

Phosphorus status and saturation in soils that drain into the Peel Inlet and Harvey Estuary of Western Australia

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Abstract. The Peel–Harvey estuarine system in Western Australia's south-west is affected by poor water quality, algal blooms, and fish kills. Phosphorus (P) discharge from agricultural activities is the main source of poor water quality. The catchment's soils are naturally infertile, but P application has increased P fertility. This paper draws on and undertakes a meta-analysis of 20 200 surface (0–10 cm) and profile (to 100 cm depth) soil samples collected in the period 1983–2018. Soil P content was high, with 70% of samples with Colwell P content in excess of agronomic requirements; Production is more likely limited by low soil pH_(CaCl2) and low K (92% and 67% of paddocks respectively). Strong P stratification in the soil is evident, particularly topsoil; sandy soils are saturated to depth; and clay soils show signs of P saturation in the topsoil. Management of P in sandy soil near the estuary is a high priority as is P stratification in highly P retentive soil. Soil P stocks increased since clearing compared with uncleared soils (1221 kg ha⁻¹ m⁻¹ and 285–694 kg ha⁻¹ m⁻¹, respectively). Thirteen percent of samples had P content in excess of agronomic requirements in 1983, rising slowly to 69% in 2018. Landholder practices need to be analysed in detail to confirm if this accumulation occurs everywhere or is only confined to actively farmed land.

Keywords: eutrophication, P saturation, P management, P loss, P efficiency, water quality, Peel–Harvey, estuary health.

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Introduction

Soils in south-west Western Australia (SWWA) were deficient in phosphorus (P) when land clearing for agriculture commenced in the 1800s. To overcome P deficiency, superphosphate application, particularly in the period 1945–1975 became an integral part of farming practice (Birch 1982; Yeates 1993) in the Peel–Harvey coastal catchment. An unintended consequence of P use in agriculture has been increased P loss to waterways, removing natural limitations to algal growth in the Peel Inlet and Harvey estuarine system (Kinhill Engineers 1988). As algae decompose, oxygen is depleted and fish kills occur (Hodgkin and Hamilton 1993). Of the coastal catchments in SWWA, the Peel–Harvey coastal catchment has the most P discharge (Ruprecht *et al.* 2013), with ~90% of the P sourced from ~210 000 ha of predominantly farmland in the coastal section of the catchment (Kinhill Engineers 1988).

Agricultural P loss has been widely reported (Sharpley and Withers 1994; Weaver and Reed 1998) and attributed to long-term P application to agricultural watersheds, leading to elevated soil P and widespread P losses from legacy P

sources (Jarvie *et al.* 2013). The diffuse loss of this legacy soil P is one of the most difficult to control (Sims *et al.* 1998).

With time, repeated P application results in a gradual increase in P diffused into particles that have adsorbed P; this increases the negative charge of soil particles and subsequently reduces P buffering capacity of the soil (Barrow *et al.* 2018). Tian *et al.* (2019) identified that 31–65% of applied P was found to have accumulated in soil P stocks when measured over 57 years. They found that excessive P application and soil P accumulation beyond agronomic requirements resulted in a P use efficiency decrease of 57% and increased P losses of 33%.

Various measures of soil P saturation have been proposed, and are typically based on measures of available P divided by measures of P sorption capacity, or other indirect measures such as ammonium oxalate extractable iron (Ammox Fe) and aluminium (Ammox Al); or Mehlich P (Nair 2014). Strong positive relationships between measures of P saturation such as the Degree of Phosphorus Saturation (DPS) and P concentration in run-off have also been identified (Nair *et al.* 2004; Tarkalson and Mikkelsen 2004; Withers *et al.* 2017; Dari *et al.* 2018).

Knowledge of P source and transport factors (Sharpley *et al.* 2008), as well as the location of soil at risk of P loss allows targeting of 'fit for purpose' management practices and resources to optimise agricultural production whilst minimising water quality impacts. Conceptual models of transport pathways such as leaching through sandy soils, surface runoff from sandy soils when the water tables rise to the surface, and surface runoff from nutrient stratified clay soils is important to couple with knowledge of the spatial and vertical distribution of P storage, P retention and saturation in order to better understand P loss risk, and management interventions with potential to reduce P loss. For example, knowledge of soil P stratification (Ryan *et al.* 2017) and the extent of subsoil P retention capacity provides insight into the potential for P-rich surface soil to be displaced from run-off pathways by incorporation into the soil profile rather than being exposed to run-off when concentrated at the surface. In addition, knowledge of temporal trends can provide insight into the impacts of agricultural practice on stored soil P (McDowell *et al.* 2021), and the potential for legacy P drawdown to contribute to improved water quality (Rowe *et al.* 2016; Withers *et al.* 2017).

Much of the knowledge of soil P retention, saturation, spatial and vertical variability of P storage, and the associated risk of loss is often acquired through dedicated research programs with clear hypotheses aimed at answering specific questions. However, opportunities to reinforce and value-add to existing knowledge also lie in meta-analysis of less prescriptive, but often large datasets from soil testing programs, which at their core are designed to promote evidence-based fertiliser decisions, rather than test a specific hypothesis. For example, government sponsored soil testing in the Peel–Harvey catchment occurred from 1983 to 1991, followed by targeted topsoil and subsoil sampling in 2006. From 2009 to 2018, government soil testing programs aimed at supporting evidence-based fertiliser decisions recommenced.

The meta-analysis of disparate soil testing programs presented here allows questions on the stocks of P in the soils, the rate and magnitude of change of P reserves, where to target intervention and how P has built up within the soil profile to be explored. In addition, the data presents an opportunity to develop pedotransfer functions for P sorption measures, which have changed during the period of this dataset. Such a dataset also allows the spatial representation of parameters that provide insight into water quality risk (P sorption, saturation and content), enabling fit-for-purpose management decisions to be more targeted.

Material and methods

Catchment environment

The Peel–Harvey coastal catchment is part of the Swan Coastal Plain, Western Australia (Fig. 1a) and is predominantly characterised by infertile Aeolian dunal systems running parallel to the coast and a narrow band of fluvial clay soils along the eastern edge of the plain beside the Darling Scarp. The fluvial clay soils are a small proportion of the catchment and are derived from the river systems running off lateritic

upland. The area's Mediterranean climate with 3–4 months of winter rainfall (up to 900 mm) results in inundation, with runoff carrying P to the Peel–Harvey estuary (Hodgkin and Hamilton 1993). The area was first settled in the early 1830s but the nutrient deficiency problems of the sandy soils were not solved until trace elements and superphosphate were introduced in the 1940s. Subsequent P fertiliser subsidies resulted in landholders on the coastal plain applying superphosphate heavily, with rates commonly up to 600 kg ha⁻¹. This coincided with further clearing and artificial drainage of the coastal areas in the 1940s and 1950s, and 75% of the area is now pasture for agriculture. Research in the 1970s and 1980s linked the loss of P to algal blooms and water quality problems in the estuarine system and efforts began to reduce excessive P application (DA Lord and Associates 1998).

Soils in the catchment are largely used to grow rain-fed subterranean clover and ryegrass pastures in a mixed sward for the purpose of grazing cattle (including dairy) and sheep. Although small areas of intensive agriculture (such as horticulture) exist, and urban development is increasing, extensive grazing activities occupy most of the landscape (Environmental Protection Authority 2008).

Soil sampling

Agricultural extension programs operated from 1983 to 1991 and from 2009 to 2018 in the Peel–Harvey coastal catchment, with the aim of providing landholders with evidence-based fertiliser recommendations based on soil sampling to 10 cm depth. In 2006, soil profiles representative of the area tested in 1983–1991 were sampled incrementally to 100 cm depth. The number of paddocks sampled and analytes tested varied each year depending on program resources and the soil testing methods prevailing at the time (Table 1). Analytical techniques are described below in chemical analysis.

1983–1991

Composite soil samples (0–10 cm) comprising 30 cores were taken using a 19 mm diameter sampler to represent each paddock. Samples were analysed for a standard set of agronomic soil tests, contemporary for the time including pH_(CaCl2) (Rayment and Lyons 2011), Colwell P (Colwell 1965), Colwell K (Rayment and Lyons 2011), and ammonium oxalate extractable iron (Ammox Fe) (Tamm 1922). The analogue soil chemical data and sample locations from this period were digitised (Fig. 1b) for 15 334 samples.

2006

A total of 314 sites representative of the 1983–1991 period were revisited and resampled (0–10 cm) using the same soil sampling equipment and protocols. In addition, a mechanised direct-push core sampler was used to take soil samples in increments of 0–5, 5–10, 10–20, 20–40 and 40–100 cm. Samples were taken from one paddock per farm and geolocated (Fig. 1b). The analytical suite was expanded to include phosphorus retention index (PRI) (Allen and Jeffery 1990), phosphorus buffering index (PBI) (Burkitt *et al.* 2002) and total P (Rayment and Lyons 2011), whilst continuing with Ammox Al and Fe (Tamm 1922).

