



Comparison of plant response and phosphorus uptake by ion exchange desorption and chemical extraction for soils under different land uses

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Abstract

Aims We quantified the relative significance of phosphorus (P) availability quantity and rate of P desorbed to plant growth using ion exchange membranes on three soils (0–10 cm), initially under native vegetation and converted to either cropping, pasture, or plantation for up to 115 years.

Methods Soil P availability parameters were measured by the widely used sodium bicarbonate test (Colwell P), anion exchange membranes and

anion + cation exchange membranes either saturated by NaHCO₃ or KCl solution. Plant P parameters measured were dry matter yield, relative yield, and P uptake by Rhodes grass (*Chloris gayana*).

Results We found that the quantity of soil P measured by the HCO₃⁻-anion exchange membrane accounted for up to 90% variability in dry matter yield and P uptake, and the rate of P desorbed by HCO₃⁻-anion exchange membrane accounted for 81% variability in yield response, while Colwell P was unsuccessful.

Conclusion Anion exchange membrane saturated with NaHCO₃ provided superior performance in predicting the availability of soil P to plants compared to the routinely used soil test under different land uses. Thus, wider use of these ion exchange membranes is recommended to provide a more accurate assessment of the amount of plant available P present in soils. This will be beneficial for improving fertiliser P management practices to increase P use efficiency in the face of decreasing P reserves. Moreover, HCO₃⁻-anion exchange membrane technique will be useful in monitoring excess P applications, and thereby devising practices to reduce environmental P pollution.

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Highlights

- Ion exchange membranes surpass routine tests in predicting soil P availability
- HCO₃⁻-AEM P showed the strongest correlation with dry matter yield
- HCO₃⁻-AEM P explained 90% variability in plant P uptake
- KCl⁻-ACEM P accounted for 79% variability in yield response in different land uses

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Keywords Forest soil · Pasture soil · Cropped soil · Anion-exchange membrane · Anion + cation exchange membrane

Introduction

In most agricultural systems, besides nitrogen (N), phosphorus (P) availability in soil is the limiting factor for plant production (Langhans et al. 2022). Therefore, ensuring an adequate supply of available P to crops, pastures, and other vegetation is critical to maintaining food and nutritional security (Brownlie et al. 2022). The availability of soil P to plants depends on several factors including the soil's capacity to replenish P absorbed by plants (quantity factor), and the rate at which P in the solution is replenished to meet plant demand (rate factor) (Yli-Halla et al. 2016; Barrow 2021). These factors are mediated by complex processes such as desorption, dissolution, and diffusion from the solid phase to the solution phase as inorganic P in the soil solution is depleted by plant uptake. Additionally, microbial mineralization of soil organic P (OP) supplies P to the soil solution, making it available for plant uptake (Sims and Pierzynski 2005).

To identify soils deficient in plant-available P, several soil tests have been developed, which variably simulate only one but not all the plant P availability factors and hence have limited success (Yli-Halla et al. 2016). Traditional soil P tests, including the Olsen P and Colwell P methods, have been

extensively utilized to estimate plant-available P. However, these tests primarily assess the quantity factor and often overlook the dynamic nature of soil P availability, which is influenced by multiple interacting factors such as replenishment rates or rate of P desorbed from soil (Frossard et al. 2000; Nuernberg et al. 1998). This limitation becomes particularly pronounced in soils undergoing land use changes, where alterations in soil properties such as organic carbon (OC) content, pH, and the composition and concentration of iron (Fe) and aluminum (Al) oxides can significantly alter P dynamics (Yi et al. 2023; Alovise et al. 2020; Asomaning 2020; Chavarro-Bermeo et al. 2022; Stutter et al. 2015). For example, conversion of forested land to agricultural land use can drastically reduce soil organic carbon (SOC) and alter pH, both of which are critical to P availability (Zhang et al. 2020, 2021).

The need for more accurate and predictive soil P tests has led to the development of ion exchange membranes, which offer a more comprehensive assessment of P availability by simulating the continuous exchange processes between soil P and plant roots (Nuernberg et al. 1998). Ion exchange membranes, including anion exchange membranes and anion + cation exchange membranes, capture a broader range of P availability factors including the quantity and rate factors compared to the routine soil tests (Cooperband and Logan 1994; Schroder et al. 2010). These ion exchange membrane-based approaches may show strong correlations with critical agronomic parameters, such as dry matter yield, relative yield response to applied P, and P uptake. This is particularly true in scenarios where traditional NaHCO_3 extraction methods may not fully capture the dynamic and complex processes of P replenishment and desorption processes (Hinsinger 2001; Brownlie et al. 2022).

Another technique that has been used to assess plant-available P is the diffusive gradients in thin films (DGT) method, which simulates P diffusion from soil mineral surfaces to a resin sink, mimicking the depletion zone near plant roots (Almeida et al. 2019) although the active role of rhizosphere in accessing P is neglected. DGT has been shown to integrate both the intensity and resupply components of P availability and was initially reported to correlate well with plant P uptake under controlled, fertilised conditions (Menzies et al. 2005). However, its

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predictive performance under field conditions has been inconsistent. For example, Burkitt et al. (2016) and Spiers et al. (2013) reported that DGT-P was not consistently better than Colwell P in predicting pasture yield or wheat yield responses to P fertiliser applications. Moreover, practical limitations such as high cost, single-use design, limited spatial representativeness, and microbial biofilm interference have constrained the widespread adoption of DGT in routine agronomic soil testing (Marrugo-Madrid et al. 2021; Wagner et al. 2022; Mohammadi et al. 2022). These challenges highlight the need to evaluate alternative and scalable methods such as ion exchange membranes under diverse soil and land use conditions.

The chemical transformations and availability of P in soil are influenced by various properties such as soil pH, organic matter content, clay content and Fe and Al oxides (Fink et al. 2016; Frossard et al. 2000; Ismat et al. 2018; Ryan et al. 1985). These soil properties significantly impact P sorption and availability, particularly in soils with varying pH and mineral composition (Sims and Pierzynski 2005; Barrow 2017; Barrow et al. 2022). Understanding these interactions is critical for refining soil testing methodologies to provide more accurate predictions of P availability across diverse agricultural landscapes (Cordell and White 2013; Syers et al. 2008), especially land converted for different land uses.

Given these considerations, there is a pressing need to develop and validate soil testing methods that account for the multifaceted nature of P availability, especially in the context of changing land use patterns and diverse soil types. This study aims to address this gap by evaluating the relative importance of different P quantity and rate of desorption/diffusion of soil P in

predicting plant growth and P uptake. By comparing traditional soil P tests with ion exchange membrane-based methods, we seek to advance our understanding of how land use changes impact soil P dynamics relevant to plant productivity and to identify the most effective strategies for managing soil P to enhance agricultural productivity and P use efficiency. The central hypothesis of this study is that ion exchange membrane techniques, particularly those involving bicarbonate or chloride saturated membranes, will offer a more accurate and reliable prediction of P availability than traditional chemical extraction methods. The most appropriate techniques to measure plant available P will contribute to the dynamic and integrative approaches to soil P testing, which are essential for increasing P use efficiency and supporting sustainable agricultural practices in the face of global P resource constraints (Cordell and White 2013; George et al. 2018).

