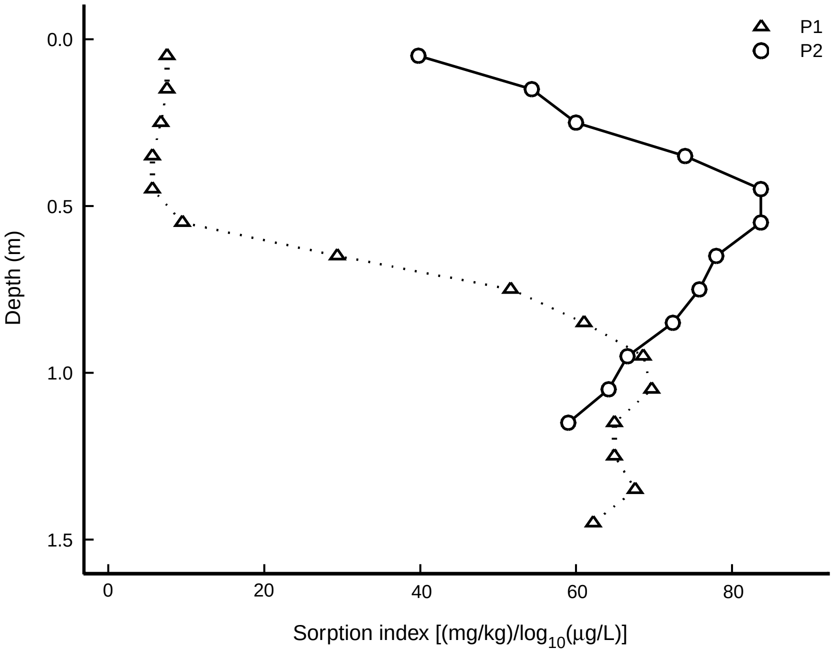

**Fig. 2.** Phosphorus sorption index data for the unirrigated profiles of both P1 and P2.

reactive P in piggery slurries. Analysis of the filtered (0.45 µm) P1 effluent indicated that it contained no detectable non-molybdate-reactive P, though the detection limit of the analysis was higher than the concentrations found by Chardon *et al.* (1997; detection limit for P1 analysis 1 mg P/L; total P concentration of the P1 filtrate was 11 mg P/L). Unfortunately, access was not available to the P2 effluent to carry out similar analyses. While mechanisms involving DOP in the transport of P may have been important, soluble organic P (as estimated by $P_{OC}$) was not found to represent a high proportion of $P_C$. A small, though significant, increase in $P_{OC}$ with effluent irrigation in the surfaces of the soil of P1 was observed to a depth of 0.4 m (Table 2), but no significant increase was observed for the P2 profiles (Table 2 and Fig. 3; significance tested at the $P = 0.05$ level; the large variability for P2 is the result of spatially irregular effluent application). In the surface 0.05 m of the P2 effluent application area, however, the proportion of $CaCl_2$-extractable P in non-molybdate-reactive forms fell sharply with effluent application (43% to 0% for P2). ICP and colorimetric analysis for molybdate-reactive P in the bicarbonate extracts from the P2 profile indicated the lack of significant quantities of non-molybdate-reactive P (significance tested at the $P = 0.05$ level). If the effluent contained significant quantities of soluble organic P in non-molybdate-reactive forms, then these may have undergone transformation to other P forms.

### *Runoff risks*

Runoff transport of P can present a greater risk of water resource contamination than does leaching through strongly P sorbing soil profiles. Source factors (effluent application management and soil P content), runoff, and erosion (Sharpley 1995) control the potential for contamination of water resources with high levels of algal available P in runoff. It is

**Table 2. Surface 0.05 m soil P characteristics for the unirrigated and effluent-irrigated areas at the P1 and P2 piggery sites**