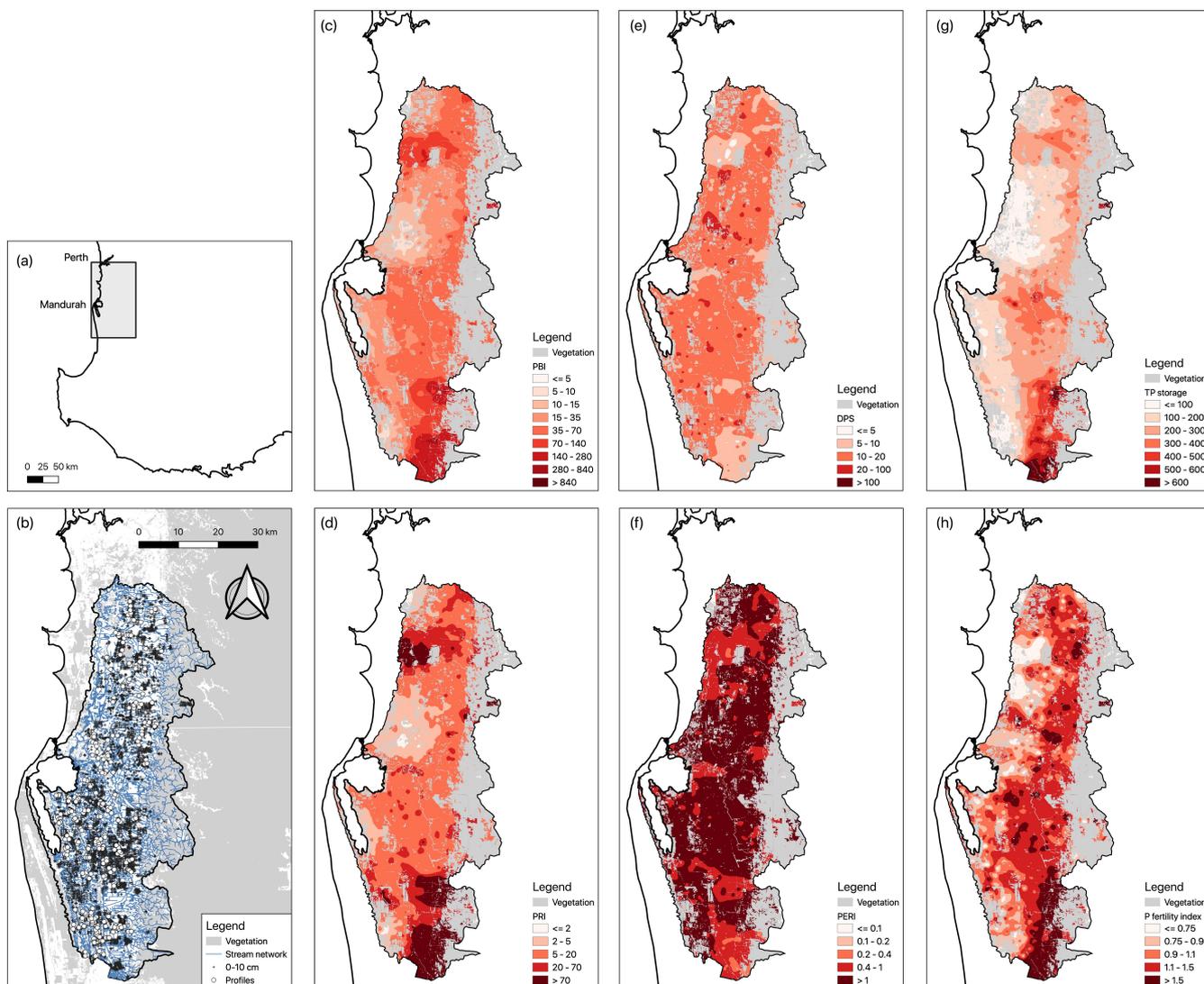


Fig. 1. (a) Overview of study area in south-west Western Australia. (b) The sampling sites (+, 1983–2018; ○, 2006 only) superimposed on the drainage system and outline of the Peel–Harvey Coastal Catchment. (c) PBI for extremely low (<5), very low (≥ 5 –10), low (≥ 10 –15), moderately low (≥ 15 –35), medium (≥ 35 –70), moderately high (≥ 70 –140), high (≥ 140 –280), very high (≥ 280 –840) and extremely high (≥ 840) categories (Gourley *et al.* 2019). (d) PRI for very weakly adsorbing or desorbing (≤ 2), weakly adsorbing (>2 –5), moderately adsorbing (>5 –20), strongly adsorbing (>20 –70) and very strongly adsorbing (>70) categories (Allen and Jeffery 1990) (e) distribution of DPS, (f) distribution of PERI, (g) distribution of TP and (h) distribution of P_{95} fertility index.

Soil in stands of remnant vegetation were also sampled at six locations in the Peel–Harvey coastal catchment but most of the uncleared land was representative only of sandy soil with $PBI < 15$. To supplement the soil samples in remnant vegetation with a $PBI \geq 15$, a further 42 locations in stands of remnant vegetation were included from sampling programs on the south coast of WA.

2009–2018

Composite 0–10 cm samples ($n = 2912$) each comprising 30 cores of soil were taken and geolocated to represent each paddock (Fig. 1b). The analytical suite was further expanded to include KCl-40 S (Blair *et al.* 1991), which was measured from 2016 to 2018 (Table 1).

Soil preparation and analyses

Following sampling, soil samples were prepared by oven drying at 40°C , sieving <2 mm and mixing before analysis. Colwell P and Colwell K were determined after extracting soil with 0.5 M NaHCO_3 at pH 8.5 for 16 h at 25°C at a soil solution ratio of 1:100 (Colwell 1965). Total P (TP) was determined after digestion in sulfuric acid in the presence of a Kjeldahl catalyst (Rayment and Lyons 2011). Phosphorus in extractions and digests was determined using the colourimetric procedure of Murphy and Riley (1962) and K was determined by atomic adsorption spectroscopy (Rayment and Lyons 2011). $\text{pH}_{(\text{CaCl}_2)}$ was determined after extracting soil for 1 h with 0.01 M calcium chloride solution at a soil solution ratio of 1:5 (Rayment and Lyons 2011). Soil organic

Table 1. Count and proportion of analytes and paddocks sampled in each year (a and c, periods of extension programs; b, research project)

Year	Count	%	Colwell P	Colwell K	Ammox Fe	Ammox Al	PRI	PBI	OC	TP	pH _(CaCl2)	KCl-40 S	
1983	1514	8.2	1503	1503	32								a
1984	3821	20.6	3819	3819	3393								a
1985	2925	15.8	2874	2874	2479						2873		a
1986	1715	9.3	1611	1611	1588						1612		a
1987	1703	9.2	1651	1651	1570						1643		a
1988	1172	6.3	1157	1157	906						1150		a
1989	1111	6.0	1108	1108	1104						1108		a
1990	738	4.0	738	738	738						729		a
1991	581	3.1	580	580	578						580		a
2006	314	1.7	1949	1949	1949	1905	1859	1898	1941	1948	1949		b
2009	387	2.1	387	387				387			387		c
2010	665	3.6	665	665				665			665		c
2011	378	2.0	374	374				374			374		c
2012	49	0.3	49	49			49	49			49		c
2013	280	1.5	280	280			267	280			280		c
2014	201	1.1	201	201			200	201			201		c
2016	274	1.5	274	274			250	274	263		274	274	c
2017	299	1.6	299	299				299	299		299	299	c
2018	379	2.0	379	379				379	379		379	379	c

carbon (OC) was estimated using the heat of dilution method (Walkley and Black 1934).

Ammox Fe and Ammox Al were determined by absorption spectrophotometry after extracting soil for 1 h at a soil solution ratio of 1:33 with Tamm's reagent (Tamm 1922; Blakemore *et al.* 1977). Phosphorus retention index was determined following incubation of soil with 10 mg P L⁻¹ at 1:20 soil:solution ratio for 16 h (Allen and Jeffery 1990) and expressed as the ratio of the P sorbed to P remaining in solution. Phosphorus buffering index was determined by incubating soil with a 100 mg P L⁻¹ at a 1:10 soil:solution ratio for 16 h and is corrected for Colwell P (Burkitt *et al.* 2002). Soil sulfur (S) was determined using the KCl-40 S method (Blair *et al.* 1991).