Materials and methods

Soils samples representing eight soil land-use combinations were collected from three locations in subtropical Australia (Table 1). The soils were Ferralsols from Lamington (28° 12' 52.92"S, 153° 6' 58.30" E, 151° 45' 8.40" E), Vertisols from Warra (26° 47' 27.01"S, 150° 53' 7.90" E), and Ferralsols from Kingaroy (26° 39' 55.57"S, 151° 45' 8.40" E); these are Lamington clay, Warra clay, and Kingaroy clay loam, respectively. The properties of these soils were previously provided by Zhang et al. (2020). Briefly, at each of these three locations, adjacent paired sites (within two hundred meters) were used to collect soils from different land uses; that is, a native (virgin)

Table 1 Soil type, soil order, and land use combinations

Soil type	Soil order	Land Use Combination	Abbreviation
Lamington clay	Ferralsol	Native vegetation	LUD
Lamington clay	Ferralsol	115-year pasture	LPS
Warra clay	Vertisol	Native vegetation	WUD
Warra clay	Vertisol	82-year cropping	WCP
Kingaroy clay loam	Ferralsol	Native vegetation	KUD
Kingaroy clay loam	Ferralsol	67-year cropping	KCP
Kingaroy clay loam	Ferralsol	33y cropping + 34y pasture	KPS
Kingaroy clay loam	Ferralsol	33y cropping + 18y pasture + 16y plantation	KPI

site paired with an adjacent cropped, pasture or plantation site developed after land use change at different times. Soil samples were collected from three sites: Lamington (native vegetation and 115 years of pasture), Warra (native vegetation and 82 years of cropping), and Kingaroy (native vegetation, 67 years of cropping, 33 years of cropping followed by 34 years of pasture, and 33 years of cropping followed by 18 years of pasture and 16 years of hardwood plantation) (Table 1). Soil samples were collected from a depth of 0–10 cm, corresponding to the tillage-affected layer. At each site, ten randomly selected subsamples were composited to form one sample, and three replicate composite samples were obtained per site. P fertilizer applications were minimal, with no P fertilizer at Lamington, 120 kg P over 82 years at Warra, and 85.6 kg P over 67 years at Kingaroy.

Soil chemical analysis is described in detail by Zhang et al. (2020, 2021). Briefly, soil pH and EC were measured using a 1:5 soil: water suspension (Rayment and Lyons 2011). Total organic C (TOC) and total N were determined by using a CN analyser (LECO Trumac CN analyser, Michigan, USA). For the soil from Warra, the soil was pretreated with 5% HCl prior to the TOC analysis to remove carbonate C. The citrate-dithionite extractable Fe (Fe_d) and Al (Al_d) concentrations were determined according to the procedure of Kuo (1996). Particle size distribution was determined using the pipette method (Gee and Bauder 1986) (Supplementary Table S1). Soil pH varied from 4.7 to 8.4; EC varied from 0.03 to 0.31 mS m^{-1} , clay content varied from 28 to 77 g kg^{-1} soil, SOC varied from 7 to 146 g kg^{-1} soil, total soil N varied from 0.6 to 8.9 g kg^{-1} soil, total P ranged between 329 and 1430 mg kg^{-1} soil and organic P between 68 and 700 mg kg^{-1} soil. The Hedley sequential extraction procedure (Hedley et al 1982) was used to fractionate soil P into resin-extractable P, NaHCO_3 -extractable P_i and P_o , NaOH-extractable P_i and P_o , and HCl-extractable P_i and P_o (Supplementary Table S2a). Solution ^{31}P NMR spectra for inorganic P and organic P were obtained for the soil extracts (NaOH-EDTA extractant) using a Varian INOVA400 NMR spectrometer (Supplementary Table S2b).

For NaHCO_3 extraction (Colwell P), soil P concentrations were determined following extraction with 0.5 M NaHCO_3 at pH 8.5 for 16 h at a soil: solution ratio of 1:100 (Colwell, 1963) (hereafter referred to as Colwell P), and the extractions were repeated for nine

times (total extraction period of 144 h) to estimate the rate of P desorption. P in the extract was measured using the molybdate blue colorimetric method (Murphy & Riley 1962).

For ion exchange resin desorption of soil P, anion exchange membranes (551642S, VWR International Ltd., UK) and cation exchange membranes (551652U, VWR International Ltd., UK) were supplied in 12.5 cm $\times$ 12.5 cm, which were cut into 2 $\times$ 6 cm strips. The anion exchange membrane and cation exchange membrane strips were submerged in the 0.5 M KCl or 0.5 M NaHCO_3 solution for 24 h to saturate with counterions and then refreshed by washing anion exchange membrane and cation exchange membrane with deionized water for three times. The following anion exchange membrane and cation exchange membrane strips were prepared for soil P desorption: The anion exchange membrane in 0.5 M NaHCO_3 (HCO_3 -anion exchange membrane P), anion exchange membrane + cation exchange membrane in 0.5 M NaHCO_3 (NaHCO_3 -anion exchange membrane + cation exchange membrane P), anion exchange membrane in 0.5 M KCl (Cl^- -anion exchange membrane P), anion exchange membrane + cation exchange membrane in 0.5 M KCl (KCl-anion exchange membrane + cation exchange membrane P). Centrifuge tubes containing 0.4 g air-dry soil and 2 strips of the membranes in 40 mL of deionized water were placed in a horizontal shaker (25 °C) and extracted for 16 h to estimate the quantity of P extracted/desorbed, and then sequentially desorbed 16 h each for nine times with two replicates to estimate the rate of P desorption from soil. The anion exchange membrane-P and anion exchange membrane + cation exchange membrane-P were extracted following the procedure of Andersson et al. (2016) except that soil: extractant ratio was 1:100, similar to the Colwell P, rather than 1:80. After shaking, the strips were removed and rinsed in deionized water, with the soil retained and returned for the next extraction step. The strips were eluted in 50 mL centrifuge tubes with 20 mL 0.5 M HCl by shaking on the end-over-end shaker for 2 h at 25 °C. The eluate was stored at 4 °C prior to analysis. These procedures were continued for nine extractions (144 h of total extraction time), until the concentration of P extracted/desorbed did not change. The concentration of P in the eluates was measured using inductively coupled plasma

atomic emission spectroscopy (ICP-OES) (PerkinElmer Optima 8000).

A glasshouse experiment with Rhodes grass (*Chloris gayana*, cv. Reclaimer) was conducted using the eight land-use soil combinations and a randomised block design during April–July 2020. Rhodes grass was chosen because its known sensitivity to P in nutrient poor soils and its strong response to N and P fertilisation (Arshad et al. 2016).

The soil samples were air-dried, sieved through a 10 mm sieve, and mixed thoroughly with P fertilizer $\text{Ca}(\text{H}_2\text{PO}_4)_2$ at a rate of 291 mg P per 1.5 L pot (spraying evenly in the form of P aqueous solution), being equivalent to a rate of *ca.* 50 kg P ha^{-1} for a depth of 0–10 cm on 14 April 2020. Soils receiving no P fertilizer were used as controls. Each treatment was replicated four times, resulting in sixty-four pots in total, filled with 1 L soil in each pot (1.5L ANOVApot® pots; Garden City Plastics, Stapylton, Queensland, Australia). The pot height was 140 mm, and average diameter was 126.5 mm (116 mm bottom and 137 mm top) (Hunter and Scattini 2014). After filling the pot with the required amount of soil, basal macronutrients (491 mg N, 273 mg K, 158 mg S, 315 mg Ca, 179 mg Mg) and micronutrients (7.68 mg Cu, 7.45 mg Zn, 20.61 mg Mn, 0.72 mg Mo, 3.79 mg B) were applied to each pot (Xiong et al. 2018). The pots were randomly placed in a naturally lit glasshouse at 25°C and allowed to equilibrate for two weeks, with water content

maintained at field capacity using a capillary matting system. On 28 April, 2020 twenty seeds were evenly sown by covering 1–2 mm of soil. On 8 May 2020, the seedlings were thinned to ten per pot when they reached about 5 cm in height, and on 11 May 2020, seedlings were further thinned to five per pot when they grew to about 10 cm in height. Then the Rhodes grass was grown for another 30 days and harvested on 11 June 2020 (first harvest) by cutting at 10 cm above ground level. Two weeks after the first harvest, on 25 June 2020, the solution containing 205 mg N and 273 mg K was added to each pot. On 11 July 2020, the second harvest was taken. At each harvest, plant shoots were weighed (fresh mass) and dried at 60 °C for two days before being weighed again (dry mass). Additionally, at each harvest, a 30 g soil sample was collected from the surface layer (0–2 cm) of each pot for subsequent soil analyses. The tissues were then milled to <0.1 mm, digested in a 1: 5 mixture of nitric acid and perchloric acid, and analyzed for P using ICP-OES. Dry matter yield and P uptake by Rhodes grass were aggregated from two harvests. Relative yield response to applied P was calculated from the dry matter yield in P0 treatment divided by dry matter yield in P50 treatment. (Arshad et al. 2016). Evidence from Arshad et al. (2016) indicates that applying 50 kg P ha^{-1} effectively achieves a yield plateau for Rhodes grass, optimizing growth and production.