Data are presented as mean±s.d. mg P/kg. $P_B$, bicarbonate-extractable P; $P_C$, dilute $CaCl_2$-extractable orthophosphate P; $P_{OC}$, dilute $CaCl_2$-extractable non-molybdate-reactive P

| Soil P fraction | Piggery | Unirrigated | Irrigated |
|---|---|---|---|
| Total-P | P1 | 190±10 | 720±70* |
| | P2 | 1720±1050 | 28100±900* |
| $P_B$ | P1 | 23±1 | 290±6** |
| | P2 | 72±48 | 3950±1960** |
| $P_C$ | P1 | 0.03±0.00 | 23.9±0.2*** |
| | P2 | 0.7±0.0 | 443±287*** |
| $P_{OC}$ | P1 | $< 0.05^{A}$ | 2.5±0.1* |
| | P2 | 0.8±0.1 | 0±12 |

* $P < 0.005$; ** $P < 0.01$; *** $P < 0.001$ for comparison with unirrigated soil.
$^{A}$ Detection limit is 0.05 mg P/kg.

likely that the surface interval of interaction with runoff water is <0.05 m thick (Sharpley *et al.* 1996). Bicarbonate-extractable P for the runoff interacting intervals (surface 0.05 m) at both piggery effluent application areas is significantly higher than the unirrigated areas ($P < 0.01$; ANOVA; Table 2). Also, $P_C$, which is strongly correlated with soil solution P (Moody *et al.* 1988), was significantly higher than that in the unirrigated areas ($P < 0.001$; ANOVA; Table 2)

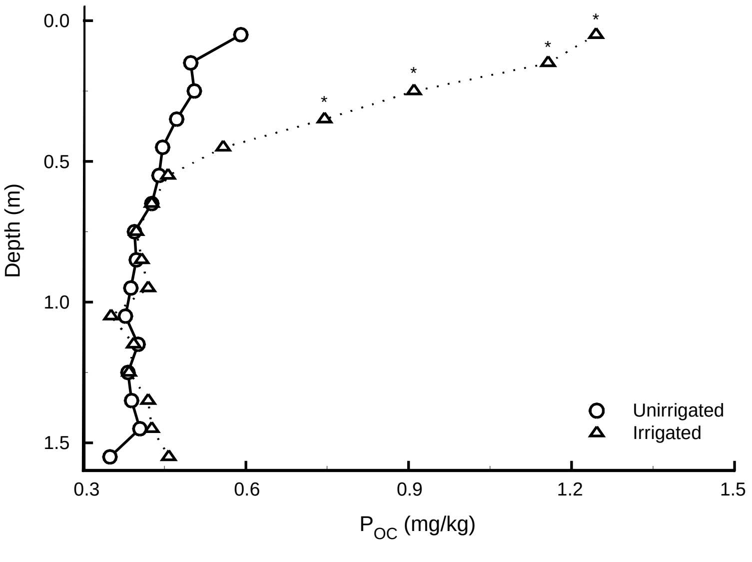

**Fig. 3.** Soil profile dilute $CaCl_2$-extractable non-molybdate-reactive P ($P_{OC}$) for the effluent-irrigated and unirrigated P1 soils. Where present, * indicates that the effluent-irrigated treatment is significantly different from the unirrigated ($P < 0.05$).