Pedotransfer functions

As each of the soil test measures were not in continuous use through the study period (Table 1), pedotransfer functions between various measures were developed using multiple linear regression (MLR) to provide a more complete spatial and temporal data series (Kleinman *et al.* 1999; Borggaard *et al.* 2004). Watmuff *et al.* (2013) propose pedotransfer functions to estimate PBI from other P sorption measures, however, sample sizes are often small for the proposed regressions, are often restricted to specific ranges of the independent variable, and do not include all of the analytes required here. For example, surrogate measures of P sorption using Ammox Fe and Al were used in the period 1983–1991, whilst single point P sorption measures such as PRI were used in the period 2006–2016, and PBI from 2006 to 2018 depending on procedures contemporary of the time. Prior to MLR, variables were log-transformed to remove skewness and approximate normal distributions (Helsel and Hirsch 1992). Transforms and MLR were prepared using DataDesk 8.2 (Data Description Inc.).

PBI was estimated from Ammox Fe using the function described by Weaver and Wong (2011). PRI was estimated from other soil variables using Eqn 1, 2 or 3, depending on which analytes were available in the timeseries.

$$\log PRI = 1.345 \times \log Ammox Fe - 0.489 \times \log Colwell P - 2.115 \quad (R^2 = 0.56, n = 4446) \quad (1)$$

$$\log PRI = 0.844 \times \log Ammox Fe - 0.449 \times \log Colwell P + 0.636 \times \log Ammox Al - 2.515 \quad (R^2 = 0.65, n = 3511) \quad (2)$$

$$\log PRI = 1.713 \times \log PBI - 0.278 \times \log Colwell P - 1.286 \quad (R^2 = 0.89, n = 9734) \quad (3)$$

Ammox Fe was estimated using Eqn 4.

$$\log Ammox Fe = 0.816 \times \log PBI + 1.388 \quad (R^2 = 0.56, n = 3470) \quad (4)$$

Total P was estimated using Eqn 5 or 6.

$$\log Total P = 0.240 \times \log PBI + 0.705 \times \log Colwell P + 0.762 \quad (R^2 = 0.70, n = 3467) \quad (5)$$

$$\log Total P = 0.240 \times \log Ammox Fe + 0.656 \times \log Colwell P + 0.568 \quad (R^2 = 0.70, n = 4199) \quad (6)$$

Derived measures

P status

The response of pasture to applied P depends on soil P sorption and Colwell P (Ozanne and Shaw 1967; Moody 2007; Gourley *et al.* 2019). Critical Colwell P values used to achieve

90–95% of relative yield (RY) were used to classify soils as P sufficient or deficient.

Measures of P saturation

A P environmental risk index (PERI) was determined as the ratio of Colwell P to PBI (Eqn 7) and is analogous to DPS and the likelihood that soluble P can be leached from the soil (Moody 2011).

$$PERI = \frac{\text{Colwell P}}{\text{PBI}} \quad (7)$$

The molar P saturation ratio (DPS) (Sims *et al.* 2002; Nair *et al.* 2004; Nair 2014) was calculated using Eqn 8 or 9, depending on what analytes were available in the timeseries.

$$DPS = \frac{\text{Colwell P/31}}{0.5 \times \text{Ammox Fe/56} + 0.5 \times \text{Ammox Al/27}} \quad (8)$$

$$DPS = \frac{\text{Colwell P/31}}{\text{Ammox Fe/56}} \quad (9)$$

P fertility index

The P fertility index (Cope and Rouse 1973) is estimated as the ratio of measured Colwell P to the critical or target Colwell P (Eqn 10) to achieve 90 or 95% RY (Gourley *et al.* 2019). The index represents the proportional contribution made by the soil to meet pasture P demand in the absence of applied nutrient, assuming no other constraints. Index values near to 1 are agronomically optimal, values less than 1 are considered deficient, and values greater than 1 are considered in excess. The amount above or below index values of 1 indicates the degree of P sufficiency or deficiency.

$$P \text{ fertility index} = \frac{\text{Measured Colwell P}}{\text{Target Colwell P}} \quad (10)$$

Data analysis

Analytes and derived variables were presented depth wise as notched box and whisker plots (Aabel NG2, Gigawiz Ltd) (McGill *et al.* 1978) and as violin plots (Igor Pro ver. 8 WaveMetrics, Inc.) (Hintze and Nelson 1998). For box and whisker plots, notches represent an area that can be visually compared to another boxplot to explore differences between factors or treatments. McGill *et al.* (1978) explain that in the absence of a formal statistical test, when notches do not overlap, the median values are ‘approximately, significantly different’. Non-linear regression (Igor Pro ver. 8) and correlation (Spearman rank; DataDesk 8.2, Data Description Inc.) were used to identify relationships between different soil analytes and variables. Soil variables and those derived from pedotransfer functions for measures of TP, P₉₅ fertility index, PBI, PRI, DPS and PERI were interpolated spatially using inverse distance weighting (ArcView 3.2 and Spatial Analyst, ESRI; QGIS 3.8, Creative Commons), and the correlation and regression between interpolated variables determined.

Results

The median Colwell P of the assembled data in the 0–10 cm topsoil was 31 mg kg⁻¹ and 8 mg kg⁻¹ in the 10–100 cm subsoil. Median TP values were 140 mg kg⁻¹ in the 0–10 cm topsoil and 57 mg kg⁻¹ in the 10–100 cm subsoil. The median Colwell K in the 0–10 cm topsoil was 70 mg kg⁻¹ compared to 33 mg kg⁻¹ in the 10–100 cm subsoil. Median KCl-40 S in the 0–10 cm topsoil was 9.5, whilst median soil pH_(CaCl2) in the 0–10 cm topsoil was 4.4 compared to 4.5 in the 10–100 cm subsoil (Table 2). Median values of PRI were 12.6 in the 0–10 cm topsoil and 55.0 in the 10–100 cm subsoil, whilst PBI was 55.0 in the 0–10 cm topsoil and 20.1 in the 10–100 cm subsoil. Median soil OC was 3.2% in 0–10 cm topsoil and 1.1% in the 10–100 cm subsoil.

Table 2. Summary statistics for soil analytes in the 0–10 cm and 10–100 cm depth ranges

Depth	Variable	Units	Count	Min	25th percentile	Median	75th percentile	Max
0–10 cm	Colwell P	mg kg ⁻¹	18 293	1.0	15.0	31.0	52.0	536
	Colwell K	mg kg ⁻¹	18 293	2.0	45.0	70.0	110	1857
	KCl-40 S	mg kg ⁻¹	982	0.8	5.8	9.5	16.1	167
	Ammox Fe	mg kg ⁻¹	12 717	5.0	170	480	1200	11 926
	Ammox Al	mg kg ⁻¹	319	5.9	133	417	996	8366
	PRI		1071	0.1	3.4	12.6	114	8300
	PBI		3226	1.0	26.9	55.0	146	772
	OC	%	1267	0.4	2.5	3.2	3.9	10.0
	TP	mg kg ⁻¹	326	9.0	67.0	140	259	1048
	pH _(CaCl2)		12 932	3.1	4.1	4.4	4.8	8.0
10–100 cm	Colwell P	mg kg ⁻¹	1623	1.0	3.0	8.0	24.0	698
	Colwell K	mg kg ⁻¹	1623	10.0	19.0	33.0	75.8	2196
	KCl-40 S	mg kg ⁻¹	ND	ND	ND	ND	ND	ND
	Ammox Fe	mg kg ⁻¹	1623	0.1	81.0	238	787	19 846
	Ammox Al	mg kg ⁻¹	1586	1.1	91.2	352	1142	19 930
	PRI		1554	0.1	1.1	3.5	29.2	19 980
	PBI		1580	1.0	8.8	20.1	62.3	1261
	OC	%	1615	0.1	0.5	1.1	2.9	10.7
	TP	mg kg ⁻¹	1622	1.0	23.0	57.0	148	2178
	pH _(CaCl2)		1623	3.2	4.2	4.5	5.0	8.3

Table 3. Spearman rank correlation matrix of soil analytes and derived variables
 Φ , not significant; *, $P < 0.05$; **, $P < 0.001$; values without symbol are significantly different at $P < 0.0001$

	Colwell P	Ammox Fe	Ammox Al	PRI	PBI	Colwell K	KCl-40 S	OC	TP	DPS	PERI	pH _(CaCl2)	P ₉₀
Colwell P	1												
Ammox Fe	0.719	1											
Ammox Al	0.537	0.823	1										
PRI	0.544	0.83	0.857	1									
PBI	0.648	0.838	0.838	0.943	1								
Colwell K	0.545	0.524	0.406	0.469	0.573	1							
KCl-40 S	0.483			0.498	0.475	0.335	1						
OC	0.518	0.322	0.157	0.081**	0.3	0.622	0.411	1					
TP	0.841	0.726	0.631	0.552	0.637	0.611		0.634	1				
DPS	0.063	-0.494	-0.627	-0.598	-0.48	-0.131		0.129	-0.026 Φ	1			
PERI	0.238	-0.228	-0.303	-0.521	-0.516	-0.016 Φ	-0.124**	0.162	0.173	0.742	1		
pH _(CaCl2)	0.228	0.255	0.228	0.341	0.302	0.287	0.175	-0.009 Φ	0.176	-0.195	-0.054**	1	
P ₉₀	0.638	-0.020*	0.314	0.313	0.411	0.286	0.375	0.505	0.729	0.737	0.497	0.114	1