$$\text{Relative yield}(\%) = 100 \times (\text{dry matter yield}(\text{g kg}^{-1}) \text{ in P0 treatment} / \text{dry matter yield}(\text{g kg}^{-1}) \text{ in P50 treatment}) \quad (1)$$

Statistical analyses were conducted using SigmaPlot and IBM SPSS Statistics 26 (IBM Corp., Armonk, NY, USA) (Pallant 2020) and Microsoft Excel 2019 (Microsoft Corp., USA). Descriptive statistics were used to summarize soil P and plant response variables. Linear and quadratic regression analyses were applied to examine relationships between soil P availability (quantity and desorption rate) and plant responses (dry matter yield, P uptake, and relative yield). Model performance was evaluated using R^2 , adjusted R^2 , and p values. Stepwise multiple regression was used to identify the most important predictors of plant responses from P availability

indices, with entry and removal thresholds set at $p = 0.05$ and $p = 0.10$, respectively. For these models, R^2 , adjusted R^2 , t -values, p values, and variance inflation factors (VIF) were reported to assess model performance and multicollinearity. Normality of regression residuals was evaluated using the Omnibus and Jarque–Bera tests. All statistical tests were considered significant at $p < 0.05$. Graphs were generated in Excel and included fitted equations, adjusted R^2 values, and significance indicators where appropriate. Figures were generated in Excel based on both Excel and SPSS outputs, with significance letters indicating treatment differences where relevant.

Table 2 Quantity of soil P extracted for 16 h by sodium bicarbonate NaHCO₃ (Colwell P, bicarbonate saturated anion exchange membrane (HCO₃-AEM P), sodium bicarbonate saturated anion-cation exchange membrane (NaHCO₃-ACEMP), chloride saturated anion exchange membrane (Cl-AEM P), sodium chloride saturated anion-cation exchange membrane (KCl-ACEM P) from three soils under different land uses (quantity factor) (mean $\pm$ se)

Site/soil type	Land use	Colwell P mg P kg ⁻¹ soil	HCO ₃ -AEM P	NaHCO ₃ -ACEM P	Cl-AEM P	KCl-ACEM P
Lamington clay	LUD	49.1 $\pm$ 1.28	75.8 $\pm$ 1.56	85.5 $\pm$ 1.90	32.0 $\pm$ 0.16	68.5 $\pm$ 1.26
	LPS	29.3 $\pm$ 0.21	46.8 $\pm$ 0.15	54.3 $\pm$ 0.15	11.8 $\pm$ 0.22	39.8 $\pm$ 0.18
Warra clay	WUD	74.7 $\pm$ 0.43	62.1 $\pm$ 7.36	82.0 $\pm$ 0.99	51.6 $\pm$ 1.14	69.5 $\pm$ 2.00
	WCP	56.4 $\pm$ 0.21	37.9 $\pm$ 1.90	61.8 $\pm$ 2.41	32.6 $\pm$ 0.43	50.2 $\pm$ 5.45
Kingaroy clay loam	KUD	34.5 $\pm$ 0.21	28.1 $\pm$ 0.46	32.8 $\pm$ 1.68	5.19 $\pm$ 0.34	25.7 $\pm$ 2.03
	KCP	72.3 $\pm$ 0.21	33.1 $\pm$ 0.23	40.1 $\pm$ 1.34	14.5 $\pm$ 0.47	35.9 $\pm$ 0.07
	KPS	45.6 $\pm$ 0.42	27.7 $\pm$ 0.70	30.1 $\pm$ 0.44	5.68 $\pm$ 0.21	23.5 $\pm$ 0.38
	KPI	23.3 $\pm$ 0.42	18.4 $\pm$ 1.23	19.2 $\pm$ 0.08	2.54 $\pm$ 0.02	14.8 $\pm$ 0.02
Mean		48.2 $\pm$ 6.71	41.2 $\pm$ 6.83	50.7 $\pm$ 8.63	19.5 $\pm$ 6.17	41.0 $\pm$ 7.20

The soils and land uses are: LUD, Lamington clay native; LPS, Lamington clay pasture; WUD, Warra clay native; WCP, Warra clay cropped for 82 y; KUD, Kingaroy clay loam native; KCP, Kingaroy clay loam cropped for 62 y; KPS, Kingaroy clay loam pasture; KPI, Kingaroy clay loam plantation

Results

Quantity of P extracted/desorbed from soils under different land uses

Soil P extracted/desorbed by different extractants during the first 16 h are given in Table 2. Overall, the Cl-anion exchange membrane extracted/desorbed the lowest amount of soil P (19.5 $\pm$ 6.17 mg P kg⁻¹ soil) and NaHCO₃-anion + cation exchange membrane desorbed the highest amount of P (50.7 $\pm$ 8.63 mg P kg⁻¹ soil). However, there were large differences in soil under different land uses. For example, in Lamington clay under native vegetation, NaHCO₃ P was 49.1 $\pm$ 1.28 mg P kg⁻¹ soil, and NaHCO₃- anion + cation exchange membrane P was 85.5 $\pm$ 1.90 mg P kg⁻¹ soil, 74% higher in the latter than the routinely used NaHCO₃ extractant (Colwell P) to estimate plant available P (Olsen, 1954; Colwell, 1963). On the other hand, in Kingaroy clay loam cropped soil, Colwell P was 72.3 $\pm$ 0.21 mg P kg⁻¹ soil, and NaHCO₃- anion + cation exchange membrane P was only 40.1 $\pm$ 1.34 mg P kg⁻¹ soil, 45% lower than the Colwell P.

There were some consistent trends under different land uses among the different extractants/desorbents (Table 2). Lamington clay under native vegetation, had higher amounts of P than the pasture soil, while Kingaroy clay loam had similar amounts in both the soils either under native vegetation or pasture, among

all the extractants/desorbents except Colwell P, where the soil under native vegetation had lower amount of P than the pasture soil (Table 1). Similarly, in Lamington clay, the soil under native vegetation had 31% lower Colwell P than the pasture soil. Land use conversion from native vegetation to pasture resulted in the decrease of extracted/desorbed P by 37–42% in all extractants/desorbents except for the Cl-anion exchange membrane P, where it was 63% lower in the pasture soil. However, in the Warra clay, the decrease in extractable P from land conversion from native vegetation to cropping was small (24–39%). Notably, the Kingaroy clay loam under plantation had the lowest extractable/desorbed P among all the extractants/desorbents, and land uses.

Except for the Colwell P and Cl-anion exchange membrane P, there was a significant linear relationship ($p < 0.01$) between the soil P extracted/desorbed for 16 h by different extractants/desorbents and the ratio of SOC and SOP, SOC:SOP ratio (Fig. 1).

