



## Mobility and lability of phosphorus from highly concentrated fertiliser bands

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### ABSTRACT

In order to improve crop nutrition, phosphorus (P) fertiliser is increasingly being applied in concentrated bands. Although information is available regarding the sequence of reactions that occur within the band itself, comparatively little is known regarding the reactions controlling P diffusion and availability further away from fertiliser bands. In particular, no previous experiments have utilised *in situ* methods to examine P speciation with increasing distance from the band. The present study used two contrasting soils in an incubation experiment to investigate the impact of soil characteristics, form of P fertiliser, and the co-application of potassium (K) on changes in P speciation and availability up to 40 mm away from the fertosphere (i.e., volume of soil which includes the fertiliser band and the fertiliser-enriched soil immediately adjacent band). Precipitation of aluminium-P (Al-P) minerals were important for regulating P availability within the fertosphere itself, with this precipitation of Al-P minerals largely driven by changes in fertosphere pH (soluble Al) and solution P. However, adsorption processes were important for controlling P diffusion from the band, primarily by decreasing concentration gradients between the fertosphere and bulk soil. The choice of P fertiliser form was more important in the soil with a low P sorption capacity, where the pH of the fertiliser saturation solution strongly influenced precipitation reactions and P availability. Co-application of K with P fertilisers had the greatest impact on P availability in the soil with a higher concentration of exchangeable cations – these cations could be displaced by the K and precipitate with P. This study therefore demonstrates that P distribution is influenced by soil characteristics, but that P availability is primarily impacted by fertiliser choice and the composition of the nutrient blend in the fertosphere – these findings have important implications for improving P use efficiency in cropping systems.

### 1. Introduction

Phosphorus (P) is an essential element in global food production due to its critical role in the photosynthetic process. Since soil supply of P to plants is often inadequate, the P demand of agricultural crops is frequently met through the addition of P fertilisers, with the latest estimates indicating an average application of 28 kg P ha<sup>-1</sup> of cropland, globally (FAO Statistics, 2021). However, the efficiency of in-season plant uptake of fertiliser P is very low (8–30 %; Blackwell et al., 2019,

Prasad et al., 2016). Crop P acquisition is particularly challenged in semi-arid agricultural systems where plants are reliant on water stored at depth for growth. In these systems, deep placement of P within the soil profile is necessary to avoid nutrient deficiencies and to overcome stratification of P in surface soil that can be dry for extended periods (Freiling et al., 2022, Singh et al., 2005). However, the cost, soil structural disruption, and water loss caused by deep P placement means that applications are made infrequently but at high rates to supply nutrients over multiple seasons. Consequently, practical deep P placement

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strategies result in fertiliser bands that are highly concentrated and characterised by increases in the local salt concentration and changes in pH that can collectively affect the dynamics of P in the fertiliser band and surrounding soil (i.e., fertosphere; [Ernani and Barber, 1991](#), [Meyer et al., 2021](#), [Werner and Strasser, 1993](#)). This modification of soil chemistry within the fertosphere of P fertiliser bands may create conditions that are hostile to plant roots ([Zhang and Rengel, 1999](#)), limiting plant access to P in the soil solution surrounding the fertiliser band ([Moody et al., 1995](#)). Accordingly, the modification of soil chemistry in response to fertiliser application, the speciation of P and the distribution of available P at increasing distance from the fertosphere of fertiliser bands are likely to be important factors influencing the efficacy of banded P fertilisation.

Diffusive transport of P from fertilisers in soil is dependent on several interdependent factors including, (i) the concentration gradient between the source (fertiliser) and the bulk soil; (ii) amount of labile P; (iii) P adsorption capacity of the soil; and (iv) the water content in the soil matrix ([Degryse and McLaughlin, 2014](#), [Eghball et al., 1990](#), [McBeath et al., 2012](#), [Olsen and Watanabe, 1963](#)). Consequently, soil physico-chemical properties which are linked to P availability and adsorption capacity are likely to have a substantial impact on the rate of P diffusion from concentrated bands. These include clay content, P buffering capacity, cation availability, pH, aluminium (Al) and iron (Fe) oxides, and calcium carbonate (CaCO<sub>3</sub>) content ([Daly et al., 2015](#), [Meyer et al., 2021](#), [Parfitt, 1979](#)). It is hypothesised that soils with lower P sorption capacities will enable greater diffusion of P from fertiliser bands (i.e., creating a greater volume of P enriched soil) due to reduced adsorption to the solid phase, whilst soils with lower cation (Al, Fe, calcium (Ca)) solution concentrations will enable greater P diffusion from the band due to decreased cation-P precipitation (Hypothesis 1).

Whilst soil properties are the dominant factor regulating P availability when the fertiliser is dispersed (mixed/incorporated) within the soil volume, the form of P fertiliser and its subsequent reactions in soil also become key aspects influencing P availability in and around fertiliser bands ([Degryse and McLaughlin, 2014](#), [Meyer et al., 2021](#)). There is a range of P fertilisers used in agricultural systems worldwide, although the most commonly used include those which are most effective at increasing the soluble orthophosphate concentration in soil solution *viz.* monocalcium phosphate (MCP), monoammonium phosphate (MAP), and diammonium phosphate (DAP) ([Sample et al., 1980](#)). The availability of P from fertilisers is largely dictated by the pH of the saturated fertiliser solution and subsequent interactions of P in the saturated solution with soil cations and solubilised organic matter ([Hedley and McLaughlin, 2005](#)). The saturated solutions of MCP (pH 1.0 – 1.5) and MAP (pH 3.5) are both highly acidic whereas that of DAP (pH 8.0) is alkaline ([Sample et al., 1980](#)). Acidic saturated P solutions, particularly that of MCP, may mobilise soil silicon (Si), Fe, Al, manganese (Mn), Ca, magnesium (Mg) and potassium (K) through partial dissolution of minerals, although concentrations and subsequent precipitation products will depend on the cation composition of the soil. Under the more alkaline conditions of saturated DAP solution, exchangeable cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup> can be displaced by NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>, increasing the likelihood of Ca- and Mg-phosphate formation ([Moody et al., 1995](#), [Sanyal and Datta, 1991](#)). Understanding the nature and distribution of precipitation products derived from saturated P fertiliser solutions is particularly important for banded P application where precipitation reactions dominate and P adsorption is not (initially) a significant factor influencing P availability ([Lombi et al., 2004](#)). However, since adsorption of P is highly important in regulating its availability and mobility in soils, determining how far the saturated solution disperses will enable identification of the zone where precipitation reactions begin to decrease, and adsorption becomes the dominant process controlling soil solution P concentrations. Low solution P concentrations would decrease the expected rate of P diffusion to soil further from the band. It is postulated that the zone of greatest P availability around bands will occur where (i) P that is in excess of the

precipitation capacity of the saturated solution (i.e., the amount of cations available to precipitate P within the fertosphere) can diffuse to, and the chemical conditions of soil enable dissolution of readily soluble precipitates; and (ii) P adsorption processes do not exceed the diffusive supply of P in solution (Hypothesis 2).

Finally, co-application of other nutrients with P fertilisers may influence P speciation dynamics and availability of P to plants. Of particular interest is the interactive effects of the macronutrient K, which is often applied as potassium chloride (KCl, muriate of potash) in blends with P fertilisers. Addition of KCl with P fertilisers has been shown to cause both increases and decreases in plant-available P, with three key reactions proposed: (i) direct precipitation of K-Al-P minerals ([Lindsay et al., 1962](#), [Taylor and Gurney, 1965](#)); (ii) indirect precipitation of P via displacement of exchangeable cations on clay minerals ([Akinremi and Cho, 1993](#), [Cho, 1991](#), [Kim et al., 1983](#)); or (iii) induced changes in soil solution electrical conductivity (EC), modifying P adsorption to soil minerals ([Ernani and Barber, 1991](#)). While recent research by [Meyer et al. \(2020; 2021\)](#) indicates that factors other than co-application of K to P fertiliser bands had greater impacts on P availability within the fertosphere, it is possible that the influence of this cation on soluble P concentrations becomes more important as the chemical environment changes with increasing distance from the fertosphere. It is hypothesised that co-application of KCl with P fertilisers may initially form more precipitates (either directly or indirectly via displacement of cations on the soil exchange) which will reduce solution P concentrations and the subsequent diffusion of P from the band. However, as pH changes are buffered and soluble P diffuses away from the saturated fertiliser solution over time, precipitates formed with K or other exchangeable cations may be readily dissolved back into solution (Hypothesis 3).

This study aims to test these three hypotheses by examining P speciation and availability dynamics within the fertosphere and up to 40 mm from the centre of the fertosphere during an incubation experiment. Synchrotron-based X-ray adsorption near edge structure (XANES) at the K-edge and thermodynamic modelling enabled *in situ* assessment of P forms, and both isotope exchange kinetics (IEK) and resin-extraction methods were used to assess the availability of P. Measurements were taken at increasing distances from the fertosphere of two P fertilisers (MAP and DAP), with and without co-applied K. These fertilisers have distinct differences in saturation solution chemistry and were deployed in soils with contrasting physico-chemical properties (Vertisol and Acrisol). Understanding of the impact of soil characteristics, P fertiliser selection, and co-application of K, on P availability within and surrounding fertiliser bands enables more efficient and sustainable P management within agricultural systems.

## 2. Materials and methods

### 2.1. Soils and nutrient application

Two soils were collected from the top 0–10 cm of the soil profile, being a Vertisol (Queensland, Australia) and a Acrisol (New South Wales, Australia) (classified according to the World Reference Base; [IUSS Working Group WRB 2015](#)). These soils are classified as a Vertisol and Kandosol in the Australian Soil Classification). These soils were selected on the basis of their contrasting physico-chemical properties ([Table 1](#)) and previously demonstrated differences in P dynamics and availability ([Meyer et al., 2020](#)). Briefly, the Vertisol has a higher pH, clay content, CEC, Al and Fe oxide content, P buffering index (PBI), total P, and measured Colwell-P (cf. the Acrisol).