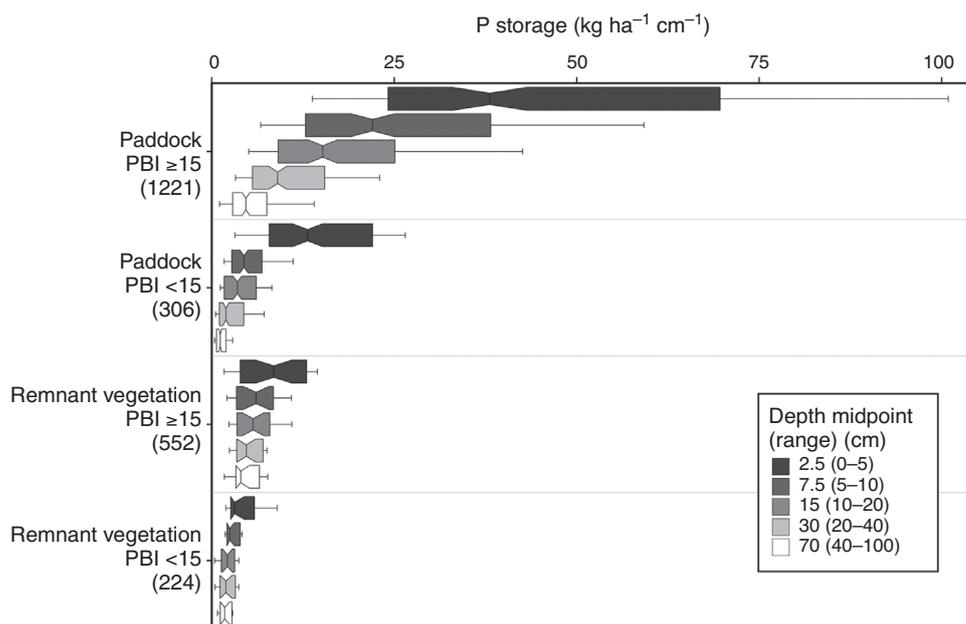


Fig. 2. Notched box and whisker plots of TP stored in the soil profile from fertilised paddocks (grouped by PBI ≥ 15); fertilised low PBI (grouped by PBI < 15) paddocks and uncleared remnant vegetation from the 2006 profile sampling (mean P stored $\text{kg ha}^{-1} \text{m}^{-1}$ in parenthesis).

Many soil analytes and derived variables were strongly correlated (Table 3). Colwell P was positively correlated with measures of P sorption, and with other soil nutrients (K, S), OC, pH and TP. Direct or surrogate measures of P sorption (Ammox Fe, Ammox Al, PBI, PRI) were all strongly positively correlated with each other ($r > 0.823$), negatively correlated with measures of P saturation (DPS, PERI), and increased with increasing Colwell K, OC, pH and TP.

Phosphorus stratification

The mean P stored in farmed soil profiles was $835 \text{ kg ha}^{-1} \text{m}^{-1}$, with a 10th and 90th percentile value of 160 and $1959 \text{ kg ha}^{-1} \text{m}^{-1}$, respectively. The mean P stored in uncleared soil profiles

was $147 \text{ kg ha}^{-1} \text{m}^{-1}$, with a 10th and 90th percentile value of 88 and $247 \text{ kg ha}^{-1} \text{m}^{-1}$, respectively.

When grouped by PBI ≥ 15 , the farmed soils stored ~ 4 times more P ($1221 \text{ kg ha}^{-1} \text{m}^{-1}$) than stored in farmed soils grouped by PBI < 15 ($306 \text{ kg ha}^{-1} \text{m}^{-1}$) and 2.2 to 5.4 times that stored in uncleared sites grouped by PBI ≥ 15 ($552 \text{ kg ha}^{-1} \text{m}^{-1}$) or PBI < 15 ($224 \text{ kg ha}^{-1} \text{m}^{-1}$) (Fig. 2).

Of the increase in soil P storage for PBI ≥ 15 , approximately one fifth occurs in the 0–5 cm layer, one third occurs in the 0–10 cm layer, and one third in the 40–100 cm layer. Of the increase in soil P storage for PBI < 15 , approximately one half occurs in the 0–5 cm layer, two thirds occur in the 0–10 cm layer, and one tenth in the 40–100 cm layer. Virgin soils associated with remnant

vegetation are mainly restricted to sands with low PBI and these maintain a relatively consistent but small P storage over the full soil profile (Fig. 2).

Using the samples collected in 2006 taken to 100 cm from across the catchment, a strong relationship was found between the TP stored in the 0–10 cm and the 0–100 cm depth of the

soil profile (Fig. 3a, b). The relationship in Fig. 3b was then used to estimate P storage to 100 cm from the larger 0–10 cm dataset.

A strong relationship between PBI in the 0–10 cm and P stored to 100 cm was also identified in the spatial data (Fig. 3c).

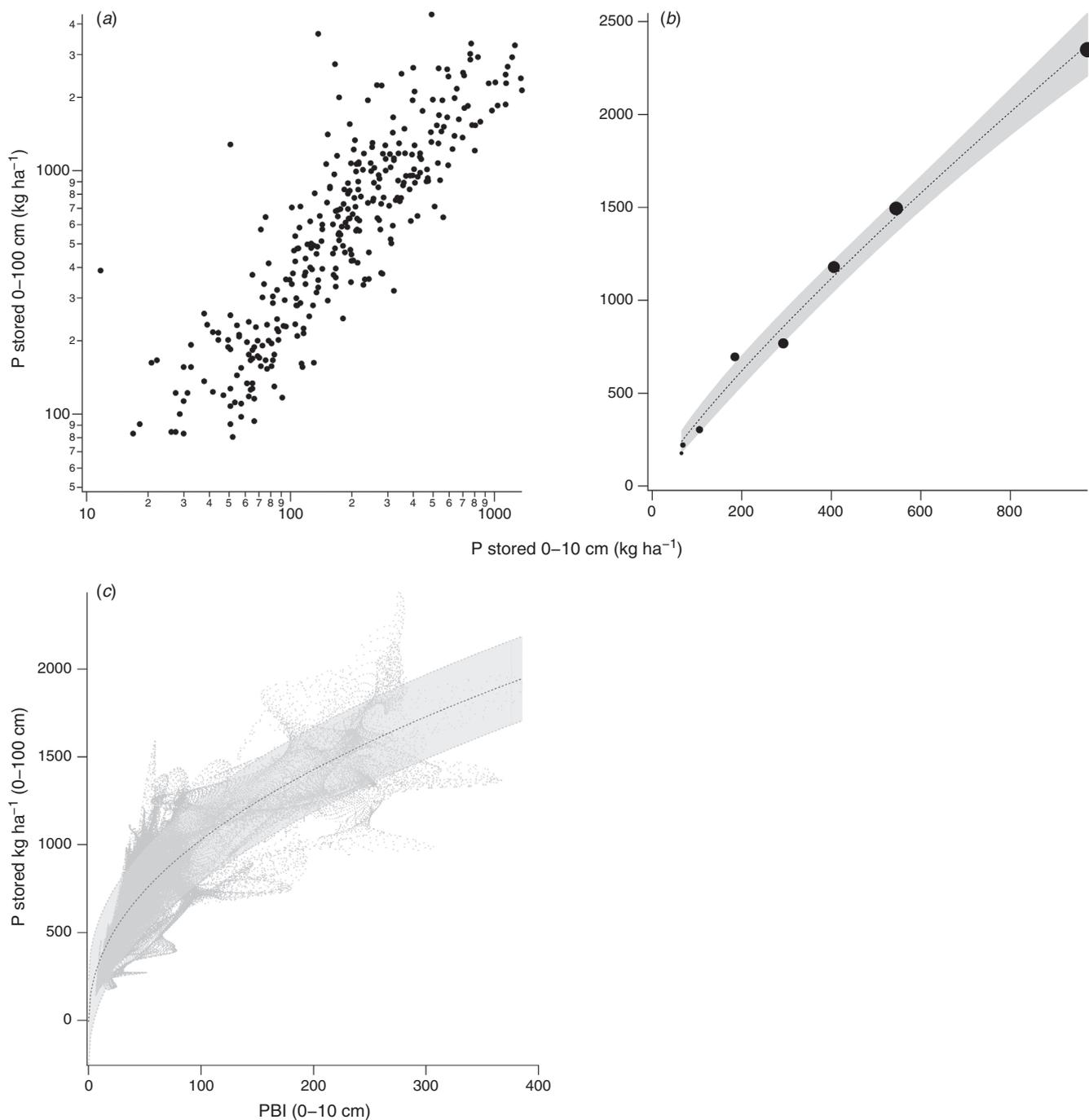


Fig. 3. The relationship between the TP storage (kg ha⁻¹) 0–10 cm depth and TP storage 0–100 cm depth (kg ha⁻¹) from the 2006 samples for (a) individual soil profiles, (b) summarised by the median P stored for PBI groups shown with increasing symbol size. The shaded area shows the 95% confidence band of the fitted curve (TP stored (0–100 cm) = 6.90 × TP stored (0–10 cm)^{0.849} *r*² = 0.99) and (c) total P storage (0–100 cm) as a function of soil PBI (0–10 cm) derived from inverse distance weighted coverages. Dashed line shows fitted curve and grey shaded area shows the 95% confidence band of the fitted curve. TP stored (0–100 cm) = -8.87 + 119 × PBI^{0.47} *r*² = 0.92.