Desorption rate of soil P by different extractants/desorbents

Desorption rate of soil P extracted by NaHCO₃ during 144 h of the extraction period was the highest (0.58 $\pm$ 0.03 mg kg⁻¹ soil h⁻¹) among all the extractants/desorbents in the Lamington clay and Kingaroy clay loam, irrespective of the land uses (Supplementary

Fig. 1 Relationship between the ratio of soil organic C (SOC) and soil organic P (OP) and P extracted by sodium bicarbonate (Colwell P), bicarbonate saturated anion exchange membrane (HCO_3^- -AEM P), sodium bicarbonate saturated anion-cation exchange membrane (NaHCO_3 -ACEM P), chloride saturated anion exchange membrane (Cl-AEM P), sodium chloride saturated anion-cation exchange membrane (KCl-ACEM P) for 16 h. **, $p < 0.01$

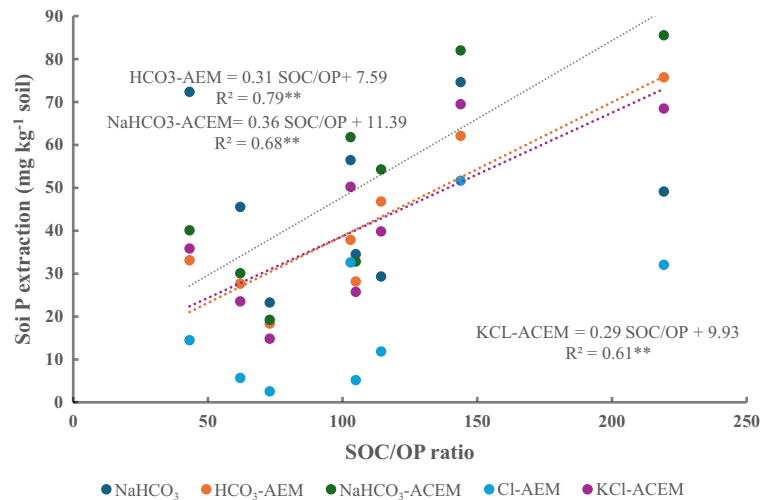


Table 3 Soil P desorption rate using sodium bicarbonate NaHCO_3 (Colwell P), bicarbonate saturated anion exchange membrane (HCO_3^- -AEM), sodium bicarbonate saturated anion-cation exchange membrane (NaHCO_3 -ACEM), chloride satu-

rated anion exchange membrane (Cl-AEM), sodium chloride saturated anion-cation exchange membrane (KCl-ACEM) extraction for up to 144 h from three soils under different land uses (mean $\pm$ se)

Site/soil type	Land use	Colwell P $\text{mg P kg}^{-1} \text{ soil h}^{-1}$	HCO_3^- -AEM P	NaHCO_3 -ACEM P	Cl-AEM P	KCl-ACEM P
Lamingtonclay	LUD	0.67 ± 0.01	0.53 ± 0.02	0.50 ± 0.02	0.29 ± 0.04	0.32 ± 0.03
	LPS	0.58 ± 0.01	0.39 ± 0.01	0.35 ± 0.01	0.19 ± 0.02	0.24 ± 0.03
Warracalay	WUD	0.56 ± 0.01	0.49 ± 0.03	0.54 ± 0.07	0.45 ± 0.07	0.54 ± 0.07
	WCP	0.48 ± 0.02	0.45 ± 0.02	0.54 ± 0.10	0.49 ± 0.08	0.59 ± 0.11
Kingaroyclay loam	KUD	0.58 ± 0.02	0.26 ± 0.01	0.30 ± 0.01	0.18 ± 0.01	0.23 ± 0.02
	KCP	0.66 ± 0.03	0.37 ± 0.02	0.46 ± 0.03	0.22 ± 0.02	0.26 ± 0.02
	KPS	0.64 ± 0.02	0.29 ± 0.01	0.36 ± 0.02	0.17 ± 0.01	0.22 ± 0.02
	KPI	0.45 ± 0.02	0.17 ± 0.01	0.19 ± 0.01	0.16 ± 0.01	0.17 ± 0.01
Mean		0.58 ± 0.03	0.37 ± 0.04	0.41 ± 0.04	0.27 ± 0.05	0.32 ± 0.06

The rate of P desorption was calculated from the linear relationship, $y = a + bt$, where y is the amount of P desorbed (mg P kg^{-1} soil) at the extraction time, t (h), b is the rate of desorption ($\text{mg P kg}^{-1} \text{ soil h}^{-1}$), and a is the regression coefficient. All R^2 values, regression coefficients and regression constants are significant at $P < 0.05$. The soils and land uses are: LUD, Lamington clay native; LPS, Lamington clay pasture; WUD, Warra clay native; WCP, Warra clay cropped for 82 y; KUD, Kingaroy clay loam native; KCP, Kingaroy clay loam cropped for 62 y; KPS, Kingaroy clay loam pasture; KPI, Kingaroy clay loam plantation

Fig. S1, Table 3). In fact, in the Kingaroy clay loam under plantation, the rate of soil P extracted by NaHCO_3 ($0.45 \pm 0.02 \text{ mg kg}^{-1} \text{ soil h}^{-1}$) was about 2.5-fold higher than the other extractants.

The effect of land use changes on P desorption rate was not consistent in all soils with different extractants/desorbents (Table 3). Conversion of Lamington clay from native vegetation to pasture decreased P desorption rate from 13.4% by NaHCO_3 to 34.4% by Cl^- -anion exchange membrane. However, the Warra

clay under native vegetation and cropping had similar desorption rates by NaHCO_3 -anion + cation exchange membrane, Cl^- -anion exchange membrane, and KCl-anion + cation exchange membrane desorbents.

Plant growth and P uptake response to native and added P to soil

Dry matter yield without P addition was the highest ($45.6 \pm 2.75 \text{ mg kg}^{-1} \text{ soil}$) in the Lamington clay

Table 4 Total plant dry matter yield, relative yield and P uptake from three soils under different land uses (mean $\pm$ se)

Soil	Land use	Dry matter yield (g kg ⁻¹)	Relative yield (%)	P uptake (mg P kg ⁻¹ soil)
Lamington clay	LUD	45.6 $\pm$ 2.75	82.2	43.4 $\pm$ 1.70
	LPS	23.5 $\pm$ 1.47	73.1	19.1 $\pm$ 0.47
Warra clay	WUD	27.8 $\pm$ 5.19	86.6	35.6 $\pm$ 3.97
	WCP	15.6 $\pm$ 0.83	92.4	18.3 $\pm$ 0.55
Kingaroy clay loam	KUD	18.5 $\pm$ 0.89	52.5	14.2 $\pm$ 0.53
	KCP	6.80 $\pm$ 0.63	76.5	6.93 $\pm$ 0.93
	KPS	13.7 $\pm$ 0.58	69.0	11.9 $\pm$ 0.35
	KPI	10.8 $\pm$ 0.44	39.3	8.32 $\pm$ 0.25

Grass dry matter yields and P uptake values are from the total of two harvests, and relative yield (%) was calculated from dry matter yields from nil P (P0) and 50 mg kg⁻¹ P (P50) application ((dry matter yield (g kg⁻¹ soil) at P0/dry matter yield (g kg⁻¹ soil at P50) $\times$ 100). The soils and land uses are: LUD, Lamington clay native; LPS, Lamington clay pasture; WUD, Warra clay native; WCP, Warra clay cropped for 82 y; KUD, Kingaroy clay loam native; KCP, Kingaroy clay loam cropped for 62 y; KPS, Kingaroy clay loam pasture; KPI, Kingaroy clay loam plantation

under native vegetation and the lowest in the Kingaroy clay loam under cropping (6.80 $\pm$ 0.63 mg kg⁻¹ soil) (Table 4). Land use changes from native vegetation to either pasture or cropping reduced dry matter yields, irrespective of soil type. The reduction in the dry matter yields varied from 63.2% in the Kingaroy clay loam under cropping, to 25.8% in the Kingaroy clay loam under pasture.

The yield response to applied P varied from 39% in the Kingaroy clay loam under plantation to 92% in the Warra loamy clay under cropping (Table 4). The lowest P uptake (6.93 $\pm$ 0.93 mg P kg⁻¹ soil) was from the Kingaroy clay loam under cropping and the highest P uptake (43.4 $\pm$ 1.70 mg P kg⁻¹ soil) from the Lamington clay under native vegetation. In fact, the dry matter yields and P uptake were closely correlated ($R^2 = 0.95$; $p < 0.001$).

Relationships between dry matter yield, yield response and P uptake, and quantity and rate of soil P desorption/extraction

Quantity of soil P

The quantity of P assessed using Hedley's sequential extraction of soil P (Supplementary Table S2a) and ¹³NMR determined organic P species (Supplementary Table S2b) were not significantly related to any of the plant parameters, except for the anion exchange membrane extractable inorganic P (resin P_i, Supplementary Table S2a), which were significantly related

to both dry matter yield and P uptake but not to the relative yield response to applied P a trend similar to HCO₃-AEM P, which is described below.

