

Valuable phosphorus retained by ironstone gravels can be measured as bicarbonate extractable P

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ABSTRACT

The > 2 mm fraction of soils is often excluded from laboratory analysis and glasshouse experiments, but is known to influence whole soil physical, chemical and biological properties. The historical focus on the < 2 mm fraction has led to a knowledge gap in analytical procedures and flow-on effect for agronomic response and advice when the > 2 mm fraction is present, especially when it is porous and chemically reactive.

An ironstone gravel soil (Endopetric Pisoplinthic Plinthosol (Arenic)) from south west Western Australia was separated into < 2, 2–4, 4–6, 6–8 and 8–10 mm fractions. Physical analysis included specific surface area (SSA), optical mineralogy, XRD and SEM. Chemical analysis included phosphorus (P) sorption, P retention index (PRI), P buffering index (PBI) and sodium bicarbonate extractable P (Cowell P) on intact and ground samples, and intact mixtures of the < 2 mm and > 2 mm fractions. Δ NaF pH was used as a surrogate P retention measure on intact mixtures of the < 2 mm and > 2 mm fractions.

P adsorbed onto the > 2 mm fraction can be measured as Colwell P, suggesting this fraction can provide P to plants. Colwell P determined on ground samples was correlated 1:1 with Colwell P on intact counterparts. Grinding of samples resulted in large increases in PRI and PBI, and is not a supported sample preparation, neither is the use of end over end shakers due to surface abrasion of the > 2 mm fraction increasing P sorption, however the use of Δ NaF pH as a surrogate measure of P sorption offers some potential.

Phosphorus adsorption decreased with increasing particle size but adsorption by the > 2 mm fraction is likely significant in the context of an entire unsieved soil and was influenced by SSA. The > 2 mm fraction had higher SSA than their physical size would imply, possibly influenced by the thickness and mineralogy of the exterior coating (rind). Our results show that the > 2 mm fraction contains reactive surfaces that can contribute to the nutrient holding capacity and plant available P of soils.

1. Introduction

Soil analysis routinely takes place on the < 2 mm (fine) fraction of soil. Typical processes include sample collection, air drying, and sieving of the soil to < 2 mm. The > 2 mm (coarse) fraction is discarded for chemical analysis as it is considered to be chemically inert, acting as a soil volume diluent (Miller and Guthrie, 1984). Equally, the > 2 mm fraction may have been discarded because of the difficulty in collecting a representative sample containing the > 2 mm fraction. However the > 2 mm fraction, if it has some porosity, or is comprised of minerals that enhance nutrient exchange, may: (1) contribute to water retention of

soils (Brouwer and Anderson, 2000), (2) be more chemically reactive than the < 2 mm fraction (Tiessen et al., 1993), (3) have higher nutrient content than the < 2 mm fraction (Abekoe and Tiessen, 1998), (4) contribute to more rapid transport of soil water and nutrients (Anamosa et al., 1990), (5) add to total soil pore space, which in turn effects air and water movement leading to impacts on soil biological activity (Ritz and Young, 2004), and (6) may contribute much more to the surface area of the soil than previously thought (Tokunaga et al., 2003).

At present there is a lack of understanding about how to incorporate information on the properties of the > 2 mm fraction to guide agronomic decisions. In some cases the > 2 mm fraction can consist of impervious