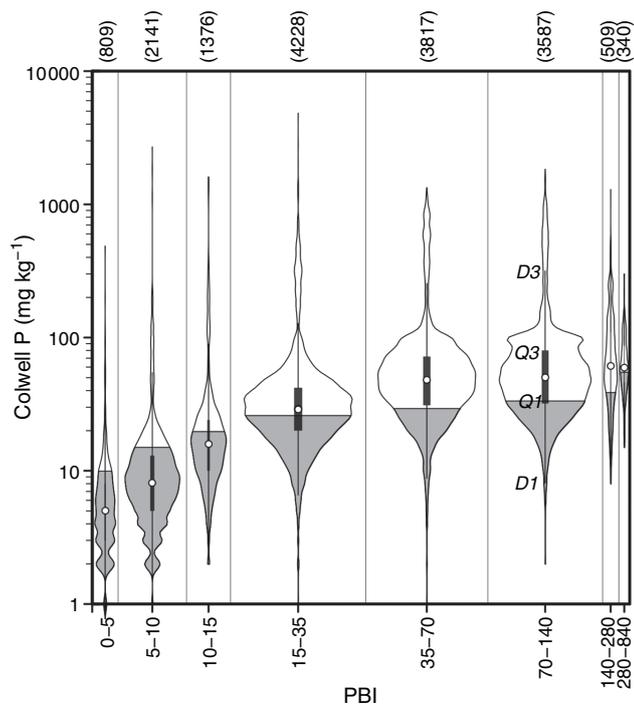


Fig. 4. Violin plots of Colwell P in each PBI group. Widths of the x-axis intervals are proportional to sample size (shaded area is soil P up to the 95% critical value P_{95} ; median soil P shown as a circle; number of samples 'n' in brackets; D, decile; Q, quartile).

P accumulation and P buffering

Colwell P accumulates in the topsoil more in high PBI soils than low PBI soils. The proportion of low PBI soils with sufficient Colwell P for 95% of RY (P_{95}) was much lower than for high PBI soils (Fig. 4).

There was systematic variation in the positive depth-wise relationships between log TP or log Colwell P and log PBI (Fig. 5a, b). The slope of the relationship decreased systematically with depth for Colwell P, but less so for TP.

There was generally a reduced P retention capacity of the topsoil relative to subsoil layers (Fig. 6a, b) with the reverse of a generally higher saturation of P in the topsoil relative to the subsoil (Fig. 6c, d).

Phosphorus retained in the topsoil increased with increasing PBI and more marked stratification shown as accumulation of P in the topsoil was found for higher PBI soils. A larger proportion of high PBI soils had more than enough P to meet the requirement for 95% RY (P_{95}) (Gourley *et al.* 2019) than lower PBI soils, which had proportionally less sites with sufficient P to reach the same critical value (Fig. 7).

Temporal variation in P fertility index

The median P_{90} fertility index was 1.13 in 1983. That is, Colwell P values were typically 13% higher than required to achieve 90% RY in 1983 (Fig. 8). The median P_{90} fertility index increased to 1.69 by 2018. The relationship between P_{90} fertility index and time between 1983 and 2018 had a significant positive slope of 0.016 (Fig. 8). This period included soil testing programs from 1983–1991 and from

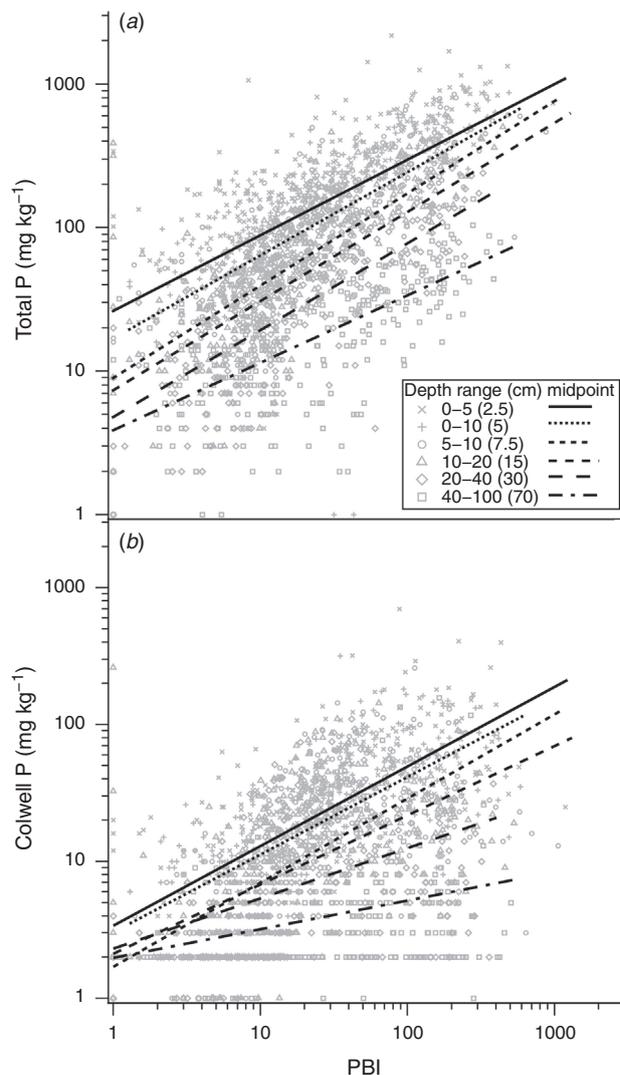


Fig. 5. (a) TP and (b) Colwell P as a function of PBI for the 2006 sampling to 1 m.

2009–2018, with a gap of 15 years (1991–2006) without a soil testing program.

Spatial distribution of P and P sorption

The spatial distribution of P sorption metrics, PBI (Fig. 1c) and PRI (Fig. 1d), were similar and were also strongly associated with each other ($r = 0.941$; Table 4), where P retention of the topsoil is low ($PRI < 5$) in the west of the catchment closest to the Peel–Harvey estuarine system.

DPS and PERI are strongly correlated ($r = 0.835$; Table 4). DPS values were mainly in the range of 10–20 while much of the catchment had PERI values greater than 1 (Fig. 1e, f).

The distribution of TP in the top 10 cm (Fig. 1g) in the catchment was correlated with PRI and PBI (Table 4). The P_{95} fertility index (Fig. 1h) shows a similar but more complex pattern than TP ($r = 0.638$; Table 4). The P_{95} fertility index was