The relationships of quantity of soil P measured by different extractants/desorbents with the grass dry matter yield, relative yield response to applied P and P uptake are shown in Fig. 2, and the detailed statistical outputs are given in Table 5. The relationships of relative yield response (%) to applied P and the soil P quantity were quadratic and those of dry matter yield and P uptake were linear with the amount of P extracted/desorbed after 16 h. Colwell P was not significantly correlated with either dry matter yield or P uptake. Also, Colwell P was not significantly correlated with the relative yield response to applied P. Soil P desorbed by HCO₃-anion exchange membrane was significantly correlated with all three plant parameters (Fig. 2a, b, c); among them, P uptake was closely and linearly correlated with HCO₃-anion exchange membrane P (adjusted $R^2 = 0.90$; $p < 0.001$). The maximum yield was achieved at 56.9 mg kg⁻¹ soil of HCO₃⁻-anion exchange membrane P. Similar relationships were shown by NaHCO₃- anion + cation exchange membrane P (Fig. 2a, b, c); the maximum yield was achieved at 68.6 mg kg⁻¹ soil of NaHCO₃- anion + cation exchange membrane P. The dry matter yield was not significantly correlated with Cl-anion exchange membrane P (Fig. 2a) although the relative yield response to applied P and P uptake were significantly correlated (Fig. 2b,

Fig. 2 Relationship between (a) dry matter yield (g kg^{-1} soil), (b) P uptake (mg kg^{-1} soil), (c) relative yield (%) of Rhodes grass and the quantity of soil P extracted by sodium bicarbonate NaHCO_3 (Colwell P), and desorbed by bicarbonate saturated anion exchange membrane ($\text{HCO}_3\text{-AEM}$), sodium bicarbonate saturated anion-cation exchange membrane ($\text{NaHCO}_3\text{-ACEM}$), chloride saturated anion exchange membrane (Cl-AEM), and sodium chloride saturated anion-cation exchange membrane (KCl-ACEM) for 16 h. The data are shown and the curves drawn for only significant relationships between plant parameters and quantity of P desorbed by ion-exchange membranes. *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$

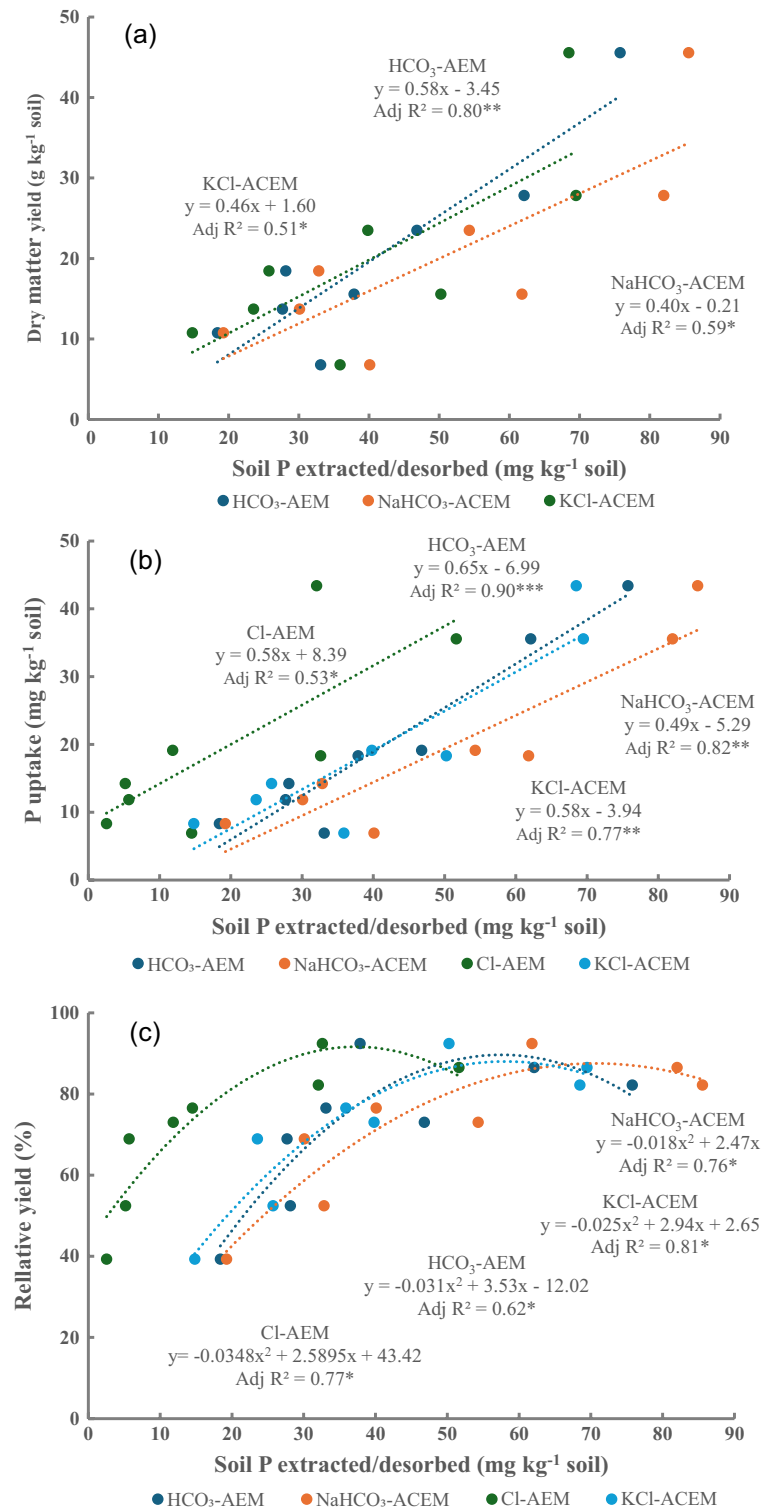


Table 5 Statistical parameters of the relationship between plant parameters and quantity of soil P extracted by Colwell P and desorbed by ion exchange membranes

Predictor	Intercept	Slope (a)	Slope (b)	R ²	Adjusted R ²	p value	F-statistic	Durbin–Watson	Omnibus P	Jarque–Bera P
Dry matter yield (g kg ⁻¹ soil) linear regression										
Colwell P	18.81	0.03		0.00	-0.16	0.91	0.01	0.81	0.08	0.47
HCO ₃ -AEM	-3.45	0.58		0.83	0.80	0.000 ***	28.58	2.43	0.72	0.75
NaHCO ₃ -AEM	-0.21	0.40		0.65	0.59	0.02 *	11.17	1.91	0.85	0.81
Cl-AEM	12.78	0.38		0.30	0.18	0.16	2.58	1.19	0.19	0.59
KCl-AEM	1.60	0.46		0.58	0.51	0.03 *	8.15	1.8	0.95	0.85
P uptake (mg kg ⁻¹ soil) linear regression										
Colwell P	9.94	0.20		0.09	-0.07	0.48	0.57	0.89	0.43	0.77
HCO ₃ -AEM	-6.99	0.65		0.91	0.90	0.000 ***	63.65	2.60	0.13	0.43
NaHCO ₃ -AEM	-5.29	0.49		0.85	0.82	0.000 ***	32.74	2.49	0.59	0.70
Cl-AEM	8.39	0.58		0.60	0.53	0.02 *	8.95	1.34	0.25	0.69
KCl-AEM	-3.94	0.58		0.81	0.77	0.000 ***	24.85	2.23	0.66	0.76
Relative yield (%) quadratic regression										
Colwell P	-150.20	-599.72	736.26	0.12	-0.06	0.68	0.18	2.14	0.57	0.73
HCO ₃ -AEM	-22.45	-400.58	416.78	0.91	0.79	0.07*	8.88	2.05	0.89	0.86
NaHCO ₃ -AEM	-6.78	-170.43	267.89	0.94	0.91	0.32	1.11	2.11	0.62	0.78
Cl-AEM	-20.12	-728.45	577.64	0.75	0.54	0.15	2.63	2.08	0.50	0.91
KCl-AEM	-32.16	-594.72	553.41	0.82	0.55	0.06*	4.69	2.09	0.95	0.85
HCO ₃ -AEM P, bicarbonate saturated anion exchange membrane; NaHCO ₃ -AEM P, sodium bicarbonate saturated anion-cation exchange membrane; Cl-AEM P, chloride saturated anion exchange membrane; KCl-AEM P, sodium chloride saturated anion-cation exchange membrane. *, $p < 0.05$; ***, $p < 0.001$										

c). The maximum yield was obtained at 37.0 mg kg^{-1} soil of Cl^- -anion exchange membrane P. There were significant correlations of the dry matter yield, yield response to applied P and P uptake with KCl -anion + cation exchange membrane P (Fig. 2a, b, c); the maximum yield was achieved at 58.8 mg kg^{-1} soil of KCl -anion + cation exchange membrane P. Thus, among all the quantity measures of soil P for the grass dry matter yield and P uptake, the HCO_3^- -anion exchange membrane P was the most closely correlated, and for the yield response to P, however, KCl -anion + cation exchange membrane P was highly significantly correlated (Fig. 2c, adjusted $R^2 = 0.81$, $p < 0.01$).