Two P fertilisers were used, namely MAP (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and DAP ([NH<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub>). These two fertilisers were chosen because of their different solution pH and their global dominance as P fertilisers (in 2020, use of products [‘000 t] was DAP [35,557] > MAP [32,313] > triple superphosphate [4,840]; [International Fertilizer Association, 2022](#)). Since K is often applied with P fertilisers to avoid deficiencies of

**Table 1**  
Key soil properties prior to fertiliser addition.

	Unit	Vertisol	Acrisol
Sampling depth	m	0.1–0.3	0.0–0.1
pH in H <sub>2</sub> O <sub>(1:5)</sub> <sup>a</sup>		7.5	5.8
pH of soil solution <sup>b</sup>		6.5	5.5
EC in H <sub>2</sub> O <sub>(1:5)</sub> <sup>a</sup>	dS m <sup>-1</sup>	0.08	0.1
EC of soil solution <sup>b</sup>	dS m <sup>-1</sup>	0.70	1.80
Clay <sup>c</sup>	g kg <sup>-1</sup>	667	175
Al <sub>ox</sub> <sup>d</sup>	mg kg <sup>-1</sup>	1489	496
Fe <sub>ox</sub> <sup>d</sup>	mg kg <sup>-1</sup>	3212	913
Total P <sup>e</sup>	mg kg <sup>-1</sup>	549	200
Colwell-P	mg kg <sup>-1</sup>	37	15
Phosphorus buffering index	PBI	144	40
Exchangeable Ca <sup>f</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	22.1	2.9
Exchangeable K <sup>f</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	0.1	1.0
Exchangeable Mg <sup>f</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	10.2	0.5
Exchangeable Na <sup>f</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	0.4	0.0
eCEC <sup>f</sup>	cmol <sub>(+)</sub> kg <sup>-1</sup>	32.8	4.4
Field capacity water content <sup>g</sup>	g H <sub>2</sub> O kg <sup>-1</sup>	452	202
Organic C <sup>h</sup>	g kg <sup>-1</sup>	6.1	8.7

<sup>a</sup> In water extracts; <sup>b</sup> In soil solution extracted using hollow fibres; <sup>c</sup> Particle size analysis – hydrometer method; <sup>d</sup> Oxalate extraction; <sup>e</sup> Digestion with HNO<sub>3</sub>/HCl/HF acids in a microwave; <sup>f</sup> No pre-treatment; <sup>g</sup> 0.1 bar pressure plate; <sup>h</sup> Du-mas high-temperature combustion with chemical pre-treatment.

this macronutrient but frequently reports mixed outcomes on P availability (Ernani and Barber, 1991, Meyer et al. 2020), the effect of K co-application was also investigated through application of reagent grade KCl. All nutrient sources were ground to <250 µm prior to application to ensure homogeneity and to avoid confounding effects associated heterogeneous distribution of granules within the fertosphere.

Fertiliser treatments were made by mixing the ground P and K sources with air-dry soil (sieved to 2 mm) to create ‘fertosphere’ soil. The fertosphere soil represents the volume of fertiliser-enriched soil, viz. the fertiliser band and the surrounding soil volume which is directly altered by the fertiliser. Phosphorus treatments were applied at a rate equivalent to 40 kg P ha<sup>-1</sup> applied in bands that were 1 m apart, resulting in a fertosphere concentration of 8.2 g P kg<sup>-1</sup> soil (total application of 245 mg P in the Vertisol and 278 mg P in the Acrisol due to varying bulk densities; see Supplementary Material Part A and Meyer et al. 2020 for full calculations). The KCl was added at a rate equivalent to 100 kg K ha<sup>-1</sup> (total application of 612 mg K in the Vertisol and 694 mg K in the Acrisol), with the equivalent in-band concentration calculated as 20 g K kg<sup>-1</sup> soil. These in-band concentrations of P and K are representative of the higher end of fertiliser application rates for these nutrients for summer row cropping in the grains industry of northern Australia.

## 2.2. Experimental design and incubation

The effect of soil properties and P form was examined by using the two contrasting soils (Vertisol and Acrisol) and the two forms of P (MAP and DAP), resulting in four treatments. The effect of K co-application was also investigated by adding KCl to both P forms in both soils, resulting in a further four treatments, being a total of eight treatments. All treatments were replicated three times giving a total of twenty-four experimental units. Individual incubations were assembled by placing air-dry soil (sieved to 2 mm) into 100 × 100 mm square Petri dishes using a partition jig and retention plates to place unfertilised soil to either side of the fertosphere (Fig. S1, see Supplementary Material, Part A). The fertiliser treatments (i.e., fertosphere soil mixtures) were applied to a 20 mm wide central strip in the 100 mm wide incubation dish (i.e., fertosphere; Fig. S1). Following placement of the fertiliser treatment, the retention plates were removed, and the soil subsequently packed to a bulk density equivalent to that in the field for each soil (Vertisol = 1 g cm<sup>3</sup>; Acrisol = 1.13 g cm<sup>3</sup>). This was achieved by using a total mass of 150 g Vertisol and 170 g Acrisol packed to a height of ca. 15 mm within

the 100 × 100 mm Petri dishes. The Petri dishes had small holes pre-drilled at 10 mm spacing across the entire bottom surface to facilitate controlled and relatively even wetting up of soil on a vertical axis to minimise the effect of water movement on horizontal P distribution (i.e., from the band). Water was added to the assembled incubations by placing individual Petri dishes in shallow water baths containing the correct volume of ultra-pure water to adjust the total soil volume of each incubation to field capacity (0.45 g g<sup>-1</sup> for the Vertisol and 0.20 g g<sup>-1</sup> for the Acrisol). Once all the water had been taken up in soil via the holes, the bottom of the Petri dishes were re-sealed and lids placed on top. The dishes were incubated in the dark at 25 °C and 80 % relative humidity until destructive sampling after 7 and 120 d. Petri dishes were regularly opened to allow gas exchange and water content was maintained on a weekly basis.

## 2.3. Non-destructive soil solution analyses and thermodynamic modelling

Non-destructive soil solution samples were taken after 7 and 120 d using hollow-fibre samplers (Menzies and Guppy, 2000), inserted through the pre-drilled holes on the side of the Petri dishes during filling with air-dry soil. Soil solution (ca. 2.5 mL) was collected under vacuum through the inserted hollow-fibres by attaching an evacuated 10 mL disposable syringe for 8 h. Three soil solution samples were collected at varying distances from the fertosphere of each experimental unit (Petri dish), viz. the centre of the fertosphere (0 mm); 5 mm from the edge of the fertosphere (15 mm from centre); and 15 mm from the edge of the fertosphere (25 mm from the centre; Fig. S1). The soil solution samples were analysed for elemental concentrations of P, K, Al, Ca, and Mg using inductively coupled plasma optical emission spectroscopy (ICP-OES), ammonium-nitrogen (NH<sub>4</sub>-N) and nitrate-N (NO<sub>3</sub>-N) concentrations using a Seal QuAatro Auto Analyzer, and pH and EC. The saturation indices (SI) of each mineral species were calculated using PhreeqcI version 3.5.0–14000, a geochemical aquatic modelling program (Parkhurst, 2020). The default PHREEQC database was used with amendments to the equilibrium constants of the various mineral P species as outlined in Lindsay (1979) (see Table S1 of Supplementary Material).

## 2.4. Solid phase analyses

Soil was destructively harvested after 120 d for analysis of the solid phase at increasing distances from the centre of the fertosphere (0–10 mm): 0–5 mm from either side of the centre (central 10 mm portion of the fertosphere); 5–10 mm (the outer 5 mm portions of the fertosphere); 10–15 mm (the unfertilised soil immediately adjacent to the fertosphere); 15–20 mm (5–10 mm beyond the edge of the fertosphere); 20–30 mm (10–20 mm beyond the edge of the fertosphere); and > 30 mm (>20 mm beyond the edge of the fertosphere; Fig. S1). Soil samples were air-dried (40 °C) and analysed for total P and K concentrations following hydrofluoric acid (HF) digestion, potentially plant-available P by both isotopic dilution and resin-extractable P methods, and *in situ* P speciation using K-edge XANES spectroscopy.

The total P and K concentrations were determined by ICP-OES following digestion of 0.1 g oven-dried (60 °C overnight) soil (ground with a ball mill) using nitric acid (HNO<sub>3</sub>), HF, and boric acid (H<sub>3</sub>BO<sub>3</sub>) in a microwave. Briefly, 9 mL of concentrated HNO<sub>3</sub> was added to microwave digestion vessels containing one soil sample each, followed by 3 mL of HF. After pre-digestion for 10 min, an additional 2 mL of HF was added, and samples were digested at 200 °C for 20 min. After cooling, 22 mL of 5 % H<sub>3</sub>BO<sub>3</sub> solution was added to samples with another digestion stage of 160 °C for 10 min. Samples were rinsed into centrifuge tubes and made up to 40 mL using ultra-pure water. Aliquots of 10 mL were used for analysis on ICP-OES. This two-stage digestion process was necessary to ensure full recovery of P and K from precipitated minerals.

An IEK approach can be used to determine the specific activity (<sup>32</sup>P/<sup>31</sup>P) of soil exchangeable P (the E-value) which is generally considered to represent the specific activity in plant shoots, the L-value

(Frossard et al., 2011), and is therefore used as a method of determining plant-available P in soil. The isotopically exchangeable P within 24 h ( $E_{24h}$ ) was measured using a 1 g soil sub-sample collected at seven distances from the fertosphere (0–40 mm) following methods described by Fardeau et al. (1991) and with modifications as outlined by Lombi et al. (2004). The calculations for P recovery in the different pools are outlined in Supplementary Material Part A.