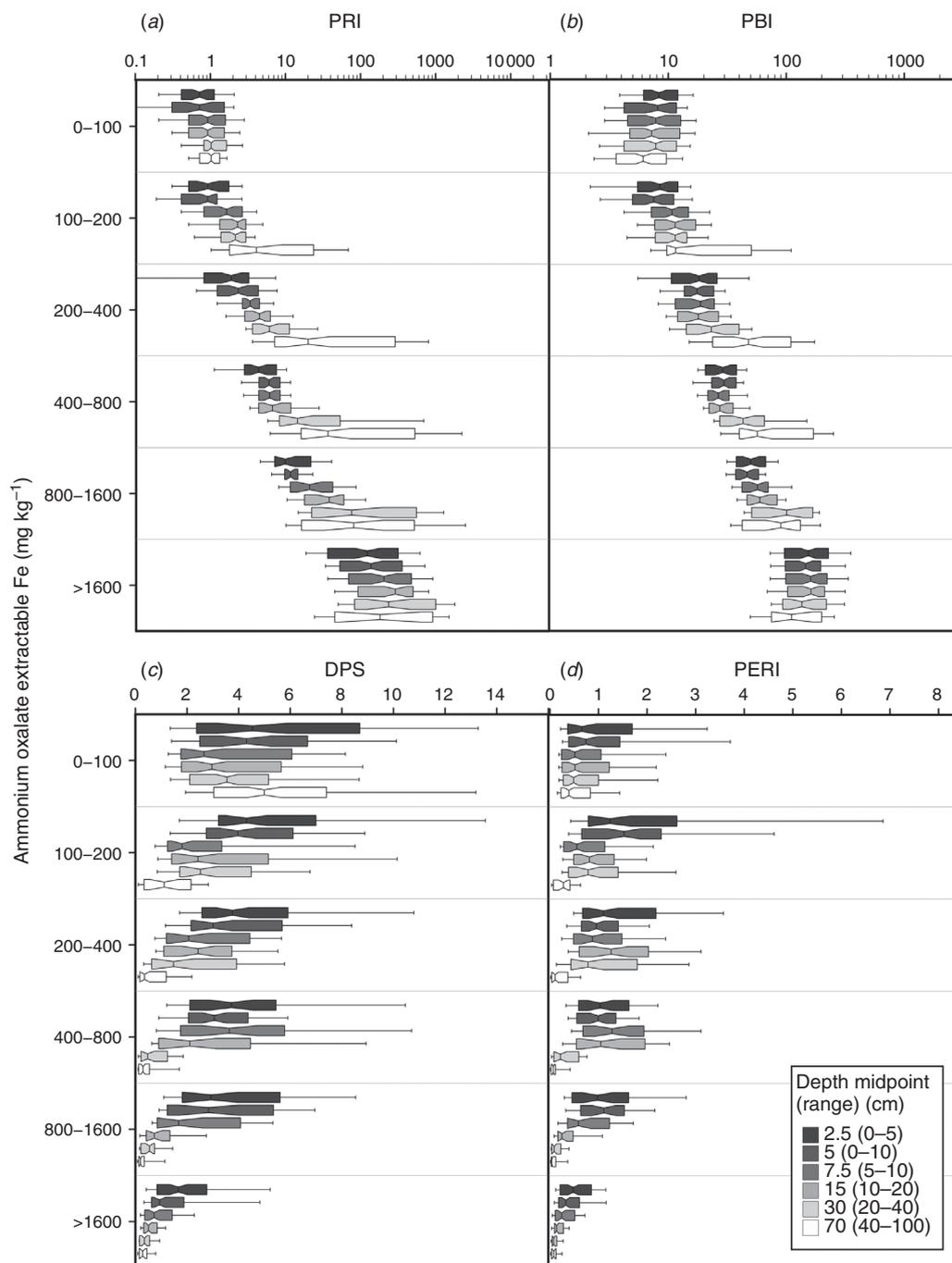


Fig. 6. (a) Phosphorus Retention Index, (b) PBI, (c) DPS and (d) PERI variation in the top metre of soil grouped by ammonium oxalate extractable Fe ranges from the 2006 sampling ($n = 1956$).

correlated with PBI and PRI (PBI: $r = 0.408$, PRI: $r = 0.307$; Table 4).

Other limiting factors

Sixty nine percent of samples had more P than required for 90% of RY, 67% of samples were K deficient, 26% were S deficient, and 92% required lime ($\text{pH} < 5.5$) for optimum pasture production (Fig. 9).

Discussion

The control of soluble P presents a major global challenge to sustainable agricultural management because high levels of P saturation of soil contribute to the release of P into watercourses (Kleinman 2017). The accumulation of P, measured as soil test P and often termed legacy P, is a well-documented threat to water quality and requires effort to draw down soil P reserves to manage the threat (Rowe *et al.*

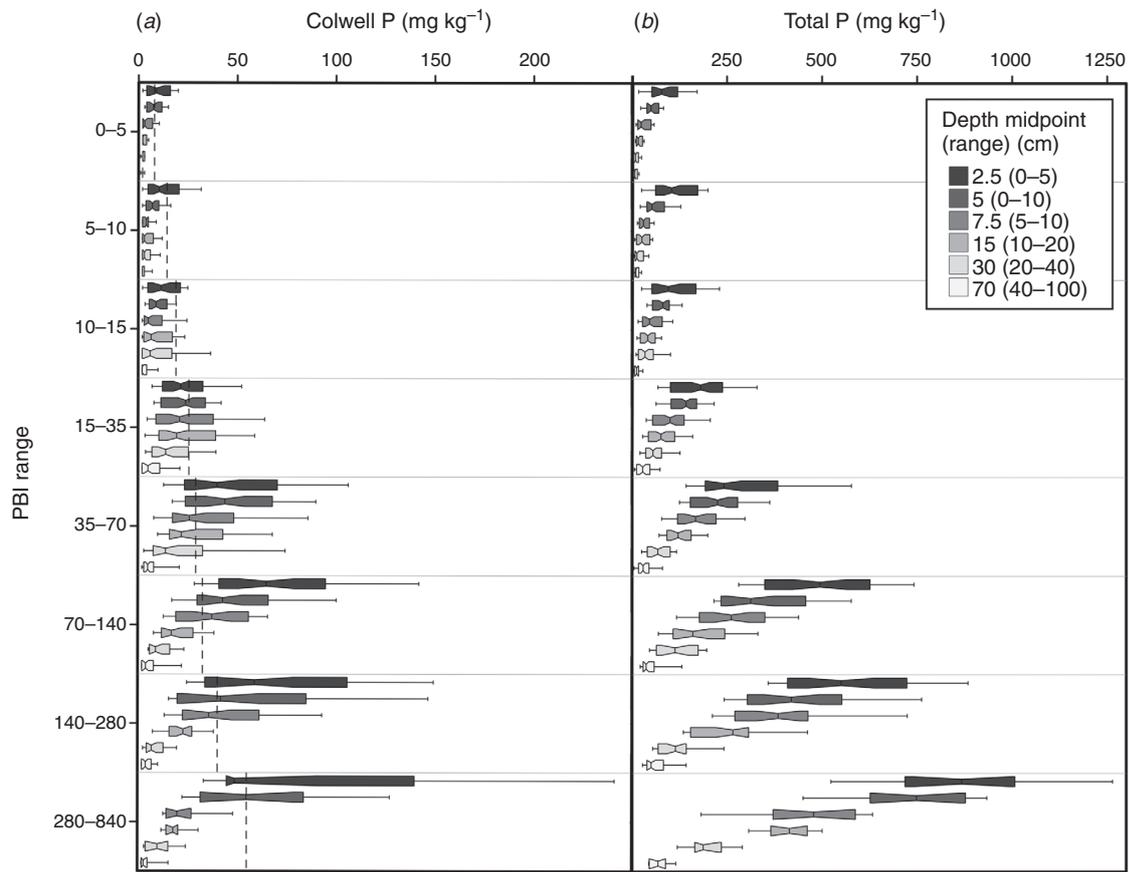


Fig. 7. (a) Colwell P and (b) TP distribution in the top metre of soil grouped by PBI ranges from the 2006 sampling ($n = 1956$). The dashed vertical line represents the critical value Colwell P at 95% RY (Gourley *et al.* 2019).

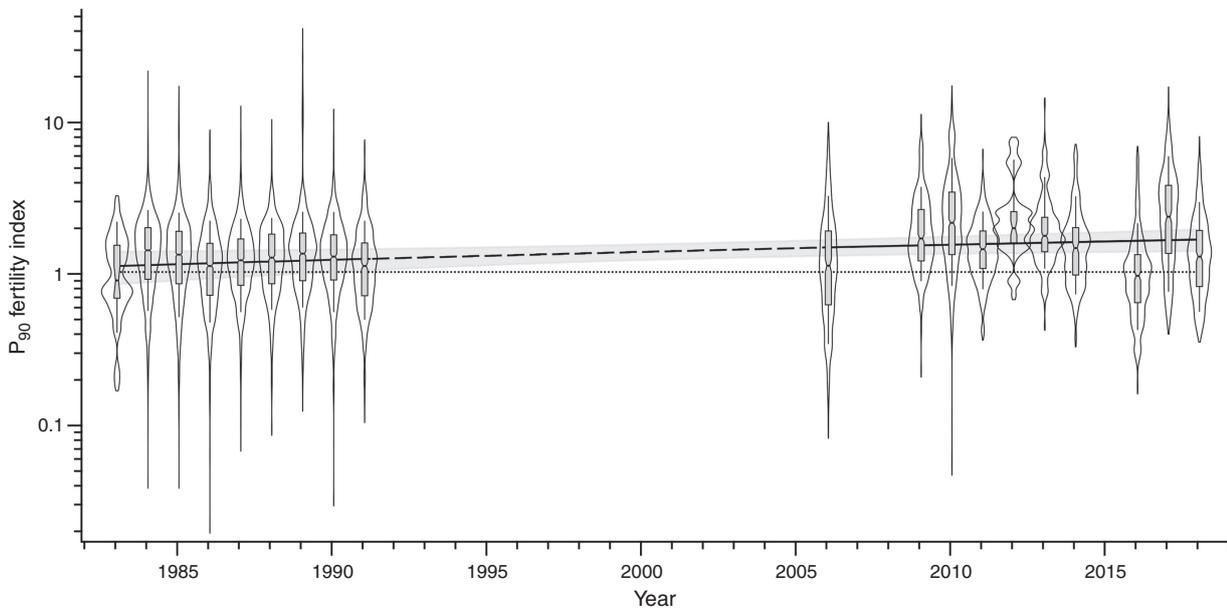


Fig. 8. Combined violin and notched boxplots showing distribution and temporal variation of P_{90} fertility index over the period of sample collection. Solid and long dashed line shows linear fit with 95% confidence interval (grey shading) to median P_{90} in each year. Dotted line shows optimal $P_{90} = 1$ for reference.