Rate of soil P desorption and plant parameters

The relationships of the plant parameters and P rate of soil P desorption estimated by different extractants/desorbents are shown in Fig. 3. The P desorption rate estimated from NaHCO_3 extractant (Colwell P rate of desorption) was not correlated with any of the plant parameters (Fig. 3a). However, HCO_3^- -anion exchange membrane P desorption rate was significantly correlated with the dry matter yield and P uptake and closely correlated with the relative yield response to applied P (Fig. 3a, b, c). Desorption rates of soil P measured from Cl^- -anion exchange membrane and KCl -anion + cation exchange membrane were significantly correlated with the relative yield response to applied P but poorly correlated with dry matter yield and P uptake (Fig. 3a, b, c).

Relative effect of quantity and rate of soil P availability to account for the variability in dry matter yield, yield response to applied P, and P uptake

The relative effect of the quantity and rate of P desorption for the dry matter yield, relative yield response to applied P and P uptake were evaluated using stepwise multiple regression analysis. The dry matter yield and P uptake were significantly correlated with the quantity of desorbed P measured by HCO_3^- -anion exchange membrane (Fig. 2a, b). The yield response to applied P was again significantly correlated with the rate of desorbed P by HCO_3^- -anion exchange membrane (adjusted $R^2 =$

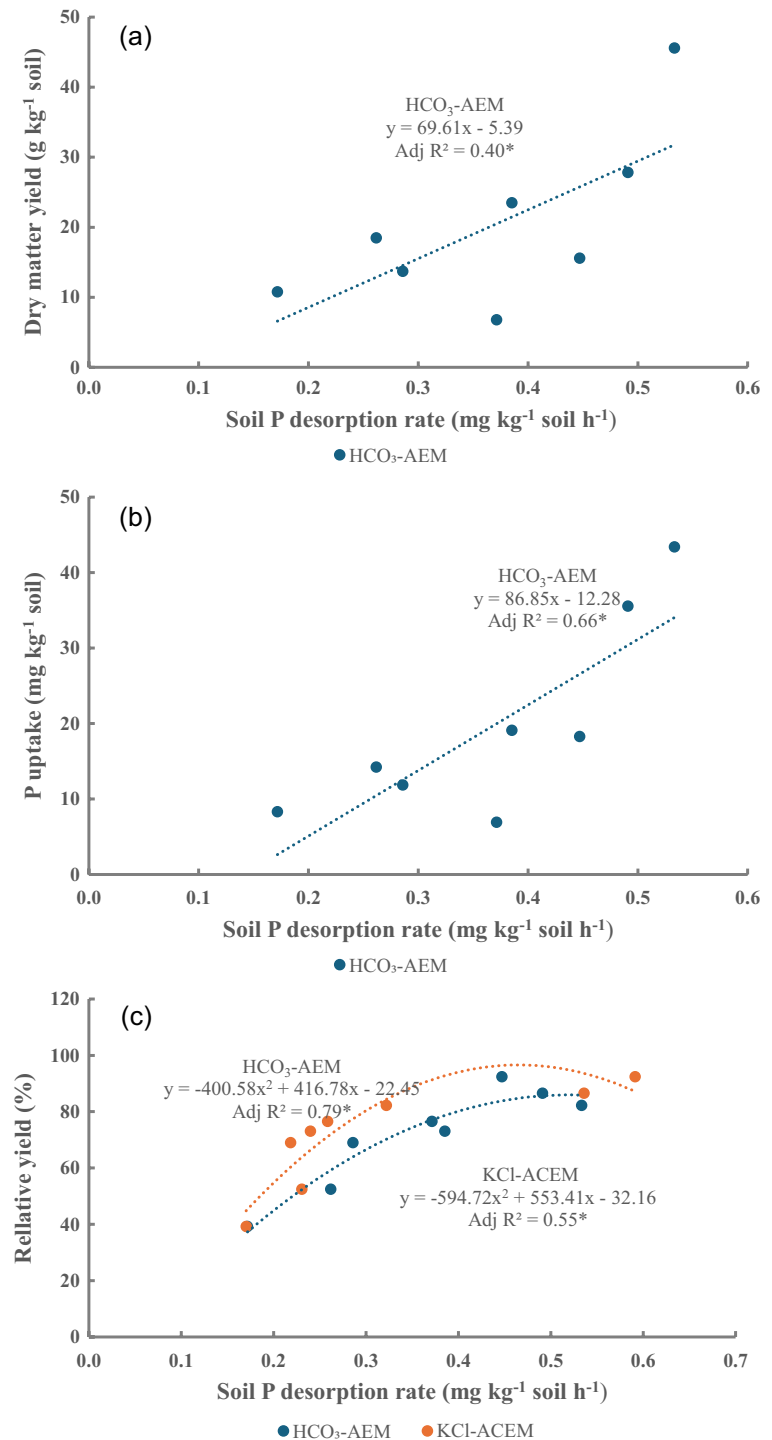
0.62; $p < 0.05$) (Fig. 3c). In the multiple stepwise regression using both P availability factors, no significant increase to the quantity of HCO_3^- -anion exchange membrane P occurred in accounting for the variability in the dry matter yield, yield response to applied P and P uptake by Rhodes grass in three soils under different land uses (Supplementary Table S4).

Among the soil properties examined, the quantity of HCO_3^- -anion exchange membrane P was positively and significantly correlated with the ratio of SOC:SOP ($R = 0.74$, $p < 0.05$) and EC ($R = 0.83$, $P < 0.01$) and negatively correlated with the crystalline Fe (Fe_d) ($R = -0.85$, $p < 0.01$) of the soils (Supplementary Table S5). However, the rate of P desorbed by NaHCO_3^- -anion + cation exchange membrane P was positively and significantly correlated with pH ($R = 0.76$, $p < 0.05$) but negatively and significantly correlated with the crystalline Fe (Fe_d) of the soils ($R = -0.78$, $p < 0.05$) (Supplementary Table S5).

Discussion

Land use changes from native vegetation to pasture and cropping significantly affects total P, inorganic P, organic P, and plant-available P, resulting in lower amounts of P in soil (Zhang et al. 2020, 2021). Land use conversion also affects other soil properties such as SOC, pH, and amorphous and crystalline Fe and Al (Dalal and Mayer 1986), all of which influence soil P availability from native, residual (legacy), and fertilizer P to plants. Therefore, routine soil P tests (Olsen, Colwell) to assess plant-available soil P may not be appropriate for all soil types and land uses. Moreover, an appropriate soil P test must implicitly measure P availability factors (quantity, and rate of desorption in different soil types and land uses) involved in P uptake by growing plants. In this study, we found that while routine soil tests (Olsen, Colwell) were inadequate to measure dry matter yield, yield response to applied P, and P uptake by plants, bicarbonate-saturated anion- as well as anion + cation exchange membranes (HCO_3^- -anion exchange membrane and NaHCO_3^- -anion + cation exchange membrane) were significantly better predictors (adjusted $R^2 \geq 0.80$; $p < 0.001$) (Fig. 4).