An alternative method for characterising plant-available P in soil is the use of an anion exchange resin, in which P is removed from solution and replaced with the anion already on the exchange resin (Amer et al., 1955). Since P uptake by plants is predominantly a one-way process of P removal from solution, the action of the resin exchange method may provide a P measurement that is more indicative of bioavailability than the phosphate-for-phosphate exchange of the IEK approach. The resin-extractable P concentrations were measured from air-dry soil as described by Hedley et al. (1982).

The analyses of *in situ* P speciation were conducted using K-edge XANES at Beamline 8 of the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand (Klysubun et al. 2020). At this beamline, the incident energy was selected using an InSb(1 1 1) double-crystal monochromator. The incident beam size was  $18 \times 2$  mm with a photon flux of  $2.19 \times 10^{11}$  photons  $s^{-1}$  ( $100 \text{ mA}^{-1}$ ). Spectra were recorded in fluorescence mode using a 13-element germanium (Ge) detector. After drying, the soil for this analysis was finely ground using an agate mortar

and pestle and placed onto polyimide tape. The samples were then placed in a sample compartment that had been purged with helium (He) to reduce X-ray absorption by the air. A total of 48 samples and 10 standards were examined using XANES across an energy range of 2050 to 2340 eV (see Supplementary Material Part A for further details). The standards were diluted to a P concentration of 1 % using boron nitride and included:  $\beta$ -tricalcium phosphate [ $\text{Ca}_3(\text{PO}_4)_2$ , TCP]; hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , HA]; iron(III) phosphate dehydrate [ $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , Fe-P]; mineral specimens taranakite, variscite, rock phosphate; K-taranakite [ $\text{H}_6(\text{K})_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$ ];  $\text{NH}_4$ -taranakite [ $\text{H}_6(\text{NH}_4)_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$ ]; and P adsorbed onto kaolinite and hematite (full details in Supplementary Material Part A). The data were processed in Athena v 0.9.26 (Ravel and Newville, 2005).

## 2.5. Statistics

Statistical analysis of solution chemical data (pH, EC, P concentration) was conducted by a four-way analysis of variance (ANOVA) with soil, time, treatment (P fertilisers, with or without K), and distance from fertosphere as factors. Values for pH were checked against the geometrical mean of  $\text{H}^+$  concentration to ensure correct interpretation (Boutlier and Shelton, 1980). Total recovery (proportion of applied) of resin-P and isotopically exchangeable P ( $E_{24h}$ ) was statistically analysed by two-way ANOVA with soil and treatment as factors. This analysis was

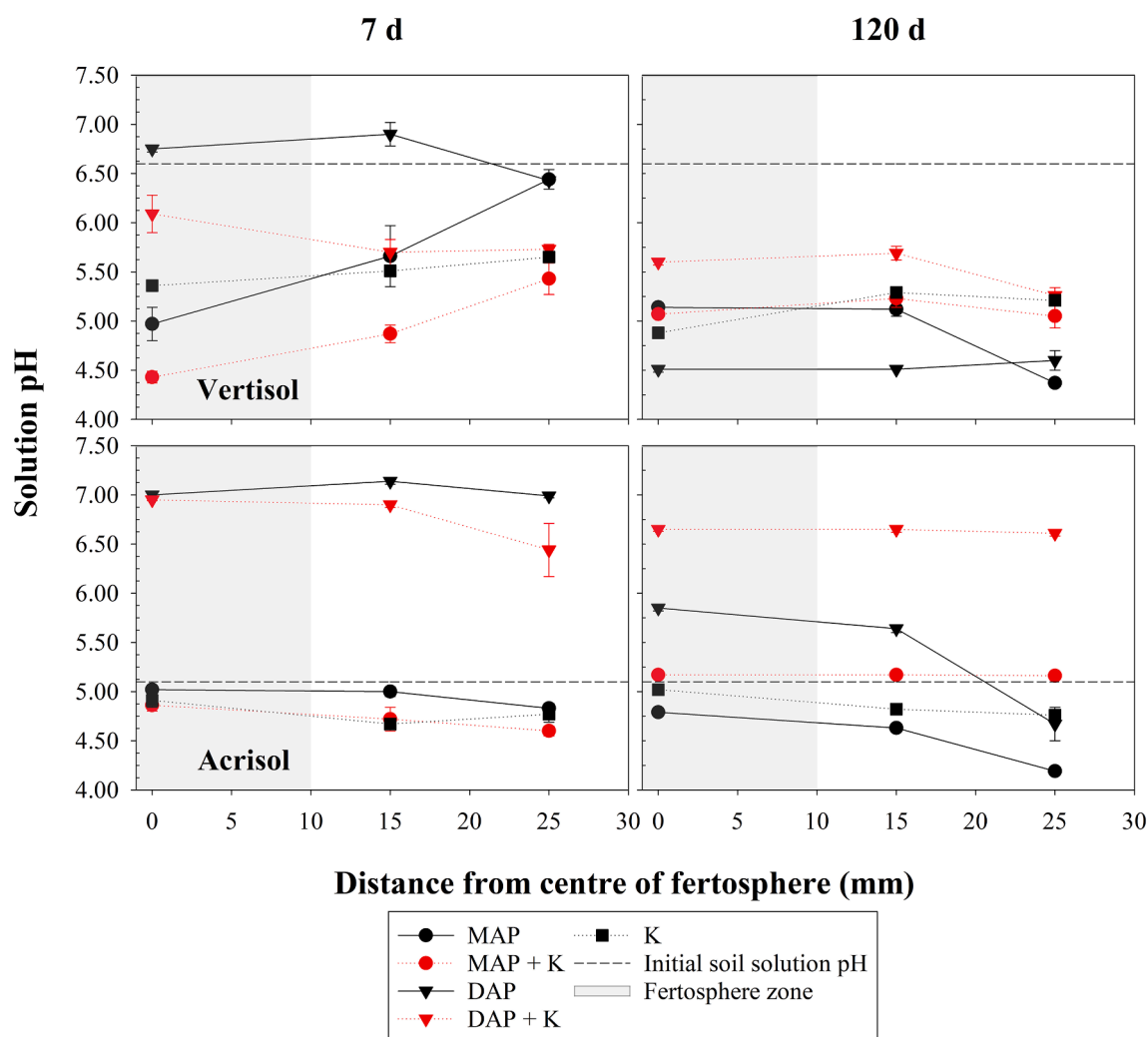


Fig. 1. Changes in soil solution pH for a Vertisol (top row) and Acrisol (bottom row) sampled at increasing distances from the centre of the fertosphere band at 7 and 120 days. The pH of the untreated soil solution is indicated by a dashed horizontal line for each soil. The position of the fertosphere band is indicated by the shaded central zone (0 to 10 mm). Error bars are the standard deviation of the mean ( $n = 3$ ).

extended to a three-way ANOVA to determine statistical differences in the distribution of resin-P and  $E_{(24h)}$  over distance from fertosphere. Tukey's honestly significant difference (HSD) test ( $P < 0.05$ ) was used to test means for significant interaction effects of all datasets tested by ANOVA.

Statistical differences in most datasets are not presented within the manuscript as the number of interactions makes graphical presentation difficult to interpret. Where appropriate, significant effects are noted in the text, with the full statistical results available in [Supplementary Material](#) (Part C).

### 3. Results

#### 3.1. Soil solution pH and EC

In both soils, the form of P fertiliser influenced the pH of the soil solution, although the magnitude of pH changes varied significantly between soils ([Fig. 1](#), [Fig. S2](#)). The pH of soil solution increased in both soils after 7 days (d) following the application of DAP, whereas the opposite was true for both soils treated with MAP where the pH decreased. For example, the pH within the DAP fertosphere and out to a distance of 15 mm increased by ca. 0.30 pH units (almost 50 % decrease in  $H^+$  concentration) in the Vertisol but by 2 units (99 % decrease in  $H^+$  concentration) in the Acrisol. In contrast, application of MAP decreased the pH in these zones by ca. 1.2 units (3800 % increase in  $H^+$  concentration) in the Vertisol but by only 0.10 units (18 % increase in  $H^+$  concentration) in the Acrisol ([Fig. 1](#)). The magnitude of change depended upon both the soil and fertiliser form, with MAP inducing greater changes in the Vertisol and DAP raising the pH to a greater extent in the more acidic Acrisol. Effectively, the largest effects on soil pH occurred where the expected pH of the fertiliser saturation solution contrasted strongly to the starting pH of the soil. In both soils, the addition of K, either alone or combined with P fertilisers, had an acidifying effect cf. the initial pH of soil solutions (ca. 1.0 pH units in Vertisol, 0.30 pH units in Acrisol) or the observed change in pH for the corresponding P fertiliser treatment (0.20–0.80 pH units for MAP, 0.30–0.90 pH units for

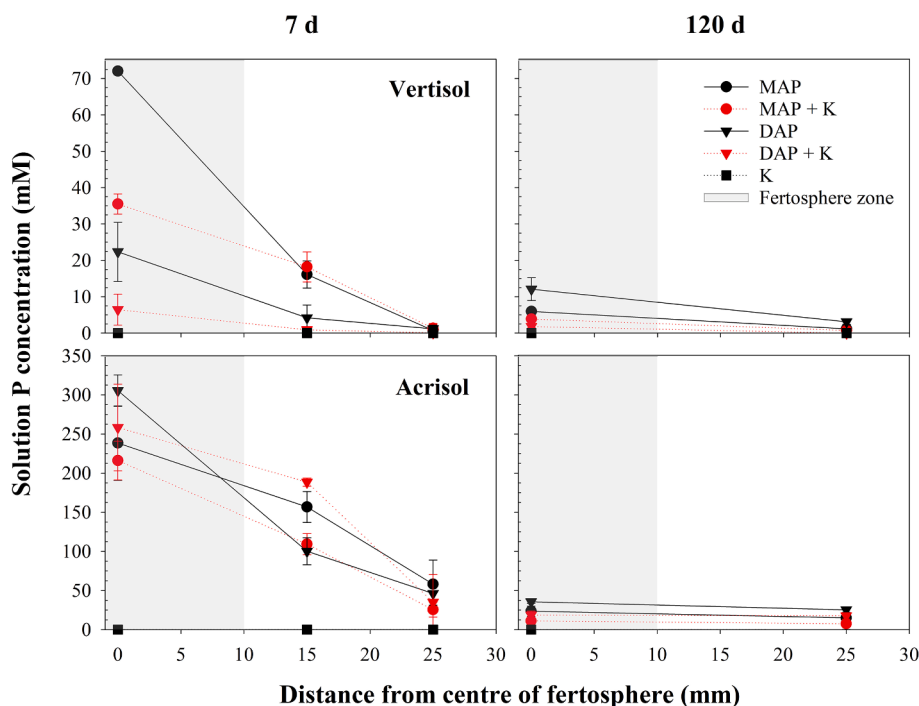
DAP, depending on soil type; [Fig. 1](#)).