Table 4. Spearman rank correlation of soil variables interpolated using inverse distance weighting. All significant at $P < 0.0001$

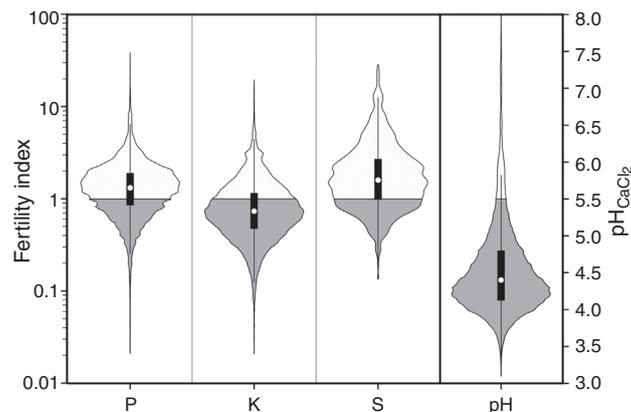
	PBI	PRI	DPS	PERI	TP	P ₉₅
PBI	1.000					
PRI	0.941	1.000				
DPS	-0.670	-0.643	1.000			
PERI	-0.506	-0.546	0.835	1.000		
TP	0.879	0.756	-0.508	-0.208	1.000	
P ₉₅	0.408	0.307	0.184	0.339	0.638	1.000

2016; Withers *et al.* 2019). This challenge posed by legacy P stores and soluble P (Summers *et al.* 2014; Weaver and Summers 2014) also exists in the Peel–Harvey coastal catchment and is a problem that is increasing with time (Figs 1g, h, 8). When coupled with other soil constraints (Fig. 9) that are likely to limit P uptake by plants (van der Ploeg *et al.* 1999), P loss in a soluble form from legacy sources represents a significant challenge in the Peel–Harvey coastal catchment.

Sandy soils with limited P retention capacity located near the Peel–Harvey estuarine system have little capacity to build up P or to stop P from entering into nearby waterbodies and are a high priority for management. In this environment, the traditional practice of riparian revegetation is ineffective at retaining P, which is transported in a soluble form (McKergow *et al.* 2003; 2006a; 2006b; Summers *et al.* 2014; Weaver and Summers 2014); therefore, minimising P application or increasing soil P retention are important strategies. Although voluntary soil testing has been used to encourage landholders to apply only the nutrients required, this appears to have had limited, if any, effect on reducing legacy P stores to date, as evidenced by gradual increases in the P₉₀ fertility index (Fig. 8). Despite this, there is some evidence emerging that soil testing programs may lead to reductions in fertiliser application (Summers *et al.* 2020).

One of the few effective and long-lasting treatments to reduce P movement from sands is soil amendment. Sandy soils can be modified to substantially reduce P losses by applying high P-sorbing materials such as bauxite residue (Alkaloam), which is produced in alumina refineries in the Peel–Harvey catchment (Vlahos *et al.* 1989; Summers *et al.* 1993; Ward and Summers 1993), or the use of clay from mineral sands mining (Summers *et al.* 2020). Soil amended with bauxite residue in 1991 reduced the P concentration from a 4300 ha catchment of the Peel–Harvey by ~70% and this has continued for more than 25 years (Summers *et al.* 2020).

The Peel–Harvey coastal catchment comprises a distinct range of soil types, which influence how P accumulates in the soil. The soils to the west have a lower P buffering capacity, and thus little capacity to retain P, resulting in soil P levels falling more quickly below target levels (Gourley *et al.* 2019) and requiring annual P applications to meet agricultural production requirements. In the east, soils have a higher P retention capacity; the erosion of high iron and aluminium soils from laterite and granitic soil origins along the Darling Scarp has contributed to their capacity for P retention. These eastern soils can support surface irrigation and the higher

**Fig. 9.** Combined violin and boxplots of Colwell P, Colwell K and KCl-40 S fertility index at 90% RY (Gourley *et al.* 2019) (shaded < 1.0) and the $\text{pH}_{(\text{CaCl}_2)}$ (shaded < pH 5.5).

productivity has favoured dairy farming. This results in a greater capacity to fund application of P and stockfeed containing P, resulting in P accumulation that exceeds the requirements for agricultural production targets.

The soils of the Peel–Harvey coastal catchment have become greatly enriched from P application since clearing and superphosphate application. Storage of $1221 \text{ kg ha}^{-1} \text{ m}^{-1}$ of P is equivalent to more than 10 tonnes of superphosphate retained by the top 100 cm of soil, or ~70 years of 140 kg of superphosphate $\text{ha}^{-1} \text{ year}^{-1}$, excluding the P removed in product (mainly beef) and lost in run-off.

Stratification of P in soils has previously been reported at two sites in the Peel–Harvey coastal catchment (Ryan *et al.* 2017) where P distribution in the top 10 cm was examined. In the current study, sampling of soil profiles at a wider scale, to greater depth, and at finer depth increments shows a similar distinct stratification of P accumulated in the topsoil, with much less P found in the subsoil (Fig. 7a, b). The median Colwell P of the assembled data in the 0–10 cm layer was 31 mg kg^{-1} while typical Colwell P values for virgin soils (0–10 cm) in SWWA are $< 2 \text{ mg kg}^{-1}$; however, soils farmed for more than 30 years had a median Colwell P of 29 mg kg^{-1} (Weaver and Reed 1998). Soils with a lower PBI were unable to retain much P, except in the top few centimetres of soil. This suggests limited P leaching to depth for soils with high PBI, but also limited capacity of soils with low PBI at any depth to increase Colwell P (Figs 2, 7). These low PBI soils accumulated a high proportion of P in the topsoils, most likely associated with organic matter in the topsoil (Tables 2, 3) rather than sorption on soil surfaces. In contrast, there was very low retention of P in the 10–100 cm subsoil of low PBI soils, which contained much less organic matter. This is of significance because organic matter breakdown over summer has the potential to release P during autumn rain and contribute to run-off into watercourses (Weaver *et al.* 1988).

The limited P enrichment of high PBI soils to depth indicates only a small degree of mixing, preferred pathways, and leaching. This has implications for the risk of P loss via different transport pathways for soils with varying

texture and PBI. Coarse textured soils with low PBI will leach P. Conversely, high PBI soils accumulate P in near-surface layers, risking the desorption of soluble P and loss via surface run-off rather than from leaching. High levels of P in topsoil also increases the risk of P loss via erosion of soil particles that carry P into waterways, with potential accumulation in streambed sediment and later release to the water column (McDowell 2015; Clarendon *et al.* 2019).

Limitations of other nutrients in the presence of excess P may contribute to reduced P uptake, reduced removal and export in agricultural product, increasing the potential for loss. While we found P stratification and accumulation beyond agronomic requirements to be widespread, other constraints (K, S, pH) were common (Fig. 9). Stratification of K is also evident but generally not sufficient to overcome deficiency. In the Peel–Harvey on the west coast of WA, we found the median Colwell K in the 0–10 cm layer was 70 mg kg⁻¹, whereas the median Colwell K for the 0–10 cm layer on soils farmed for more than 30 years on the south coast of WA was 106 mg kg⁻¹ (Weaver and Reed 1998). Colwell K values to achieve 95% RY range from 126 to 161 mg kg⁻¹ (Gourley *et al.* 2019), suggesting that despite accumulation of K in the topsoil there remains K deficiency in both topsoils and subsoils. A median KCl-40 S value of 9.5 in the 0–10 cm layer slightly exceeds the critical S value of 8 to achieve 95% RY (Gourley *et al.* 2019). Soil pH_(CaCl2) median values of 4.4 in the topsoil and 4.5 in the subsoil indicates acidic conditions that are likely to adversely affect plant growth and nutrient uptake (Truog 1918). These values are similar to those previously reported on the south coast of WA (Weaver and Reed 1998; Weaver *et al.* 2020). Soil tests for Colwell P, Colwell K and KCl-40 S increased with increasing soil pH, following the general trend of increased nutrient availability as pH increases from acidic values (<4.5) to neutral pH (Truog 1918). Median soil OC values in topsoil were around three times those in subsoils and very similar to those reported by Weaver and Reed (1998); that is, 3.1% for soils farmed for more than 30 years.