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chemically inert materials such as quartz, but others such as ironstone gravels may have chemically reactive surfaces (Weaver et al., 1992) with varying degrees of micro-porosity (Ashby et al., 1984; Coile, 1953). Moreover, it is uncertain as to whether soil test properties relevant to agronomic decision-making can be derived from the > 2 mm fraction. In some cases, estimates of the proportion of the > 2 mm fraction of soil are used to adjust soil test calibration curves and fertiliser recommendations with little justification (Bowden, 2014a; Bowden, 2014b). Also, the volume or mass of the > 2 mm fraction is rarely measured in field experiments, almost always excluded in glasshouse experiments and discarded in commercial soil analysis. This constrains our ability to relate it to crop and pasture responses in the field. For example, in determining critical soil phosphorus (P) levels for crop production, Bell et al. (2013b) noted that the > 2 mm fraction of soil can comprise up to 60% of the soil mass but is discarded and only the < 2 mm fraction is used for soil analysis. Whilst there is a small amount of information on P adsorption by the > 2 mm fraction of ironstone gravels in south west Western Australia (SWWA) (Weaver et al., 1992), its paucity does not allow for development of empirical models, nor the improvement of agronomic decisions, or justification for inclusion of the > 2 mm fraction in soil testing. The > 2 mm fraction of ironstone gravel soils in SWWA often consists of rounded or subrounded particles, sometimes called pisolites or nodules, that have an interior core similar to weathered substrate or surrounding soil, often silica- and kaolinite-rich (Gasparatos et al., 2004; Singh and Gilkes, 1996). Mottles (Singh and Gilkes, 1996) and iron coatings on root channels (Verboom and Pate, 2006) are preliminary segregations of sesquioxides and are precursors to ironstone nodules forming in some cases. The exterior coating or rind minerals on ironstone particles are usually different from the interior core mineralogy (Leopold et al., 2018; Singh and Gilkes, 1992; Singh and Gilkes, 1996).

Recent improvements in digital soil mapping in SWWA have more clearly mapped the presence or absence of coarse fragments, particularly ironstone gravels at different depths (Holmes et al., 2021). To add value to this mapping and improve our understanding of how to optimise agronomic decisions on ironstone gravel soils, the process-based work which has been completed for the < 2 mm fraction needs to be undertaken for the combined properties of the < 2 mm and > 2 mm fractions. This requires some understanding of the basic properties of the > 2 mm fraction of these ironstone gravel soils, as well as applicability of common agronomic tests of the > 2 mm fraction in isolation from, and in the presence of the < 2 mm fraction.

There are already well established soil chemical procedures to measure bicarbonate-extractable P for the < 2 mm fraction (Colwell, 1965) and for measures of P buffering index (PBI) (Burkitt et al., 2002) or P retention index (PRI) (Allen and Jeffery, 1990). For pasture based systems in Australia, both Colwell P and PBI are necessary to inform agronomic decisions around P requirements (Gourley et al., 2019), whilst for cropping systems a dependency of critical Colwell P values on soil PBI is not as clear (Bell et al., 2013b; Moody, 2007).

It is not known whether a mixture of the < 2 mm and > 2 mm fraction of ironstone gravels would lead to a different measure of plant available nutrients, or whether the processing of these materials through grinding to suit common laboratory procedures would alter the chemical behaviour of such mixtures, though this is likely to be the case for P sorption measures (Clarendon et al., 2019). In some studies, ironstone gravel particles were ground prior to chemical analysis (Clarendon et al., 2019; Gasparatos et al., 2006) however, this may expose surfaces not normally subject to chemical reactions and extractants in laboratory analysis. Some approaches such as the measurement of pH change when the entire unsieved soil is incubated with sodium fluoride (Δ NaF pH) may offer alternatives as surrogates for P sorption measures (Gilkes and Hughes, 1994; Summers et al., 2020). Additionally, ironstone gravels may have fine particles adhering to the surface of the > 2 mm fraction, which some authors removed by gentle but thorough shaking in sieves, prior to grinding (Abekoe and Tiessen, 1998). However, shaking in sieves may abrade the gravel surface, exposing fresh surfaces for

nutrient exchange, hence procedures for preparing the > 2 mm fraction for analysis need to be thoroughly investigated. Furthermore, some authors (Tiessen et al., 1993; Tiessen et al., 1991) claim that end over end shaking, a common procedure used for extraction and adsorption, did not result in disintegration of gravels, however there needs to be supporting evidence for appropriate methods of analysis given these authors used 0.5–2 mm particles that are less likely to abrade in an aqueous media than larger size fractions. In other words, the morphological and geochemical diversity of the > 2 mm fraction needs to be considered. Chemical procedures that estimate available nutrients or nutrient retention may need to consider passive approaches that avoid shaking to ensure laboratory results mimic field conditions (Mason et al., 2010). If wet chemistry methods are used to assess nutrient supply from the entire unsieved soil, larger volumes of extractant and significantly larger masses of material may be required for sampling (Buchter et al., 1994) and analysis to reduce variability in results caused by the heterogeneity of the properties of ironstone gravel particles.