Over time (i.e. after 120 d), the pH around the MAP and DAP bands decreased in both soils, although the magnitude of this change was much greater for DAP and occurred more rapidly in the Vertisol (measurements also taken at 30 d; data not shown). Notably, soil solution as far as 25 mm from the fertosphere was also acidified and this was particularly evident around MAP bands ([Fig. 1](#)). Whilst the pH of the K only treatment tended to remain relatively stable from 7 to 120 d in the Acrisol, some continued acidification was observed in the Vertisol over this period. The changes in solution pH of both P fertiliser + K treatments were also somewhat more subdued cf. P fertiliser only treatments in both soils over the 120-day incubation period.

The addition of P fertilisers significantly increased the EC in both soils (being substantially higher in the Acrisol), with the addition of K further increasing the magnitude of this effect. The EC was typically highest within the fertosphere, although EC values had decreased by 120 d. The EC was ca.  $15 \text{ dS m}^{-1}$  higher in DAP-treated soil (cf. MAP), although this trend was not evident until later in the incubation (120 d; see [Supplementary Material](#), [Fig. S3](#)).

#### 3.2. P concentration in soil solution

Application of P fertilisers significantly increased initial solution P concentrations within the fertosphere and up to 25 mm away ([Fig. 2](#)). Soil characteristics strongly influenced solution P, with concentrations significantly higher (both within the fertosphere itself as well as with increasing distance) in the Acrisol cf. Vertisol. For example, fertosphere P concentrations reached approximately 240 mM P (MAP) and 305 mM P (DAP) and were increased by ca. 50 mM P as far away from the fertosphere as 25 mm in the Acrisol at 7 d. In contrast, solution P concentrations within the fertosphere of MAP (72 mM P) and DAP (22 mM P) in the Vertisol were substantially lower, and diffusion of P from the fertosphere was also considerably reduced (ca. 1 mM P at 25 mm; [Fig. 2](#)). Thus, P source also had an impact on P diffusion from bands, with higher solution P concentrations generally observed at 15 mm from the fertosphere for MAP (cf. DAP) in both soils. The effect of K co-



**Fig. 2.** Changes in soil solution P concentration (mM) for a Vertisol (top row) and Acrisol (bottom row) sampled at increasing distances from the centre of the fertosphere band, at 7 and 120 days. Note the varying y-axis scales for the two soils. The position of the fertosphere band is indicated by the shaded central zone (0 to 10 mm). Error bars are the standard deviation of the mean ( $n = 3$ ).

application to P fertilisers on solution P was greater in the Vertisol, where initial fertosphere concentrations were significantly decreased by 51 % (MAP) and 71 % (DAP), cf. the Acrisol where the decrease was only 9 % (MAP) and 15 % (DAP) (Fig. 2). The addition of K to DAP in the Vertisol and MAP in the Acrisol reduced diffusion from the band, probably due to overall lower solution P concentrations. However, despite reduced solution P in the fertosphere, concentrations were higher further from the band for MAP + K in the Vertisol and DAP + K in the Acrisol (Fig. 2).

Over time, the solution P concentration decreased significantly in both soils treated with MAP and DAP. However, where solution P arising from MAP bands decreased by ca. 90 % by 120 d in both soils and by a similar amount for DAP in the Acrisol, the decrease was much less pronounced for DAP in the Vertisol. In this soil, 46 % of the solution P present in the fertosphere of DAP at 7 d remained in solution at the end of the incubation. The proportion of P no longer in solution at 120 d when K was co-applied was similar to that of the corresponding P fertiliser treatment without K, with the exception of DAP in the Vertisol, where co-application of K increased the magnitude of P removed from solution by 25 % (Fig. 2).

### 3.3. Mineral N in soil solution

The higher N content of DAP meant that mineral N concentrations were higher in both soils treated with DAP (cf. MAP; Figs. S8, S9). While the total production of  $\text{NO}_3\text{-N}$  was higher for DAP, especially in the Vertisol, the proportion of mineral N that was nitrified by 120 d was similar for both fertilisers in the Vertisol (ca. 95 %) and the Acrisol (ca. 51 %). The addition of K to P fertiliser treatments increased the amount of extractable  $\text{NH}_4\text{-N}$  in the early stages (i.e., at 7 d). However, subsequent nitrification appeared to be inhibited somewhat (i.e., at 120 d), with decreases of ca. 78 % (Vertisol) and 88 % (Acrisol) in total  $\text{NO}_3\text{-N}$  production cf. to that of P fertilisers without K. Data for mineral N dynamics is supplied in [Supplementary Material](#) (Part B).

### 3.4. Resin-extractable P

The distribution of resin-extractable P differed markedly between soil types after 120 d, with wider distribution (Fig. 3) but significantly lower recovery (ca. 26 %; Fig. S5) in the Acrisol compared to the Vertisol for both P fertilisers. In the Vertisol, resin-extractable P was highest in the 0–7.5 mm zone (i.e., within the fertosphere), with 62 % (MAP) and 56 % (DAP) of the total resin-extractable P found in this zone. Resin-P decreased significantly with distance from the fertosphere for both P fertilisers in the Vertisol. In contrast, the amount of resin-extractable P did not vary significantly across distance in the Acrisol, with only small decreases of ca. 1–2 % between the fertosphere and the outermost measured zone (Fig. 3). The co-application of K generally did not significantly impact the total recovery (Fig. S5) or distribution of resin-P (Fig. 3). The exception to this occurred when KCl was co-applied with DAP in the Vertisol, where resin P increased significantly by 56 % within the fertosphere of the DAP + K treatment whilst it decreased by an average 70 % in the zones outside the fertosphere (Fig. 3).

### 3.5. Isotopically exchangeable P

The proportion of potentially plant-available P ( $E_{(24h)}$ ) from applied P fertiliser was similar for MAP in both soils (ca. 35 %; Fig. 4). While  $E_{(24h)}$  from the DAP-treated Vertisol did not vary significantly from that of MAP, significant differences were observed in the Acrisol, where  $E_{(24h)}$  was significantly higher (9 %) for DAP cf. MAP. The co-application of KCl produced different responses in the two soil types, with small and non-significant increases in  $E_{(24h)}$  in the Acrisol. In contrast, co-application K produced decreases in  $E_{(24h)}$  from both P fertilisers in the Vertisol (Fig. 4). While the changes in  $E_{(24h)}$  for MAP + K in the Vertisol were not significant (-4%), co-application of KCl with DAP in the Vertisol resulted in much larger and significant decreases in  $E_{(24h)}$  (i.e., a 59 % reduction; Fig. 4).

The distribution of  $E_{(24h)}$  after 120 d decreased with distance from the fertosphere for all treatments, although higher  $E_{(24h)}$  in the fertosphere and lower values at 40 mm meant that the decrease was greater

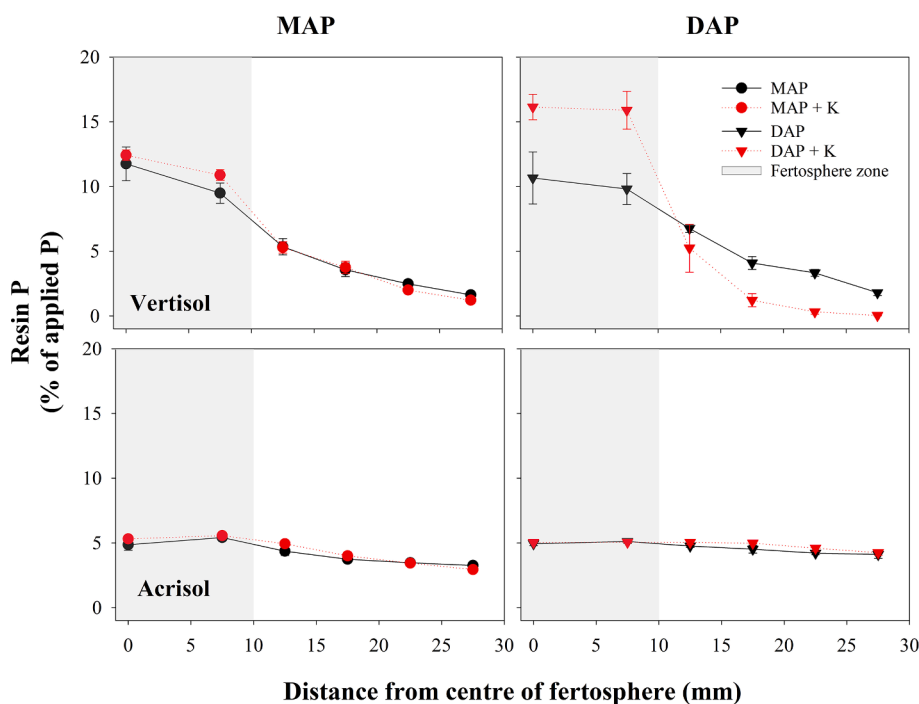
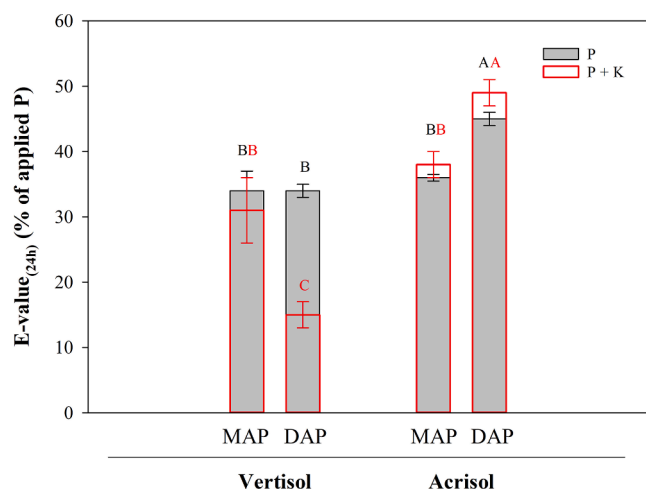


Fig. 3. Distribution of total resin-extractable P (% of applied fertiliser-P) from fertiliser bands of MAP and DAP, with and without co-application of KCl in the Vertisol and Acrisol at 120 days. The position of the fertosphere band is indicated by the shaded central zone (0 to 10 mm). Error bars are the standard deviation of the mean ( $n = 3$ ).