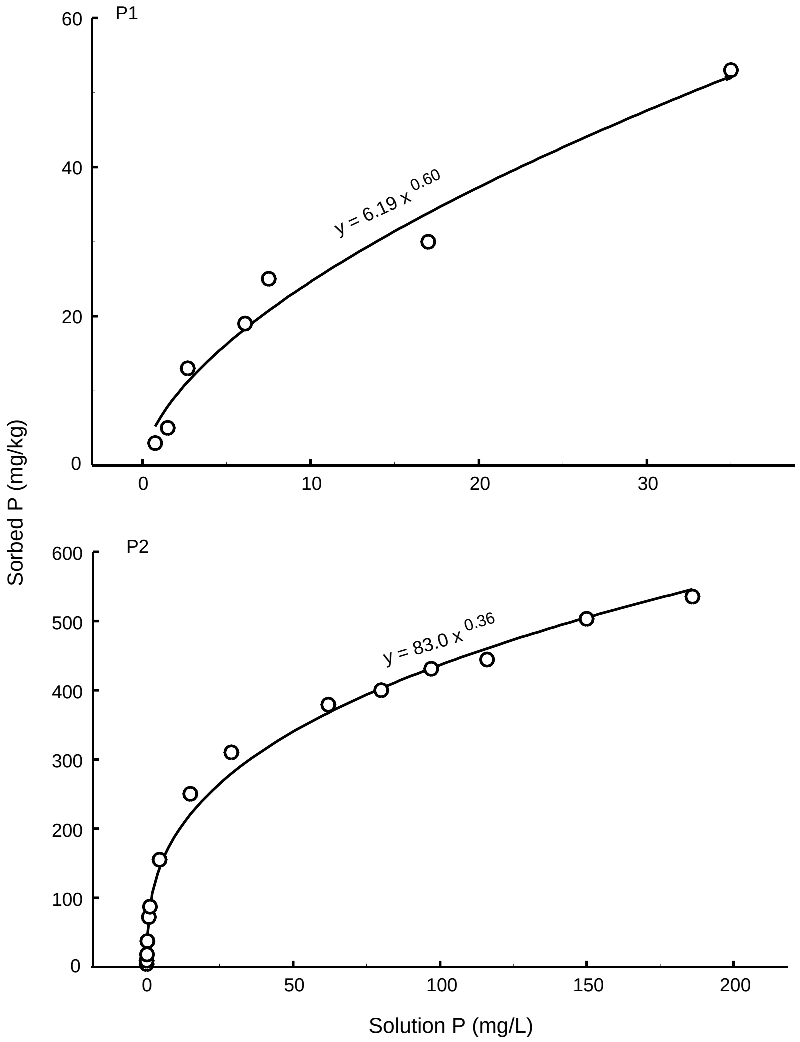

**Fig. 4.** Phosphorus sorption with increasing equilibrated total P concentrations for the unirrigated soils from piggeries P1 and P2.

The $P_B$ contents of these soils have been increased well above the level expected to produce a significant positive response in crops. For example, Baker and Eldershaw (1993) recommend that crop responses to fertiliser applications would be expected in soils in the range from deficiency to about 40 mg $P_B$/kg for the surface 0.10 m. It is likely that increases in $P_B$ levels in a soil will be indicative of increased algal-available P should runoff reach surface water bodies. Pote *et al.* (1999) found that a wide range of published soil test determinations of P were significantly ($P < 0.01$) related to runoff dissolved molybdate-reactive P, with most relationships exhibiting correlation coefficients in excess of 0.90 ($r$). Pote *et al.* (1999) investigated 3 Ultisols in their trial, and included the Olsen *et al.* (1954) bicarbonate extract amongst the soil tests studied. Other researchers have also indicated that soils that contain high levels of P from excessive fertiliser application can become an