As a contribution to some of the knowledge gaps identified above (Gasparatos et al., 2019), this paper explores the application and variation of common and novel analytical procedures to measures of P sorption and plant available P for the < 2 mm and > 2 mm fraction of ironstone gravel soils. The following hypotheses targeting ironstone gravels are tested:

1. The specific surface area (SSA) of ironstone gravels > 2 mm is smaller than the < 2 mm fraction and is linearly correlated with the physical size of particles.
2. If SSA increases with decreasing particle size, then P sorption will increase with decreasing particle size and increasing surface area.
3. If P is adsorbed by the > 2 mm and < 2 mm fractions, then Colwell P can be determined on the intact (unground) and ground equivalents of these materials.
4. P retention measures such as PBI and PRI for ground gravels and < 2 mm fraction will be greater than for intact equivalents.
5. If conventional incubation methods such as an end over end shaker are used to determine PRI on intact < 2 mm and > 2 mm fractions, then PRI will increase as the proportion of gravel increases. The converse will be supported if incubation occurs quiescently.
6. If P adsorbed by the > 2 mm fraction is less than the < 2 mm fraction, then PRI of mixtures of the < 2 mm and > 2 mm fraction will decrease with increasing > 2 mm content and will be positively correlated with Δ NaF pH.

2. Materials and methods

2.1. Soil collection and preparation

Approximately 5 tonnes of ironstone gravel soil (0–30 cm) were collected from West Dale (−32.327233 S 116.509133 E), around 90 km south east of Perth Western Australia. The soil was part of the Eastern Darling Range Zone where there is a moderately to strongly dissected lateritic plateau on granite with eastward-flowing streams in broad shallow valleys, and some surficial Eocene sediments (Beard, 1999). Today's soils are often formed in colluvium derived from lateritic profiles but may also represent in-situ weathered laterite over granite. This zone represents around 45% of the 2.7 M ha of the gravelly soils used for crop and pasture production in SWWA. Colloquially known as Yalanbee soil, it is described as a very gravelly deep sandy soil under the Western Australian soil groups classification (Schoknecht and Pathan, 2013). Using the Australian soil classification, the soil is described as a sesquimodular tenosol (Isbell et al., 2021), and under the World Reference Base the soil is classified as an Endopetric Pisoplinthic Plinthosol (Arenic) (IUSS Working Group WRB, 2015) and referred to hereon as ironstone gravel. The < 2 mm fraction colour was very pale brown (10YR 7/3), had a pH measured in CaCl₂ of 5.4 and a soil organic carbon content of 0.89%. The soil, which was never used for agricultural production and

thus never received applications of fertiliser, was taken from a cleared area amongst remnant vegetation (*Eucalyptus accedens* (Powderbark Wandoo) with an understory of *Banksia sessilis* (Parrotbush)).

An infographic providing an overview of the treatments, processes, incubations and physical and chemical measurements made on different size fractions contributing to each hypothesis is provided in Fig. 1.

2.1.1. Soil physical analysis

Following air drying at ambient temperature, a subsample of the soil was passed through 2 mm, 4 mm, 6 mm, 8 mm, 10 mm, 20 mm, 31.5 mm, 40 mm and 50 mm sieves to determine particle size distribution (Fig. 1). Particle size distribution was also determined on the < 2 mm fraction (Indorante et al., 1990).

The specific surface area (SSA) of the < 2 mm, 2–4 mm, 4–6 mm, 6–8 mm and 8–10 mm size fractions was determined (Fig. 1) using nitrogen adsorption (Brunauer et al., 1938). Each size fraction was analysed following standard vacuum preparation techniques of 48 h at approximately 10×10^{-3} Torr at 80 °C under helium flow. Samples were analysed using a Autosorb-1 analyzer (Quantachrome, Syosset, USA) using nitrogen gas at 77° K. The partial pressure adsorption range was over 11 points between 0.05 and 0.28. The physical surface area of each size fraction was estimated from mass-volume relationships based on median size and assumed sphericity of intact particles (Pennell, 2016).