**Fig. 4.** Sum of the percent of applied P that is isotopically exchangeable P ( $E_{24h}$ ) within the fertosphere and in each sampled zone out to 40 mm in Vertisol and Acrisol treated with MAP, DAP, and co-application of KCl (K) with P fertilisers at 120 days. Error bars are the standard deviation of the mean ( $n = 3$ ). Capital letters indicate the statistically significant ( $P < 0.05$ ) variation in  $E_{24h}$  as determined by Tukey's HSD test.

in the Vertisol (Fig. 5). Higher  $E_{24h}$  values were observed further from the band for both P fertiliser treatments in the Acrisol, but this was especially obvious for DAP where the total recovery of fertiliser-P as  $E_{24h}$  in the 17.5–40 mm zone was 38 % higher than the equivalent zone in the Vertisol. A pronounced decrease in  $E_{24h}$  observed at 12.5 mm (i.e., just outside the fertosphere) for MAP in the Vertisol was not observed in other treatments (Fig. 5). In the Vertisol, co-application of KCl significantly lowered the availability of P at all distances from the fertosphere but had minimal impact on overall  $E_{24h}$  in and around banded MAP (Fig. 5). In the Acrisol, small but non-significant increases in  $E_{24h}$  were observed at most distances from P-bands when K was co-applied.

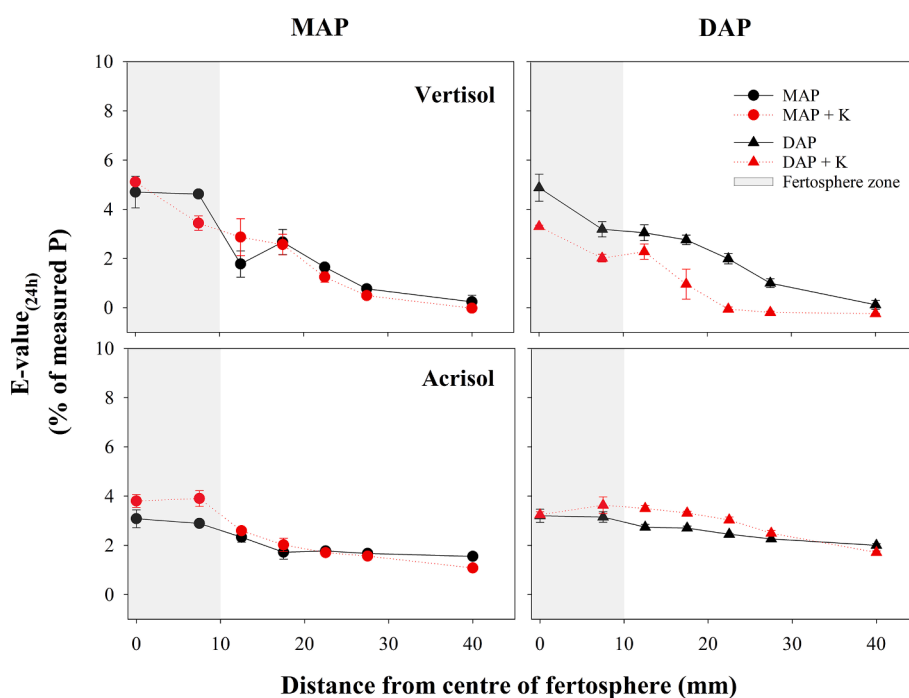
### 3.6. Thermodynamic modelling

We examined the SI values from thermodynamic modelling, with SI values of zero indicating saturation and values greater than zero indicating super-saturation. Formation of Al-P minerals (taranakites) was predicted to dominate in all treatments, both within the fertosphere and at 25 mm from the centre of the fertosphere in both soils (Fig. 6). Supersaturation of most P-minerals was observed in the Acrisol but was not as pronounced in the Vertisol. When K was co-applied, SI values for Ca-P minerals (e.g., hydroxyapatite) tended to increase and persist for longer cf. P fertilisers alone. Over time and with increasing distance from the fertosphere, supersaturation of P minerals decreased (Fig. 6). This effect was more evident over distance in the Vertisol (i.e., fertosphere cf. 25 mm from the fertosphere), and with time in the Acrisol (i.e., 7 d cf. 120 d).

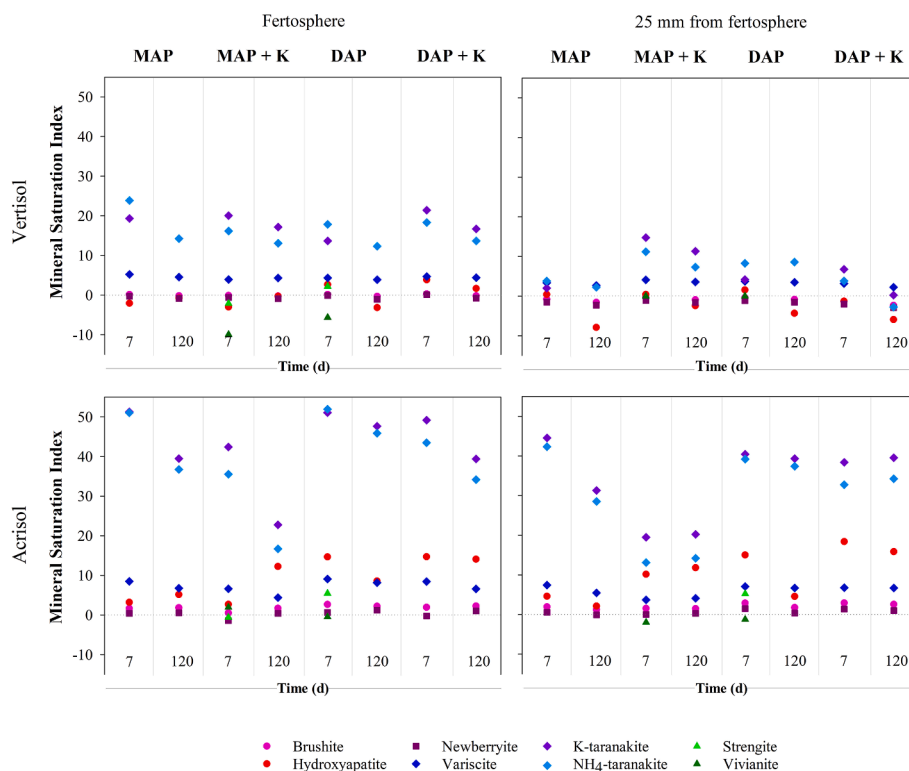
### 3.7. XANES analysis of P speciation

First, we examined the XANES spectra of the standard P compounds. Differences were observed for the P K-edge XANES spectra, depending on the form of P (Fig. S10 in Supplementary Material, Part B). The energy corresponding to the white line peak of Ca-P compounds (hydroxyapatite, dibasic Ca-P dihydrate) was ca. 2154.1 eV, whereas that of Al-P (K-taranakite, variscite) compounds was at 2154.7 eV, and Fe-P (strengite, P onto hematite) compounds was at 2154.6 eV. The intensity of the white line peaks also varied between P standards, with adsorbed forms of P demonstrating considerably higher white line peaks, even when the energy of the peak remained constant. Other notable spectral features included a pronounced pre-edge shoulder at ca. 2151.0 eV for Fe-P compounds, which was not present for Al or Ca-P compounds. Similarly, Ca-P compounds exhibited a distinct post-edge shoulder at ca. 2156.5 eV. Standards of Al-P and adsorbed phosphates did not demonstrate any pronounced distinguishing spectral features (Fig. S10).