Fig. 3 Relationship between (a) dry matter yield (g kg^{-1} soil), (b) P uptake (mg kg^{-1} soil), and (c) relative yield (%) of Rhodes grass and rate of soil P desorbed by bicarbonate saturated anion exchange membrane ($\text{HCO}_3\text{-AEM}$), and sodium chloride saturated anion + cation exchange membrane (KCl-ACEM) for 16 h. The data are shown and curves are drawn for only significant relationships between plant parameters and rate P desorbed by ion-exchange membrans. *, $p < 0.05$



This confirms findings from previous studies (Fernandes and Coutinho 1997; Mallarino and Atia 2005; Menezes-Blackburn et al. 2018) and further

clarifies which P availability measures most strongly influence plant responses in different soils under varying land uses.

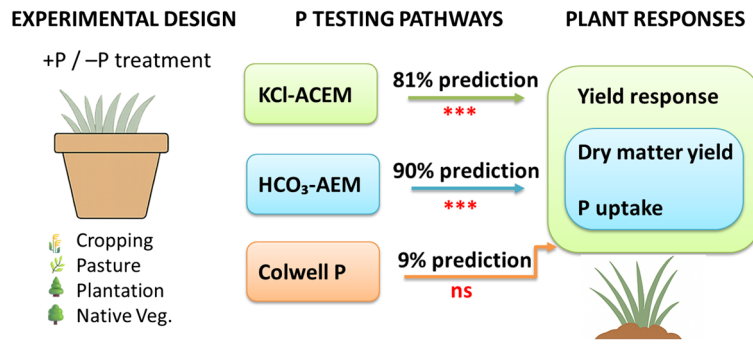


Fig. 4 Summary diagram of the experiment and key findings. Quantity of soil P extracted by sodium bicarbonate NaHCO_3 (Colwell P), soil P desorbed by bicarbonate saturated anion

exchange membrane ($\text{HCO}_3\text{-AEM}$), and potassium chloride saturated anion-cation exchange membrane (KCl-ACEM). ***, $p < 0.001$; ns, not significant

Effect of land use on plant available P assessed by ion exchange membranes

Conversion of native vegetation to agricultural land, such as pasture or cropping, typically results in reduced P availability due to the depletion of SOM and increased concentrations of Fe and Al oxides that strongly adsorb P (Zhang et al. 2020). This reduction in P availability was particularly evident when assessed using ion exchange membranes, such as $\text{HCO}_3\text{-anion}$ exchange membrane and $\text{NaHCO}_3\text{-anion} + \text{cation}$ exchange membrane, which provide a more dynamic measure of soil P compared to traditional extraction methods such as Colwell P. The findings of this study are consistent with previous research indicating that land use changes can significantly alter soil properties and consequently affects P dynamics (Hinsinger 2001; Zhang et al. 2021). The observed reduction in P availability under pasture and cropped soils compared to native vegetation underscores the critical role of organic matter in sustaining soil fertility. The correlation between the ratio of SOC and OP, and the amount of P extracted by ion exchange membranes highlights the importance of maintaining SOC to support P availability, particularly in systems where organic matter is a key contributor to P cycling (Bünemann 2015; George et al. 2018).

However, the interaction of ion exchange membranes with various P compounds, particularly organic and inorganic forms, can complicate the interpretation of results. While ion exchange membranes are effective in measuring readily exchangeable phosphate, their interaction with different P forms must be carefully managed to avoid overestimation of bioavailable P (Cooperband and Logan 1994; Nuernberg et al. 1998). However, the

soil P values obtained from ion exchange membranes in this study (range in mean values, from 19.50 ± 6.17 to 50.73 ± 8.63 , Table 3) are comparable to ion exchange membrane P measured using the molybdate blue colorimetric method (Murphy and Riley 1962) (reported in the Supplementary Table S2 as resin P_i , 33.04 ± 3.65) for the same soil samples (Zhang et al 2020). Thus, the ion exchange membrane P was the primarily sorbed inorganic P from the soil since the extract containing organic P was discarded and any adhering soil particles were removed by washing the ion exchange membranes with deionised water, before eluting the sorbed P for P analysis using ICP-OES. Moreover, the ion exchange membrane P can be confidently compared with the Colwell P using the molybdate blue colorimetric method (Murphy and Riley 1962), which also measures inorganic P in the NaHCO_3 extracts (Colwell P). Thus, ion exchange membranes remain valuable tools for capturing the ongoing processes of P desorption and replenishment, which are crucial for understanding P dynamics under different land uses.

Soil properties influencing plant available P

Soil properties such as pH, organic C content, and the concentration of Fe and Al oxides play crucial roles in determining the availability of P in soils (Ahmed et al. 2019; Fink et al. 2016; Penn and Camberato 2019). We found strong correlations between these soil properties and the quantity and rate factors of P availability, as measured by ion exchange membranes (Table S3). For instance, soil pH was positively correlated with increased P desorption rates, assessed by the $\text{NaHCO}_3\text{-anion} + \text{cation}$ exchange membrane method.

This observation aligns with established knowledge that higher pH levels enhance the solubility of P compounds, thereby increasing their availability for plant uptake (Penn and Camberato 2019; Sims and Pierzynski 2005). Conversely, in more acidic soils, P tends to be more tightly bound to Fe and Al oxides, reducing its availability to plants (Agbenin and Tiessen 1995; Hernon et al. 2019; Ismat et al. 2018; Santoro et al. 2024).

The observed negative correlation observed between P availability and crystalline Fe (Fe_d) concentrations supports this understanding (Yi et al. 2023; Zhang et al. 2021). Additionally, liming has been shown to enhance P availability by raising soil pH, thereby reducing the adsorption of P by Fe and Al oxides and increasing the proportion of P in more plant-available forms (Curtin and Syers 2001; Simonsson et al. 2018).

Moreover, the positive correlation between SOC:OP ratio and P desorbed by HCO_3^- -anion exchange membrane suggests that organic matter plays a pivotal role in maintaining a labile pool of P that is readily accessible to plants. This finding is consistent with previous research, indicating that maintaining or enhancing SOM through practices such as reduced tillage or the application of organic amendments could be vital strategies for sustaining P availability in agricultural soils (Crystal-Ornelas et al. 2021; Zhu et al. 2018). The influence of SOC on P availability through microbial activity and organic matter decomposition is supported by studies on land use changes and their impact on soil properties (Jindo et al. 2023). This is particularly important in sustainable agricultural systems, where preserving soil organic matter (SOM) is key to ensuring long-term fertility (Fageria 2012; Gamage et al. 2023; Krull et al. 2004). Given these complex interactions, it is crucial to evaluate and optimize P management strategies with a comprehensive understanding of soil pH, SOC content, and Fe and Al oxides. This study highlights the superior performance of HCO_3^- -anion exchange membrane and NaHCO_3^- -anion + cation exchange membrane over traditional chemical extraction methods in capturing the dynamics of P availability.

Relative performance of P quantity and rate of P availability in predicting dry matter yield, yield response to applied P, and P uptake

Building upon the observed influences of land use and soil properties, we next examined the predictive performance of specific quantity and rate of P

availability in relation to plant growth responses. The relative importance of quantity and rate of P availability varies depending on the specific plant response being measured. In this study, the quantity of desorbed P measured by HCO_3^- -anion exchange membrane, was found to be the most significant predictor of dry matter yield and P uptake (Table 5, Fig. 3a, b, c). This aligns with previous findings that available P quantity is a key determinant of plant growth, especially in low-P soils (Shen et al. 2011; Vance et al. 2003).