The < 2 mm, 2–4 mm, 4–6 mm, 6–8 mm, 8–10 mm, 10–20 mm, 20–31.5 mm, 31–50 mm and 40–50 mm fractions were examined by polished thin section to identify particle morphology and estimate thickness and volume of outer coatings or rinds, and also by X-ray diffraction (XRD) to explore semi-quantitative mineral composition. A selected few size fractions (4–6 mm, 6–8 mm, 8–10 mm, 20–31.5 mm) were also examined by field emission Scanning Electron Microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) to compare the elemental composition (Al_2O_3 , SiO_2 , Fe_2O_3) of the rind to the interior of the > 2 mm fraction (Fig. 1).

2.1.2. Soil chemical analysis

The soil was sieved and the > 2 mm fractions were gently washed to remove adhering surface soil and air dried at ambient temperature. Subsamples of the < 2 mm, 2–4 mm, 4–6 mm, 6–8 mm, 8–10 mm, 10–20 mm and > 20 mm size fraction were ground in a puck and ring mill for 30 s to facilitate chemical analysis. Intact and ground samples of the < 2 mm and > 2 mm fractions were analysed for Colwell P (Colwell, 1963), Phosphorus Buffering Index (PBI) (Burkitt et al., 2002), and Phosphorus Retention Index (PRI) (Allen and Jeffery, 1990) (Fig. 1). Both PBI and PRI are single point P sorption indexes that are determined by equilibrating the soil with a known initial P concentration and soil:solution ratio. The index is determined as the ratio of P adsorbed to the equilibrium P concentration. Differences between PRI and PBI are that the former has less P applied to the soil (200 mgP kg^{-1}) than the latter ($1000 \text{ mg P kg}^{-1}$) and is better suited to soils with low P sorption capacity. Additionally, PBI is adjusted for P already adsorbed by the soil measured as Colwell P, whereas PRI does not. As a result, PBI will estimate P sorption capacity of the soil prior to the addition of P, whilst PRI estimates the soils capacity to adsorb P beyond what it already stores. The following differences from standard methods for PRI and PBI were made for analysis of intact > 2 mm fractions. For PRI the same concentrations of 10 mg P L^{-1} and solution:soil ratio of 20:1 was used, however the volume was increased from 100 mL typically used in commercial laboratories to 1000 mL. Consequently, the mass of the > 2 mm fraction used was 50 g compared to 5 g. For PBI the same concentrations of 100 mg P L^{-1} and solution:soil ratio of 10:1 was used, however the volume was increased from 50 mL typically used in commercial laboratories to 200 mL. Consequently, the mass of the > 2 mm fraction used was 20 g compared to 5 g. For both PRI and PBI incubation occurred by gentle agitation of the > 2 mm fraction and P solution at the start and finish of the 16 hr incubation period (Fig. 1).

Colwell P determination on the intact < 2 mm fraction and all ground fractions was identical to that described by Colwell (1963) and Rayment and Lyons (2011). Adjustments were made to these methods to