Next, the soils to which the P fertilisers (in the absence of the co-application of K) had been added were examined. First, it was noted



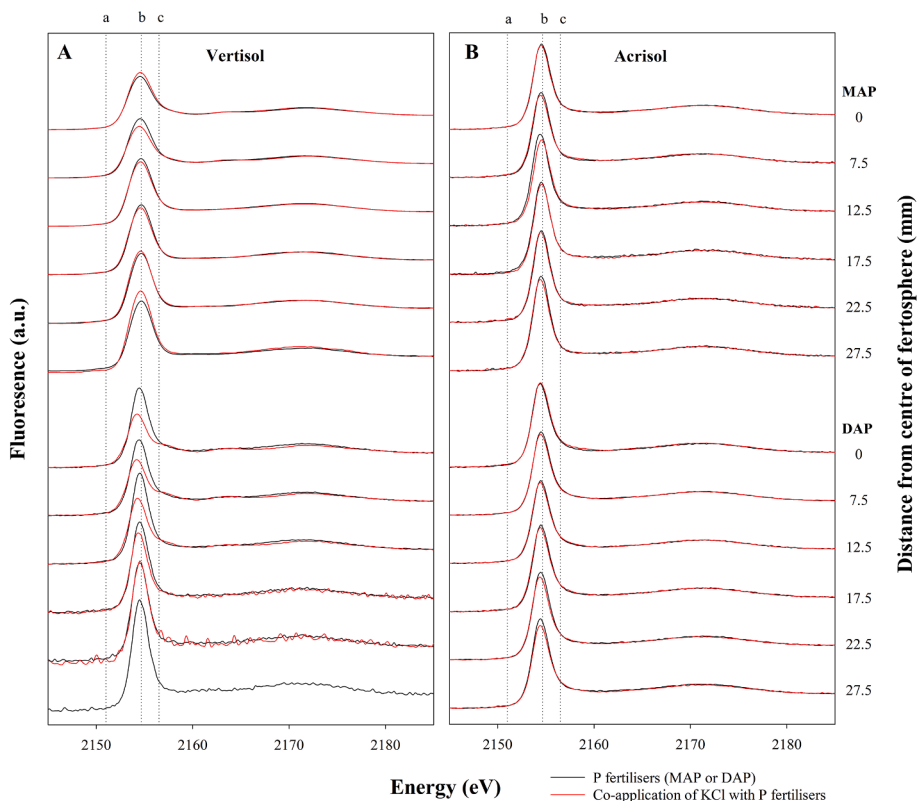
**Fig. 5.** Distribution of exchangeable P ( $E_{24h}$ ) as a percent of the P applied in fertiliser bands of MAP and DAP, with and without co-application of KCl in the Vertisol and Acrisol at 120 days. The position of the fertosphere band is indicated by the shaded central zone (0 to 10 mm). Error bars are the standard deviation of the mean ( $n = 3$ ).



**Fig. 6.** Modelled saturation indices of calcium, magnesium, aluminium, and iron -P species in the fertsphere (left plates) and at 25 mm (right plates) from P fertilisers in a Vertisol (top plates) and Acrisol (bottom plates) after 7 and 120 d. Fertiliser treatments include monoammonium phosphate (MAP) with KCl addition (MAP + K) and diammonium phosphate (DAP) with KCl addition (DAP + K).

that none of the spectra had a pre-edge shoulder at ca. 2151.0 eV which would have been indicative of Fe-P compounds, and hence Fe-P compounds were not likely of importance in any of these samples. Secondly,

we examined the energy corresponding to the white line peak, with both of the soils treated with P fertilisers having white line peaks in the range of ca. 2154.5–2154.6 eV regardless of whether the sample was from



**Fig. 7.** Stacked P K-edge XANES spectra of (A) Vertisol and (B) Acrisol, fertilised with either monoammonium phosphate (MAP) or diammonium phosphate (DAP), with and without co-application of KCl. Numbers on the right-hand side indicate the distance (mm) from centre of the fertiliser band. Dashed vertical lines indicate the average energy position of (a) the pre-edge shoulder for Fe-P compounds, (b) the white line peak of Al-P compounds, and (c) the post-edge shoulder for Ca-P compounds.



within the fertosphere or with increasing distance (Fig. 7). This indicates that it was not Ca-P compounds that dominated in any of these samples, but rather, Al-P compounds or adsorbed phosphates. We also examined the intensity of the white line peaks, with this found to increase with distance from the fertosphere in all treatments, although the overall range in intensity was greater in the P-treated Vertisol. These differences in the intensity of the white line peak indicate that the P within the fertosphere was likely dominated by Al-P compounds whilst adsorbed P became more important with increasing distance from the fertosphere.

We also examined soils where K was co-applied with the P. For these treatments, pronounced effects were observed within the fertosphere for the Vertisol receiving DAP but not for the other treatments (Fig. 7). For the DAP within the Vertisol, the energy corresponding to the white line peak shifted from 2154.6 eV for DAP alone to 2154.2 eV following application of K (DAP + K). Furthermore, a pronounced post-edge shoulder at ca. 2157 eV and an oxygen oscillation at 2164 eV was also evident and is consistent with the spectral features of Ca-P compounds (Fig. S10). Thus, for the DAP Vertisol treatment, co-application of K caused the pronounced formation of Ca-P compounds, especially within the fertosphere itself. In contrast, the co-application of K with MAP (both soils) and DAP in the Acrisol caused only small changes in white line peak intensity (Fig. 7). In general, the white line peak intensity decreased with increasing distance from the fertosphere of both P fertilisers in the Acrisol, while the reverse was true for MAP in the Vertisol. Co-application of K in these treatments did not indicate the formation of any Ca, Mg, or Fe-P minerals at any distance from the fertosphere.

## 4. Discussion

### 4.1. Soil characteristics impact P availability and distribution

#### 4.1.1. P availability within concentrated fertiliser bands is influenced by precipitation of Al-P minerals

Precipitation of Al-P minerals was found to be important within the fertosphere of all P treatments as demonstrated by soil solution saturation indices and XANES analyses (Figs. 6, 7), indicating that this is a key reaction controlling fertosphere P availability, even in soils and P-sources of contrasting physiochemistry. This supports earlier research by Meyer et al. (2021) where Al-P minerals were found to be the dominant factor controlling fertiliser-P transformations within concentrated bands across a wide range of soils and P-sources. In particular, taranakites are likely to be the main mineral formed during Al-P precipitation reactions (Fig. 6), with the prevalence of this mineral previously demonstrated in several other studies (Lindsay et al., 1962, Meyer et al., 2020, Taylor and Gurney, 1965). The dominance of Al-P precipitation in the fertosphere of P fertiliser bands highlights the importance of understanding factors which regulate this reaction. The influence of pH for regulating Al-P reactions in the fertosphere was recently demonstrated across a range of soils and P fertilisers (Meyer et al., 2021) and this study demonstrated the impact that solution P concentrations have on Al-P precipitation reactions. The predicted SIs for Al-P formation following P fertiliser application in the Vertisol were significantly lower (cf. the Acrisol; Fig. 6) despite larger decreases in pH. In the Vertisol, the high P sorption capacity of this soil (also confirmed by the resin and lability data; Figs. 3, 5) removed a substantial proportion of the fertiliser-P from solution (Fig. 2) which had the effect of decreasing Al-P precipitation reactions. Thus, although the solubility of Al-P minerals in soil solution is also dictated by pH and  $Al^{3+}$  concentrations, soil characteristics which influence solution P concentrations may have some impact on Al-P formation in the fertosphere.

Interestingly, despite the Vertisol having lower solution P concentrations (Fig. 2), P availability was significantly higher within the fertosphere of banded P fertilisers for the Vertisol than for the Acrisol (Figs. 3, 5). It is hypothesised that this effect was due to the greater amount of sorbed fertiliser-P in the Vertisol, which was potentially more readily available than the sparingly soluble P reaction products formed

during precipitation reactions. While some precipitates may re-dissolve back into solution as the chemical conditions of the saturated solution dissipate (i.e., changes in pH, increased P concentration, etc.), this takes some time (Penn and Camberato, 2019). Conversely, P that is only weakly sorbed to soil mineral surfaces may readily re-supply solution P, maintaining the equilibrium between solution and adsorbed or solid phase P pools (Moody and Bolland, 1999). Thus, in soils with a high sorption capacity, precipitation reactions may be less prevalent in the fertosphere and sorption to the soil solid phase may be a useful process to “protect”, then slowly “release” P back into solution.

#### 4.1.2. Adsorption regulates P diffusion outwards from fertiliser bands

The movement of P from the band into the surrounding soil was influenced by soil type (Fig. 2), and more specifically, soil characteristics which contribute to sorption capacity (i.e., clay content,  $Fe_{ox}$  and  $Al_{ox}$  content, and PBI). The impact of soil sorption on P distribution from fertiliser bands was twofold. Firstly, sorption that occurred within the fertosphere removed P from solution, lowering the concentration gradient to the bulk soil solution and reducing the net movement of P away from the fertosphere. This effect was clearly demonstrated in the soil with the higher sorption capacity (i.e., the Vertisol) whereby significantly more P was removed from solution, lowering the concentration gradient between the fertosphere and soil 25 mm away ( $\Delta$  20–70 mM P at 7 d) compared to that of the Acrisol ( $\Delta$  180–260 mM P at 7 d; Fig. 2). Secondly, as P moved outwards from the fertosphere to zones of soil solution with lower P concentrations, the likelihood of P precipitation decreased (Fig. 6) and interaction with unsaturated P sorption sites increased. This effect was also most evident in the Vertisol, with higher white line peak intensities further from the fertosphere (Fig. 7) suggesting that sorption became an increasingly dominant process regulating P availability at distance from the fertosphere in this soil. In contrast, the lower sorption capacity and sandier texture of the Acrisol created a less tortuous diffusion pathway (Olsen and Watanabe, 1963), permitting wider and more rapid distribution of the saturated fertiliser solution (Figs. 1, 2). However, while P diffusion occurred over a wider volume in this soil, precipitation likely continued to regulate P availability up to 25 mm from the fertosphere (Fig. 6), with only small differences in solution (Fig. 2, 120 d) and plant-available (Figs. 3, 5) P detected over these distances. These findings partially support Hypothesis 1 – the soil with the lower P sorption capacity (i.e., the Acrisol; Table 1) demonstrated greater diffusion of P, and this was largely due to reduced adsorption to the solid phase. However, in contradiction to the hypothesis, P precipitation was not reduced in the soil with a lower concentration of cations. Rather, because a greater proportion of applied P remained in solution, P was more vulnerable to this process, even up to 25 mm from the fertosphere. This suggests that the concentration of precipitating cations in soils may be less important for P availability around fertiliser bands, at least in soils with a moderate to high sorption capacity.

The impact of soil characteristics on P diffusion from the fertosphere may also influence P availability. The second hypothesis suggested that a zone of greatest P availability would occur outside of the immediate fertilizer band. However, the relatively linear decreases in P availability from the fertosphere to 40 mm in both soils (Figs. 3, 5) did not indicate the presence of the hypothesized transitional zone between the fertosphere and bulk soil. It's likely that dominance of either sorption or precipitation processes in the two examined soils did not permit development of this zone, and examination of soils with intermediate characteristics may reveal a zone of enhanced P availability outside the fertosphere.