The superior performance of ion exchange membranes over traditional soil P tests like Colwell P and Olsen P lies in their ability to simulate both the quantity of extractable P and the dynamic replenishment of P in the soil solution, which is critical for plant uptake (Frossard et al. 2000; Nuernberg et al. 1998). By acting as ion sinks, ion exchange membranes mimic the continuous exchange processes between soil and roots, reflecting both quantity and rate measures. This allows for a more realistic assessment of soil P availability under variable soil conditions, including differences in pH, organic carbon, and Fe/Al oxide content (Cooperband and Logan 1994; Myers et al. 2005; Penn and Camberato 2019). These methods simulate the plant-root environment more accurately than chemical extractions and can better capture the effects of changing soil management or environmental conditions (Myers et al. 2005). Unlike the Olsen or Colwell method, which may be less effective in soils with high P sorption capacity (e.g., high Fe content), ion exchange membranes capture both weakly and tightly adsorbed P pools, providing a more integrated measure of soil P availability. This supports more accurate fertilizer recommendations and improves P use efficiency (Frossard et al. 2000; Nuernberg et al. 1998). For example, in alkaline Vertisols and acidic Ferralsols, where Ca-P and Fe/Al-P interactions dominate, ion exchange membranes were more effective in simulating rhizosphere conditions and predicting P release (Andersson et al. 2016; Sherrod et al. 2002). The variability in critical Olsen or Colwell P values across soil types, especially in acidic soils like Kingaroy clay loam underscores the limitations of traditional methods (Tandy et al. 2021). Furthermore, ion exchange membranes have shown similar effectiveness to isotopically exchangeable P in capturing soil P dynamics (Schneider and Morel 2000).

The rate of P desorption, measured by NaHCO_3^- -anion + cation exchange membrane, emerged as the best predictor of yield response to applied P. This

suggests that the soil's capacity to resupply P as it is taken up by plants is crucial for maintaining yields under P-limited conditions (Hinsinger 2001; Khan et al. 2023; Menzies et al. 2005). The relationship between desorption rate and plant growth is well established (Daly et al. 2001; Nuernberg et al. 1998; Yang et al. 2019; Yan et al. 2018), and our findings support this linkage. The effectiveness of traditional Olsen or Colwell NaHCO_3 extraction methods is also influenced by soil pH, texture, and Fe/Al oxide content, which may limit their ability to reflect dynamic P processes (Braun et al. 2019; Cooperband and Logan 1994; Tandy et al. 2021; Wuenscher et al. 2015). Colwell P, while measuring the quantity of available P, does not adequately account for P replenishment, leading to reduced accuracy under diverse soil and land use conditions (Tandy et al. 2021; van Doorn et al. 2024). In contrast, our study shows that ion exchange membranes, especially those saturated with bicarbonate, provide a more robust and integrated assessment of both quantity and rate of available P, thereby enhancing the precision of P diagnostics and informing better P management practices.

The stepwise multiple regression analysis demonstrated that the quantity of available P measured by HCO_3^- -anion exchange membrane and NaHCO_3 -anion + cation exchange membrane accounted for up to 90% of the variability in dry matter yield and P uptake (Figs. 2a, b, c; Table 5). The rate factor measured by KCl-anion + cation exchange membrane accounted for 81% variability in relative yield response to applied P. This emphasizes the importance of assessing not just the labile P pool but also the replenishment rate to improve P management. Given the finite nature of global P resources and the push for sustainable intensification of agriculture, approaches that reflect both aspects of P availability are critical (Scholz et al. 2013; Brownlie et al. 2022; Cordell and White 2013). Therefore, incorporating ion exchange membrane-based testing into routine soil fertility evaluations could help tailor site-specific fertilizer strategies, particularly in soils where the performance of traditional tests is limited.

Despite the strong predictive performance of ion exchange membrane-based methods observed in this study, several methodological limitations warrant consideration. First, ion exchange membranes may extract not only readily available phosphate ions but also a portion of weakly sorbed or slowly

desorbing P, particularly under favourable desorption conditions or extended extraction times. This can result in an overestimation of the plant-available pool, especially in soils with high P buffering capacity or strong mineral P binding (Sato and Comerford 2006; Li and Xu 2020). Second, ion exchange membrane performance is highly sensitive to experimental parameters such as membrane surface area, soil to solution contact conditions, and deployment configuration. Even minor differences in membrane handling can influence P desorption kinetics and compromise inter-laboratory comparability (Sato and Comerford 2006). Furthermore, the predictive capacity of ion exchange membranes is soil-dependent. Zehetner et al. (2018) reported strong correlations between ion exchange membrane extractable P and plant uptake in acidic soils but weak or non-significant relationships in calcareous soils, likely due to Ca–P precipitation and limited desorption, most likely due to low ion exchange capacity of the membranes used in the study. Lastly, potential co-adsorption of competing anions and re-adsorption artifacts, particularly when using hybrid or modified membranes may further complicate the interpretation (Li and Xu 2020). These caveats underscore the importance of site- and plant-specific calibration and caution when applying ion exchange membrane derived indices in routine fertility assessments, broad-scale agronomic recommendations, and monitoring of environmental P pollution.

Although DGT was not directly assessed in this study, its comparison with the ion exchange membrane methods is pertinent. DGT was initially shown to reflect P resupply dynamics and correlate well with plant uptake in highly fertilized soils (Menzies et al. 2005), but subsequent field studies have reported inconsistent performance. For example, in calcareous soils, Colwell P performed equally well in wheat crops (Spiers et al. 2013) or even better than DGT P in predicting pasture yield responses to fertiliser P applications (Burkitt et al. 2016). Moreover, the application of DGT is limited by several operational constraints, including single-use configuration, high cost, limited soil contact area, and biofilm interference (Marrugo-Madrid et al. 2021; Wagner et al. 2022; Mohammadi et al. 2022). In contrast, the ion exchange membranes approaches used in this study, especially the HCO_3^- -saturated anion exchange membranes and KCl-saturated anion + cation exchange membranes are reusable, cost effective, and

well suited for high throughput applications. Their ability to capture both the quantity and rate dimensions of P availability (Nuernberg et al. 1998; Cooperband and Logan 1994) makes them a more practical and scalable solution for routine soil fertility diagnostics and enhanced P use efficiency studies.

It is important to note that this study evaluated phosphorus availability using only the Colwell P and IEM-based methods. While these methods are commonly used, our findings should not be generalized to all routine P tests. Other chemical extractants, such as Olsen P or Mehlich 3, may yield different predictive relationships with plant responses. Future studies incorporating a broader range of extraction techniques would provide wider applications. In addition, this study was conducted using a single plant species (*Rhodes grass*). Plant responses to phosphorus are highly species-specific due to differences in root morphology, P demand, and uptake strategies. Therefore, caution should be taken when extrapolating these findings to other crop species.

Conclusion

We evaluated the soil P quantity and rate of soil P availability on the dry matter yield, relative yield response to 50 mg kg⁻¹ soil of P application, and P uptake by *Rhodes grass* grown for 70 days on three soils, which were under different land uses (native vegetation, pasture, crops, and plantation). We found that the widely used NaHCO₃ extractant (Olsen, Colwell tests) for soil P availability was poorly related to any of the measured plant parameters. However, the soil P extracted/desorbed by the anion and anion + cation exchange membranes, initially saturated by either HCO₃⁻, or KCl, were more successful than the Colwell P in accounting for the variability in the dry matter yield, yield response to applied P and P uptake. The quantity of available P measured by HCO₃-anion exchange membrane was the best predictors of dry matter and P uptake, and KCl-anion + cation membranes accounted for the highest variability in yield response of *Rhodes grass* to P application. These extractants/desorbents were also significantly correlated ($P < 0.01$) with the SOC:SOP ratio in these soils, and the rate factor was positively correlated with pH and negatively with crystalline Fe (Fe_d)

concentration in these soils. Given their strong predictive performance and responsiveness to soil properties, bicarbonate-saturated IEMs have high potential for integration into routine soil testing. Therefore, adoption of bicarbonate-saturated ion exchange membranes by soil testing laboratories and agricultural advisory services could improve P fertilizer recommendations, enhance P use efficiency, and support the development of sustainable P management practices. Moreover, HCO₃-anion exchange membrane technique will be useful in monitoring excess P applications, and thereby devising practices and policies to reduce environmental P pollution.

However, as this study focused only on the Colwell P and IEM-based methods and used a single plant species (*Rhodes grass*), the findings should be interpreted with caution. Future work incorporating a wider range of soil P tests and plant species would provide broader applications.

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Data availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Code availability Not applicable.

Declarations

Ethics approval The research did not involve human participation or animals.

Competing interests The authors have no relevant financial or non-financial interests to disclose.

Conflicts of interest The authors declare no conflicts of interest.

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