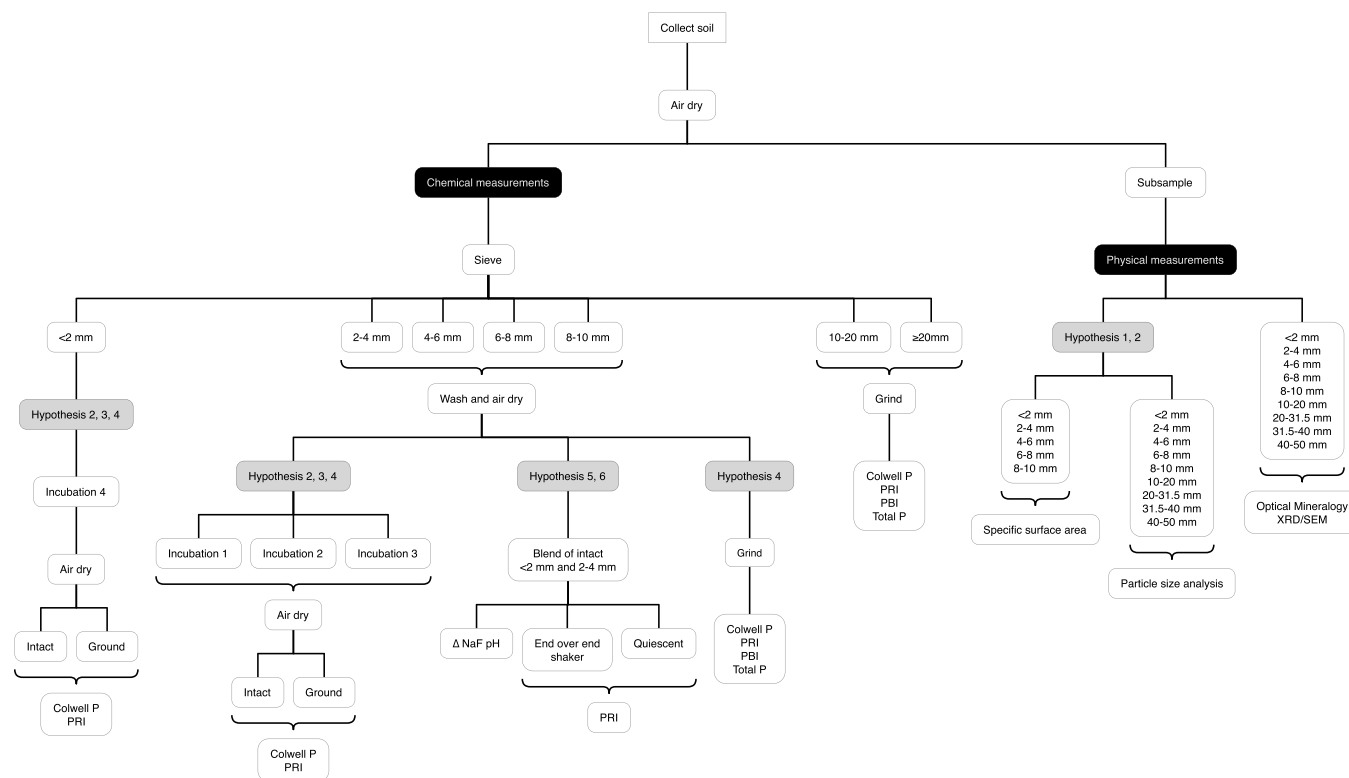


Fig. 1. Infographic depicting the treatments, processes, incubations and physical and chemical measurements made on different size fractions contributing to each hypothesis.

accommodate Colwell P analysis of the intact > 2 mm fractions. The same solution:soil ratio of 100:1 was used, however the volume of 0.5 M NaHCO₃ was increased from 50 mL or 100 mL typically used in commercial laboratories to 1000 mL. Consequently, the mass of the intact > 2 mm fraction used was 10 g compared to 0.5 g or 1 g used in a commercial laboratory setting. Because of the increased volumes, and the potential for abrasion of the surface of gravels by using of end over end shaking (Barrow and Shaw, 1979; Stone and Mudroch, 1989), extractions occurred by gentle agitation of the extracting solution at the start and finish of the 16 hr extraction period (Fig. 1). This decreased the risk of secondary P adsorption due to surface abrasion and exposure of fresh P sorbing surfaces (Barrow and Shaw, 1976a; Barrow and Shaw, 1976b; Barrow and Shaw, 1976c).

2.2. Phosphorus incubation

The washed intact 2–4 mm, 4–6 mm, 6–8 mm and 8–10 mm fractions, and the < 2 mm fraction were incubated with P solutions with differing P concentrations and at differing solution:soil ratios described below (Fig. 1). Soil materials incubated with P are from here on termed P enriched, and those not incubated with P are termed untreated. Common to each incubation, solutions prepared using KH₂PO₄ were sampled at the commencement and conclusion of the incubation period and analysed for Filterable Reactive P (FRP) using the methods of John (1970) or Hanson (1950). Incubation occurred at ambient temperatures either in a fluvarium (Clarendon et al., 2019), or quiescently in 190 L polyethylene drums where incubating solutions in contact with soil materials were agitated occasionally. At the end of the incubation period, solutions were decanted, materials drained, and the P enriched < 2 mm and > 2 mm fractions were air dried at 40° C. Subsamples of the P enriched < 2 mm and > 2 mm fractions, ground or intact, were analysed for Colwell P and PRI as described above. Ground samples and the < 2 mm fraction were analysed at CSBP (<https://www.csbp.com.au>) soil and plant analysis laboratory. Ground samples typically had the size distribution > 400 µm (1%), 300–400 µm (5%), 212–300 µm (12%), 150–212 µm (11%), <150 µm (71%) by weight.