Notably, the availability of P to plants is also regulated by the chemical conditions of the soil, in addition to P dynamics. For example, soils which retain much of the applied P within the fertosphere may limit plant access, whereby the modified pH, high salt concentrations and increased aqueous ammonia (due to co-applied N with MAP and DAP) can be toxic to plant roots (Moody et al., 1995, Zhang and Rengel, 1999).

It is therefore plausible that the proportion of applied P accessible to plant roots is greater in the Vertisol, where changes in soil chemistry were not as great as those in the Acrisol (Fig. 1, Fig. S3, S8, S9).

#### 4.2. Fertiliser type also influences P availability around bands in soils where precipitation reactions dominate

The general patterns of P distribution from the fertosphere were not impacted by P fertiliser form within each soil (Figs. 2, 3, 5), indicating that soil characteristics were the dominant factors dictating P transport from fertiliser bands. However, the overall availability of P differed between P fertilisers over time (Fig. 4, Fig. S5), although these differences were only significant in the Acrisol when assessed by IEK (Fig. 4). In the Acrisol, significantly higher solution P concentrations around DAP bands (cf. MAP; Fig. 2) were likely due to the increase in pH to ca. 7.0 after DAP application. At this neutral pH, the interactions between P and precipitating cations in solution would have been minimised, leaving more P in solution and consequently “available” (Penn and Camberato, 2019). As the pH remained elevated in the Acrisol, the availability of P from DAP bands also persisted for up to 120 d in this soil (Figs. 2-5). This contrasted to the decreasing pH around banded MAP (Fig. 1) which, in the already acidic Acrisol, accentuated conditions conducive to precipitation of Al- and Fe-P (Fig. 6). Interestingly, the modelled SI values suggest that precipitation of these cations with P was more likely in and around DAP (Fig. 6), which appears to be a result of higher P,  $\text{NH}_4^+$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  concentrations in solution (data not shown). It is not clear why Al and Fe concentrations in soil solution increased following DAP application. The introduction of greater amounts of  $\text{NH}_4^+$  with DAP (cf. MAP) may have resulted in other cations (including  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) being displaced from the exchange complex. However, as the pH remained neutral to alkaline around DAP bands, precipitation of P with these cations was minimal despite being present in high concentrations. This hypothesis requires further investigation.

In the Vertisol, the decrease in pH (Fig. 1) around MAP bands likely facilitated some dissolution of pre-existing Ca-P or primary P minerals, resulting in higher initial solution P concentrations (cf. DAP; Fig. 2). In contrast, the increased alkalinity from banded DAP meant that precipitation of Ca-P minerals was probable (Fig. 6) and the removal of P from solution was likely greater (cf. MAP). Over time, the soil pH within and around the fertosphere of both P fertilisers became more acidic, and this was especially obvious for DAP (Fig. 1), where a greater nitrification response (Figs. S8, S9) likely drove these changes. By 120 d, the concentration of P in solution (Fig. 2) was higher for DAP in the Vertisol, with some of this P possibly derived from dissolution of recently formed Ca-P minerals during the acidification process. Interestingly, the overall availability of P determined by IEK (i.e., the amount of  $\text{E}_{(24\text{h})}$  within 40 mm of the band; Fig. 4) was similar for both P fertilisers in this soil, indicating that the total labile pool of P did not differ significantly between P fertilisers, despite differences in solution P. It is suggested that desorption of P that was weakly sorbed to the solid phase within and surrounding MAP bands in the Vertisol meant that P availability was higher than indicated by solution P concentrations. Notably, the resin-exchange approach showed that the availability of P from DAP in the Vertisol was slightly higher (cf. MAP; Fig. S5), with this method likely capturing the differences in P immediately available in solution.

#### 4.3. Co-application of K causes variable effects on P availability

The application of KCl initially had an acidifying effect in the soil matrix (i.e., after 7 d, Fig. 1), with the observed pH decreases likely occurring via two main mechanisms, including: (i) hydrolysis of  $\text{Al}^{3+}$  coming off the soil exchange due to displacement by K ions (Wang et al., 2003), and (ii) proton production during precipitation of Ca and P (i.e.,  $\text{Ca}^{2+} + \text{H}_2\text{PO}_4 \leftrightarrow \text{CaHPO}_4 + \text{H}^+$ ), where  $\text{Ca}^{2+}$  in solution is increased due to displacement by K (Du et al., 2010). In the more acidic Acrisol, it's likely the displacement of acidic cations (i.e.,  $\text{Al}^{3+}$ ,  $\text{H}^+$ ) on the soil

exchange drove the observed pH decreases. In contrast, substantially higher exchangeable  $\text{Ca}^{2+}$  in the Vertisol (cf. Acrisol; Table 1) may have increased the likelihood of Ca-P precipitation, and thus the production of protons. This was especially likely with DAP application in the Vertisol, where the high pH of the DAP saturation solution, combined with displaced  $\text{Ca}^{2+}$ , created conditions favourable for Ca-P mineral formation (cf. DAP alone; Fig. 6). However, the largest effect of KCl was seen over time, where increased Cl concentrations had an inhibitory effect on nitrification (Megda et al., 2014; Fig. S8, S9). By inhibiting nitrification around the fertosphere of P fertiliser bands, a higher pH was maintained (Fig. 1), reducing the likelihood of Al-P and Fe-P precipitation (cf. respective P fertilisers alone; Fig. 6). In the acidic Acrisol, co-application of K therefore appeared to have a somewhat positive effect on P availability (Fig. 4) and only a small impact on distribution (Figs. 3, 5). However, in the Vertisol, displacement of a greater concentration of exchangeable cations meant that the likelihood of precipitation was increased (Fig. 6). In particular, the maintenance of a higher pH and considerable displacement of  $\text{Ca}^{2+}$  from the soil exchange around DAP + K bands meant that Ca-P minerals were likely to persist within the fertosphere and out to 12.5 mm for an extended period (Fig. 7). Thermodynamic modelling also indicated that co-application of K with DAP increased the likelihood of formation of Mg and K-Al-P minerals within the fertosphere (Fig. 6). Combined with significantly higher total P in the fertosphere zone of DAP + K treatments (cf. DAP alone; Fig. S4), these results suggest that the addition of K to DAP exacerbates both direct and indirect precipitation reactions in the fertosphere, consequently decreasing both the availability and the distribution of P in this soil (Figs. 3-5). Interestingly, resin-extraction did not demonstrate the same trend of reduced P recovery for DAP + K, with resin-P significantly higher within the fertosphere of the Vertisol (cf. DAP; Fig. 3). This observation suggests it may be possible for some of the newly formed P precipitates to re-dissolve back into solution under the depleting conditions of this method (i.e., removal of P from solution by the resin exchange) and is supported by spectral features which closely match that of more soluble Ca-P forms (i.e., monetite, Fig. S10; see also Lombi et al., 2006). In this case, P availability to plants may not be as impacted by K co-application as indicated by isotopic exchange measurements (Figs. 4, 5).

These findings partially support Hypothesis 3 in that co-application of KCl did increase the likelihood of P precipitation, and this occurred by both direct and indirect displacement of cations on the soil exchange.

## 5. Conclusions

Our findings demonstrate the importance of soil characteristics, the form of P fertiliser, and co-application of K, in regulating P distribution and availability from highly concentrated fertiliser bands. Specifically, significant modification of the fertosphere pH and solution P concentrations are the primary drivers of precipitation reactions, especially Al-P formation, which is the dominant process controlling P availability within the fertosphere. Soils with a high sorption capacity may modify these dynamics, potentially increasing the availability of P in the fertosphere by excluding P from precipitation reactions but decreasing the volume of soil enriched with P by reducing diffusion to the bulk soil. In soils where little P adsorption occurs, precipitation reactions are greater and more widely distributed. In these soils, the selection of P fertiliser type is more important as changes to the local pH in response to the fertiliser saturation solution exacerbate P precipitation, lowering availability. A slight trend for higher P availability following banded DAP application (cf. MAP) in both soils indicates that this fertiliser may be a broadly superior choice in cropping systems which utilise concentrated fertiliser bands. Co-application of K with P fertilisers modifies pH dynamics and displaces cations from the soil exchange. Both the concentration of precipitating cations and the interaction of the initial soil pH with that of the P fertiliser saturated solution determine the extent of precipitation reactions and, consequently, a net positive or negative

impact on P availability. Fertiliser choice and nutrient blend compositions are therefore more important in soils where precipitation reactions dominate and which have a high proportion of exchangeable cations which may precipitate with P under the modified pH conditions of the fertsphere. Collectively, these findings improve understanding of the impact of soil characteristics, P fertiliser selection, and co-application of K, on P dynamics within and surrounding fertiliser bands. This knowledge may underpin agronomic advice for more efficient and sustainable P management within agricultural systems.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2022.116248>.