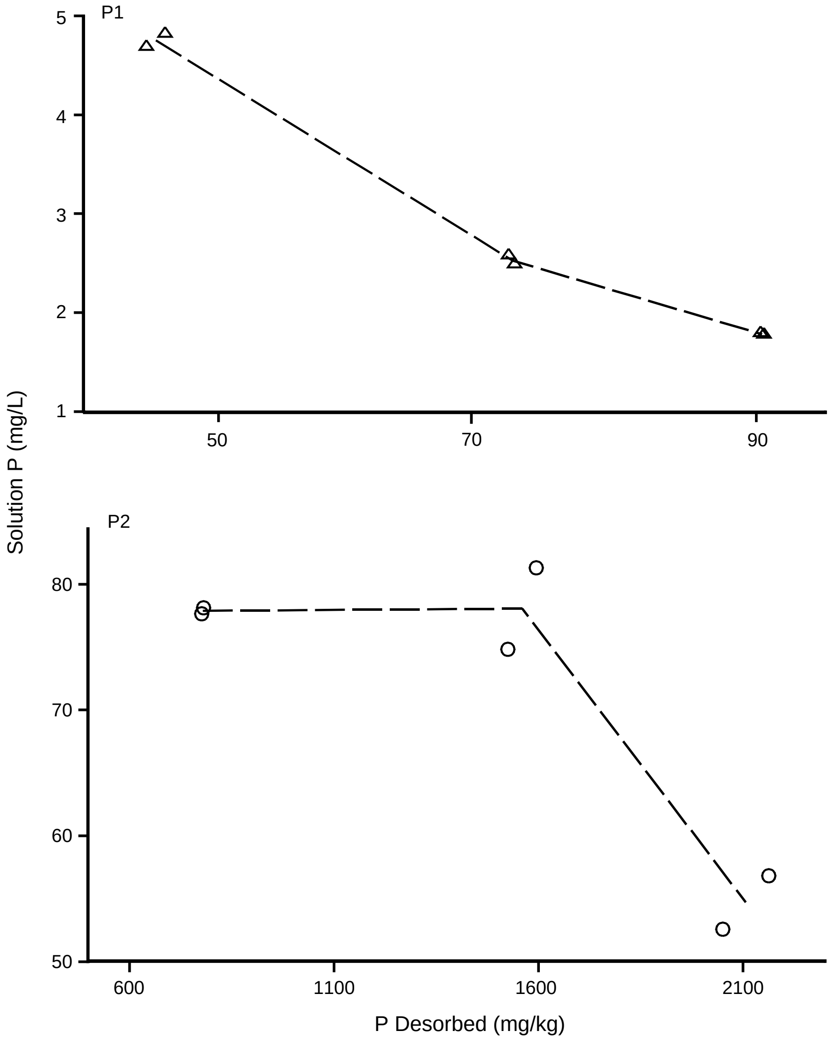

**Fig. 5.** Total phosphorus desorption with successive extractions for the effluent-irrigated soils from piggeries P1 and P2. Concentrations of the equilibrated solutions are plotted against the cumulative quantity desorbed.

important source of dissolved molybdate-reactive P in runoff (Edwards *et al.* 1993). The extreme elevation of $P_B$ in the interval of runoff water interaction (surface 0.05 m of the soil) has substantially increased the risk of runoff containing excessive loads of algal-available P.

### *Sorption and desorption*

Phosphorus sorption curves were determined for the unirrigated soils with equilibrated solution concentrations between 0.75 and 35 mg P/L for P1, and between 0.10 and 186 mg P/L for P2 (Fig. 4). Freundlich equations (Barrow 1978) of the form $y = ac^n$ were fitted to the sorption isotherm data (Fig. 4; where a and n are parameters, c is the equilibrated solution P concentration in mg/L, and $y$ is the sorbed P content in mg/kg). For the unirrigated area at P1, the parameters observed were a = 6.19±1.12 and n = 0.600±0.058 (estimate±s.e.; $r^2 = 0.99$, $P < 0.05$). For the unirrigated area of P2 the estimated parameters were a = 83.0±7.1 and n = 0.36±0.02 (estimate±s.e.; $r^2 = 0.99$, $P < 0.05$).

Phosphorus was observed to have accumulated in the surface soil (0–0.05 m) to concentrations exceeding those expected from the sorption curves. Several processes are not represented by the laboratory sorption procedure and may result in such accumulation, for example, precipitation, evaporative concentration of P in solution at the soil's surface, slow sorption processes (as discussed by Barrow 1992 and Holford 1997), and effects on sorption capacity related to the addition of effluent constituents (e.g. formation of complexes between P, P-reactive cations, and effluent OC, as suggested by Holford *et al.* 1997). Desorption studies were directed at finding information about the nature of P storage in these piggery effluent irrigated soils (Fig. 5). The total P concentration of the desorption extracts of P1 ranged from 1 to 5 mg/L. These concentrations correspond to sorption of <20 mg/kg on the P1 sorption curve (Fig. 4). Calculations indicate, however, that the effluent-irrigated samples from P1 contain approximately 500 mg/kg more P than the corresponding unirrigated samples (Table 2). This increase in P includes pools in equilibrium with soil solution and those that are not labile (for example, P diffused into mineral surfaces as suggested by Barrow 1992). A similar situation is evident for P2 with desorption extracts ranging in concentration from 50 to 80 mg total P/L, corresponding to <400 mg/kg of sorbed P on the P2 sorption curve, whereas total P has been increased due to effluent irrigation by 23000 mg/kg.