Median values of measures of P sorption in both topsoil and subsoil suggests that the soils are weakly to moderately adsorbing (Allen and Jeffery 1990) or classified as moderately low to medium sorbing when using PBI (Gourley *et al.* 2019). All these measures were skewed with low P sorption values being favoured. Total P values in subsoils were around half that of topsoils and are typical of the limited P sorption capacity of soils in the region.

Researchers have long recognised that the P sorption characteristics of soils influence plant-available P and soil P status (Ozanne and Shaw 1967; Brennan *et al.* 1994; Weaver and Reed 1998; Burkitt *et al.* 2002; Moody 2007; Gourley *et al.* 2019). Soil PBI accounts for the accumulation of P in the soil, and therefore provides an indication of the P sorption potential of the soil before P is added. Soil PRI is a measure of the current soil P sorption potential, which reduces after repeated P application and accumulation in the soil. Like PBI, Ammox Fe is an indirect measure of P sorption potential of the soil and is not expected to be impacted by soil P content. As such, PBI and Ammox Fe are measures of P sorption that would be expected to remain constant with

repeated P applications. Soil PRI shows a steeper trend by depth than PBI in most Ammox Fe groups (Fig. 6a, b) demonstrating the cumulative effect of P applications on reducing soil P sorption potential. This accumulation of P and subsequent reduction in P sorption has been explored by Barrow *et al.* (2018) and the continued application of P causes accumulation to very high levels in high PBI soils where the P sorption capacity can be overwhelmed and P may begin to desorb as soluble P into run-off (Rivers 2012). Poor P retention capacity of low PBI soils, along with propensity to lose P by leaching or run-off, is likely to have contributed to low Colwell P and TP.

The greatest P enrichment of the soil has occurred in the top 5 cm as would be expected for surface-applied fertiliser on permanent pasture, but enrichment continues deeper into the soil profile indicating leaching, occasional incorporation, or P movement via preferred pathways in all soil types.

Phosphorus saturation of the topsoil is widespread, as shown by the spatial distribution of DPS and PERI (Fig. 1e, f). Most of the catchment has a PERI of >0.4, which is considered to maintain soil solution P concentrations of 0.2 mg P L⁻¹, consistent with optimum soil solution P concentrations for plant growth of 0.15–0.3 mg L⁻¹ (Asher and Loneragan 1967; Russell and Russell 1973). Threshold values of DPS above which P loss increases significantly for a range of soils have been reported previously as being within the range of 10–20 (Nair 2014). Much of the catchment is within this range (Fig. 1d). The good correlation between DPS and PERI (Tables 3, 4) suggests that PERI may be a useful analogue for DPS and draws on more contemporary and direct P sorption measures such as PBI (Burkitt *et al.* 2002).

The heavier, highly P retentive soils that have built up P in the topsoil (Fig. 7a, b) have been shown to be losing P by desorption, especially in intensively grazed irrigation areas in the south-east of the Peel–Harvey coastal catchment (Rivers 2012), similar to observations elsewhere in Australia (Nash and Murdoch 1997; Dougherty *et al.* 2006; Nash *et al.* 2007; Kleinman 2017). In inundated areas or where there is strong stratification of P in the soil, PERI or DPS from a 0–10 cm soil sample may not provide an appropriate indication of P loss risk. Soils that are highly P stratified with P saturation in the top few centimetres may desorb P into run-off water, resulting in soluble P concentrations of 4 to 6 mg P L⁻¹ (Dougherty *et al.* 2006; Rivers 2012). Laboratory assessment of PERI or DPS from a 0–10 cm soil sample saturated with P at the surface would be diluted with higher PBI soil less saturated with P from deeper parts of the sample when collected for analysis for agronomic purposes. The homogenisation of the stratified sample would mask the highly P saturated surface and give the appearance of a soil that could retain more P rather than desorb P. This highlights the importance of collecting soil samples that are fit for purpose for the question being asked, whether that is agronomic or environmental.

Clay soils saturated with P have been managed elsewhere by laser grading irrigation paddocks to disturb and bury the P saturated surface soil and expose P-sorbing subsoil material (Nash *et al.* 2007). Similarly, increasing the P sorption of stream sediment by using highly P retentive materials to control soluble P has been identified as an option in the

Peel–Harvey coastal catchment and south-eastern Australia (Barlow *et al.* 2003; 2004; Summers *et al.* 2014).

Combining soil P fertility mapping (Fig. 1h) with hydrological data to identify critical source areas will help target management interventions, minimising its cost and maximising its effectiveness (Cassidy *et al.* 2019). This is important in catchments of the south-west of WA such as the Peel–Harvey coastal catchment, where run-off has reduced by more than 50% over the study period; this reduction has been attributed to climate change (Kauhanen *et al.* 2011). Reduction in run-off greatly focuses the efforts to reduce P losses in the critical source areas near drains and watercourses. The westernmost areas have the lowest P retention capacity, they are also saturated with P and are closest to the Peel–Harvey estuarine system, where there is little opportunity to attenuate P loss by overland flow or retention in the drainage system before run-off reaches the estuary.

Although typical P application rates in the Peel–Harvey coastal catchment decreased from 8.1 to 7.7 kg P ha⁻¹ between 1983 and 1991 (Kinhill Engineers 1988; Arkell 1989; Peek and Arkell 1992), these decreased rates are still likely to be in excess of P requirements to maintain optimum production when soils have a P fertility index of 1. By comparison, the median removal of P by cattle is ~2 kg P ha⁻¹ (Weaver and Wong 2011). Even if landholders follow the advice to apply less P, P application is still too high and P is building up, albeit at a slower rate (Fig. 8).

The apparent accumulation of P over the 35-year study period may appear to be a threat to water quality; however, the sampling methodology may have masked some underlying changes in how representative the samples were. The earlier sampling period (1983–1991) aimed to soil test all properties in the catchment, was resourced accordingly, and was widely adopted with 15 309 samples taken from most of the farmed catchment area. Between 2006 and 2018, sampling occurred for only 10 years, with only 3232 samples taken. In this later sampling period, advertising that offered free soil testing to landholders meant that farmers self-selected for inclusion in the program. Crawford *et al.* (2020) identify some potential issues of bias associated with the use of legacy data rather than from randomly selected sites. In addition, over the period of the study, two distinct farmer groups can be identified, commencing with all farmers in the period 1983–1991, followed by self-selected farmers from 2006 to 2018. Some of these issues along with changes in land ownership, urbanisation and a reduction in the actively farmed area and thus the P applied may contribute to bias. Preliminary assessment of the 2005–2017 fertiliser sales in the Peel–Harvey coastal catchment (Summers *et al.* 2020) showed reduced fertiliser use in the south of the catchment area, with the lowest fertiliser sales in the northern peri-urban area. This land use change may mean these peri-urban property owners in the north would have little interest in soil testing and would be unlikely to be in the self-selected group who are soil testing. Therefore, there may be a growing area of the catchment that potentially could be reducing the soil P store but the landholders did not come forward for testing. The results may also mean that those landholders who are still

farming and fertilising have had their soils tested over the entire sampling period and represent a part of the catchment that is slowly accumulating P in their soil. A different methodology that incorporates a more representative sample to include those farms that were no longer fertilising would be required to investigate this aspect.

Management of all soil types is essential to minimise the build-up of P where undesirable levels of P already occur (Fig. 1h), or where the agronomic optimum for Colwell P at 95% RY is exceeded (Fig. 7a). The continued increase and widespread nature of high P status soils in the study area (Figs 1f, 7) suggests that the long-term subsidised and voluntary approach to soil testing and fertility management has not achieved sufficient behavioural change. This is a concern because soil testing can identify financial savings by reducing P application, which can be diverted to addressing other limiting factors for pasture production, such as K, S, and pH (Fig. 9). Increased productivity, greater water use, greater removal of P in agricultural products, and improved water quality are likely to result from adopting evidence-based fertiliser decisions that are based on soil testing.

In conclusion, this meta-analysis of spatially explicit soil test data from the Peel–Harvey catchment allowed improved understanding of changes in soil P stocks, and the rate and magnitude of the temporal change of metrics such as P fertility index. In addition, the stratification of soil P and depthwise changes in P sorption and saturation have been identified, reinforcing and expanding on the conventional wisdom around the loss of P via different transport pathways. The spatial representation of soil P parameters via pedotransfer functions and regression models has assisted to confirm areas of increased water quality risk, much of which is consistent with existing understanding of P loss risk.

Conflicts of interest

The authors declare no conflicts of interest

Declaration of funding

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