### References

- Akinremi, O., Cho, C., 1993. Phosphorus diffusion retardation in a calcareous system by coapplication of potassium chloride. *Soil Sci. Soc. Am. J.* 57, 845–850. <https://doi.org/10.2136/sssaj1993.03615995005700030035x>.
- Amer, F., Bouldin, D.R., Black, C.A., Duke, F.R., 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P<sup>32</sup>-equilibration. *Plant Soil* 6, 391–408.
- Blackwell, M., Darch, T., Haslam, R., 2019. Phosphorus use efficiency and fertilizers: future opportunities for improvement. *Front. Agric. Sci. Eng.* 6, 332–340. <https://doi.org/10.15302/J-FASE-2019274>.
- Boutillier, R., Shelton, 1980. The statistical treatment of hydrogen ion concentration and pH. *J. Exp. Biol.* 84, 335–339.
- Cho, C., 1991. Phosphate transport in calcium-saturated systems: I. Theory. *Soil Sci. Soc. Am. J.* 55, 1275–1281. <https://doi.org/10.2136/sssaj1991.03615995005500050013x>.
- Daly, K., Styles, S., Lalor, D., Wall, D.P., 2015. Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties. *Eur. J. Soil Sci.* 66, 792–801. <https://doi.org/10.1111/ejss.12260>.
- Degrise, F., McLaughlin, M.J., 2014. Phosphorus diffusion from fertilizers: visualization, chemical measurements, and modeling. *Soil Sci. Soc. Am. J.* 78, 832–842. <https://doi.org/10.2136/sssaj2013.07.0293>.
- Du, Z., Zhou, J., Wang, H., Chen, X., Wang, Q., 2010. Soil pH changes from fertiliser site as affected by application of monocalcium phosphate and potassium chloride. *Commun. Soil Sci. Plant Anal.* 41, 1779–1788. <https://doi.org/10.1080/00103624.2010.492064>.
- Eghball, B., Sander, D.H., Skopp, J., 1990. Diffusion, adsorption, and predicted longevity of banded phosphorus fertilizer in three soils. *Soil Sci. Soc. Am. J.* 54, 1161–1165. <https://doi.org/10.2136/sssaj1990.03615995005400040041x>.
- Ernani, P.R., Barber, S.A., 1991. Predicted soil phosphorus uptake as affected by banding potassium chloride with phosphorus. *Soil Sci. Soc. Am. J.* 55, 534–538. <https://doi.org/10.2136/sssaj1991.03615995005500020041x>.
- FAO Statistics. 2021. *Fertilizer Indicators* [Online]. Food and Agriculture Organization of the United Nations. Available: <https://www.fao.org/faostat/en/#data/EF> [Accessed].
- Fardeau, J.C., Morel, C., Boniface, R., 1991. Cinétiques de transfert des ions phosphate du sol vers la solution du sol: paramètres caractéristiques. *Agronomie* 11, 787–797. <https://doi.org/10.1051/agro:19910909>.
- Freiling, M., Tucher, S.V., Schmidhalter, U., 2022. Factors influencing phosphorus placement and effects on yield and yield parameters: a meta-analysis. *Soil Tillage Res.* 216, 105257. <https://doi.org/10.1016/j.still.2021.105257>.
- Frossard, E., Achat, G. L., Bernasconi, S. M., Bunemann, E. K., Fardeau, J. C., Jansa, J., Morel, C., Rabeharisoa, L., Randriamanantsoa, L., Sinaj, S., Tamburini, F., Oberson, A., 2011. The user of tracers to investigate phosphate cycling in soil-plant systems. In: BUNEMANN, E., OBERSON, A. & FROSSARD, E. (eds.) *Phosphorus in Action: Biological Processes in Soil Phosphorus Cycling*. Heidelberg, Germany: Springer Berlin Heidelberg.
- Hedley, M., McLaughlin, M. 2005. Reactions of phosphate fertilizers and by-products in soils. In: SIMS, T. & SHARPLEY, A. N. (eds.) *Phosphorus: Agriculture and the Environment*. Madison, WI: American Society of Agronomy, Crop Science Society of America, Soil Science Society of America.
- Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46, 970–976. <https://doi.org/10.2136/sssaj1982.03615995004600050017x>.
- International Fertilizer Association, 2022. Supply Reports: Phosphate Products. Available: <https://www.ifastat.org/supply/Phosphate%20Products/Processed%20Phosphates>.
- IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014. World Soil Resources Reports No. 106. Food and Agriculture Organization of the United Nations. Available: <https://www.fao.org/3/i3794en/i3794en.pdf>.
- Kim, Y.K., Gurney, E.L., Hatfield, J.D., 1983. Fixation kinetics in potassium-aluminum-orthophosphate systems. *Soil Sci. Soc. Am. J.* 47, 448–454. <https://doi.org/10.2136/sssaj1983.03615995004700030011x>.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. John Wiley & Sons, Chichester, UK.
- Lindsay, W.L., Frazier, A.W., Stephenson, H.F., 1962. Identification of reaction products from phosphate fertilizers in soils. *Soil Sci. Soc. Am. J.* 26, 446–452. <https://doi.org/10.2136/sssaj1962.03615995002600050013x>.
- Lombi, E., McLaughlin, M.J., Johnston, C., Armstrong, R.D., Holloway, R.E., 2004. Mobility, solubility and lability of fluid and granular forms of P fertiliser in calcareous and non-calcareous soils under laboratory conditions. *Plant Soil* 269, 25–34. <https://doi.org/10.1007/s11104-004-0558-z>.
- Lombi, E., Scheckel, K.G., Armstrong, R.D., Forrester, S., Cutler, J.N., Paterson, D., 2006. Speciation and distribution of phosphorus in a fertilized soil: a synchrotron-based investigation. *Soil Sci. Soc. Am. J.* 70, 2038–2048. <https://doi.org/10.2136/sssaj2006.0051>.
- Mcbeath, T.M., McLaughlin, M.J., Kirkby, J.K., Armstrong, R.D., 2012. Dry soil reduces fertilizer phosphorus and zinc diffusion but not bioavailability. *Soil Sci. Soc. Am. J.* 76, 1301–1310. <https://doi.org/10.2136/sssaj2011.0431>.
- Megda, M.X.V., Mariano, E., Leite, J.M., Megda, M.M., Trivelin, P.C.O., 2014. Chloride ion as nitrification inhibitor and its biocidal potential in soils. *Soil Biol. Biochem.* 72, 84–87. <https://doi.org/10.1016/j.soilbio.2014.01.030>.
- Menzies, N., Guppy, G., 2000. In-situ soil solution extraction with polyacrylonitrile hollow-fibers. *Commun. Soil Sci. Plant Anal.* 31, 1875–1886. <https://doi.org/10.1080/00103620009370544>.
- Meyer, G., Bell, M.J., Doolette, C.L., Brunetti, G., Zhang, Y., Lombi, E., Kopittke, P.M., 2020. Plant-available phosphorus in highly concentrated fertilizer bands: effects of soil type, phosphorus form, and coapplied potassium. *J. Agric. Food. Chem.* 68, 7571–7580. <https://doi.org/10.1021/acs.jafc.0c01287>.
- Meyer, G., Bell, M.J., Lombi, E., Doolette, C.L., Brunetti, G., Novotny, E.H., Klysubun, W., Zhang, Y., Kopittke, P.M., 2021. Phosphorus speciation in the fertsphere of highly concentrated fertilizer bands. *Geoderma* 403, 115208.
- Moody, P. W. Bolland, M. D. A. 1999. Phosphorus. In: PEVERILL, K. I., SPARROW, L. A. & REUTER, D. J. (eds.) *Soil analysis: An interpretation manual*. Collingwood, Australia: CSIRO Publishing.
- Moody, P.W., Edwards, D.G., Bell, L.C., 1995. Effect of banded fertilizers on soil solution composition and short-term root growth. II. Mono- and Di-ammonium phosphates. *Aust. J. Soil Res.* 33, 689–707. <https://doi.org/10.1071/SR9950689>.
- Olsen, S.R., Watanabe, F.S., 1963. Diffusion of phosphorus as related to soil texture and plant uptake. *Soil Sci. Soc. Am. J.* 27, 648–653. <https://doi.org/10.2136/sssaj1963.03615995002700060024x>.
- Parfitt, R.L., 1979. Anion adsorption by soils and soil materials. *Adv. Agron.* 30, 1–50.
- Parkhurst, D. 2020. Phreeqc 3.5.0. ed.: United States Geological Survey.
- Penn, C., Camberato, J., 2019. A critical review on soil chemical processes that control how soil pH affects phosphorus availability to plants. *Agriculture* 9 (6), 120.
- Prasad, R., Shivay, Y. S., Majumdar, K., Prasad, S. 2016. Chapter 5: Phosphorus Management. In: LAL, R. & STEWART, B. A. (eds.) *Soil Phosphorus*. 1 ed.: Taylor & Francis Group.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFFFIT. *J. Synchrotron Radiat.* 12, 537–541. <https://doi.org/10.1107/S0909049505012719>.
- Sample, E.C., Soper, R.J., Racz, G.J. 1980. Reactions of phosphate fertilizers in soils. In: KHASAWNEH, F. E., SAMPLE, E. C. & KAMPFRATH, E. J. (eds.) *The role of Phosphorus in agriculture*. Madison, WI, USA: American Society of Agronomy, Inc.; Crop Science Society of America, Inc.; Soil Science Society of America, Inc.
- Sanyal, S. K. Datta, S.K.D. 1991. Chemistry of Phosphorus Transformations in Soil. In: STEWART, B. A. (ed.) *Advances in Soil Science*. New York: Springer-Verlag New York Inc.
- Singh, D.K., Sale, P.W.G., Routley, R.R., 2005. Increasing phosphorus supply in subsurface soil in northern Australia: Rationale for deep placement and the effects with various crops. *Plant Soil* 269, 35–44. <https://doi.org/10.1007/s11104-004-2475-6>.
- Taylor, A., Gurney, E., 1965. Precipitation of phosphate by iron oxide and aluminum hydroxide from solutions containing calcium and potassium. *Soil Sci. Soc. Am. J.* 29, 18–22. <https://doi.org/10.2136/sssaj1965.03615995002900010008x>.

Wang, H., Zhou, J., Chen, X., Li, S., Du, C., Dong, C., 2003. Interaction of NPK fertilizers during their transformation in soils: I. Dynamic changes in soil pH. *Pedosphere* 13, 257–262.

Werner, W., Strasser, B. 1993. Phosphorus dynamics and mobility in the diffusion zone of band-applied phosphorus fertilizers. In: FRAGOSO, M. A. C. & BEUSICHEM, M. L. V. (eds.) *Optimization of Plant Nutrition*. Klumwer Academic Publishers.

Zhang, X., Rengel, Z., 1999. Gradients of pH, ammonium, and phosphorus between the fertiliser band and wheat roots. *Aust. J. Agric. Res.* 50, 365–373. <https://doi.org/10.1071/A98134>.