When effluent concentrations are used to predict sorbed P levels by reading directly from the conventionally determined sorption curves, predictions grossly underestimated the levels of P in the surface of the effluent-irrigated soil. Analyses of P1 effluent-soluble orthophosphate-P, both in 1995 and in 1999, showed little variation in soluble forms. Total effluent P was approximately 45 mg P/L, while soluble P forms were 10±0 mg P/L (mean±s.d.). Sorption curve sorbed-P values for equilibrated concentrations ranging from 10 to 45 mg P/L were much less than the calculated increase in P contained in the surface soil. A similar situation is likely for P2, since sorption appears to reach a maximum of approximately 600 mg P/kg, though effluent concentrations were not measured. Single chemical phase P sorption equilibrated over a short period (18 h) does not represent well the accumulation of P in piggery effluent irrigated surface soils. This finding is consistent with that of Menzies *et al.* (1999), which questioned the effectiveness of P adsorption curves for predicting the life of sewage effluent disposal sites.

Since the desorption curve for the first 2 extractions from the effluent-irrigated P2 soil does not indicate a decrease in solution concentration, it is possible that the desorption extracts are extracting some sparingly soluble precipitated phase. Dissolution of sparingly soluble precipitated phases leads to desorption curves that tend to be parallel to the sorbed P axis (e.g. Basta and Tabatabai 1992). The desorption extract orthophosphate concentrations and the soil pH of both soils fall in the range where Lindsay (1979; pp. 163–204) found that several P phases may precipitate in mineral or soil systems (including a range of calcium phosphates).

The accumulation of P in effluent application area soils to contents greater than can be explained as short-term sorption is an important issue, and is a subject requiring further study. Depending on the mechanisms involved this may indicate a greater capacity to retain P against leaching than would be suggested by short-term sorption processes. The additional storage of P close to the soil surface may also introduce increased potential for transport of P by runoff water.

## Conclusions

Both of the case study effluent application areas are examples of the impact of management techniques widely considered acceptable in the past. Irrigation site P1, however, represents changing management practices with time, and there is no evidence of significant P leaching from the soil profile. The data reported here indicate that the greatest potential for environmental harm at P1 is related to surface mobilisation of soluble and algal bio-available P forms, as surface soil contents of these forms are significantly elevated. Careful management of cropping at this site will probably minimise this potential. At the P2 irrigation area, where the waste management ethos over the last 30 years has largely been one of effluent disposal, leaching losses of P below the soil profile have probably already occurred. Surface runoff from this irrigation site also poses a high risk to receiving water quality. It is unlikely that normal cropping and agricultural management practices would have a large impact in ameliorating the contamination potential of this site in the short term.

Effluent application was observed to slightly increase soluble organic P forms (estimated by $P_{OC}$) in the P1 effluent application area. Increased $P_{OC}$ contents extended some distance down the profile, but not to the same depth as the increased $P_B$. No significant increase in soluble organic P species was observed in the effluent-irrigated P2 profile.

Both of the irrigation areas displayed high contents of P in surface soils that would not be predicted by routine P sorption isotherm techniques similar to those employed here. In particular, evidence of control of solution P concentrations by sparingly soluble solid phases was found for P2. The relationship between laboratory sorption isotherm data and long-term sorption in effluent systems requires further investigation.

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