2.2.1. Incubation 1

39.6 kg of the 2–4 mm, 4–6 mm and 6–8 mm fractions was placed in separate channels of a 9.8 m long, 0.2 m wide fluvarium (Clarendon et al., 2019) to 3 cm depth and 396 L of 100 mg P L⁻¹ was cycled continuously over each size fraction for 3.3 days.

2.2.2. Incubation 2

Each of the 2–4 mm, 4–6 mm, 6–8 mm and 8–10 mm fractions was incubated separately with 5, 10, 20, 40 and 100 mg P L⁻¹ for 10 days at a solution:soil ratio of 10:1 (120 L:12 kg) in 190 L polyethylene drums.

2.2.3. Incubation 3

The 2–4 mm, 4–6 mm, 6–8 mm and 8–10 mm fractions were incubated separately with 150 L of 2, 20 and 100 mg P L⁻¹ for 10 days in 190 L polyethylene drums at solution:soil ratios of 43:1, 24:1, 20:1 and 13:1 respectively.

2.2.4. Incubation 4

The < 2 mm fraction was incubated with 2, 5, 10, 20, 40 and 100 mg P L⁻¹ for 10 days at a solution:soil ratio of 10:1.

2.3. Phosphorus retention measures of intact gravel

Sodium fluoride (NaF) pH (Gilkes and Hughes, 1994) was determined on untreated mixtures of < 2 mm and 2–4 mm fractions (0, 20, 40, 60, 80, 100%) at a soil:solution ratio of 1:20 as a surrogate for P sorption. pH measurements occurred after 1 hr of incubation, and Δ NaF pH was determined as the difference in pH for solutions with or without added soil mixtures. In addition, PRI was measured on mixes of the 2–4

mm and < 2 mm fractions using an end over end shaker, and quiescently with the latter incubation occurring by gentle agitation of the soil and P solution at the start and finish of the 16 hr incubation period (Fig. 1).

2.4. Data analysis

Chemical analysis data from the various experiments were pooled and relationships between analytical tests for enriched and untreated, ground and intact fractions, and fraction mixtures were explored using linear and non-linear regression. Igor Pro V8 (WaveMetrics, Inc) and DataDesk 8.2 (Data Description Inc.) were used as exploratory analysis, statistical, curve fitting and presentation tools.

3. Results

Eighty one percent of the soil mass was > 2 mm in size (Table 1). The < 2 mm fraction was 7% clay (<2 µm), 4% silt (2–20 µm) and 89% sand (20–2000 µm), with a texture classification of coarse sand. Specific surface area measured by the BET method with N₂ sorption decreased with increasing particle size (Fig. 2a, Table 1) and was well described by a linear fit for the particle sizes that were measured. The 2–4, 4–6, 6–8 and 8–10 mm fractions had 84%, 73%, 64% and 53% respectively of the SSA of the < 2 mm fraction. Physical surface area also decreased with particle size (Table 1), however the ratio of SSA to physical surface area increased with increasing particle size. Specific surface area of the < 2 mm fraction was around 300 times the physical surface area whilst the SSA of the 8–10 mm fraction was around 90,000 times the physical surface area (Fig. 2a). Specific surface area was linearly correlated with rind volume, and both SSA and rind volume increased with decreasing particle size (Fig. 2b). A similar relationship (not shown: $SSA = 34.5 \times RindVolume + 5.1$; $r^2 = 0.99$) between SSA and rind volume was observed when rind volume was expressed on a volume/volume basis rather than a volume/weight basis.

The main minerals identified by optical mineralogy and XRD were quartz, gibbsite and oxide/hydroxide minerals such as boehmite, hematite and maghemite. Other minerals present, usually accessory, ie. < 10%, were goethite, kaolinite, muscovite, rutile, anatase, ilmenite and corundum. For iron-based minerals, there was a much greater abundance of hematite and maghemite than goethite. In the larger size fractions for aluminium-based minerals, boehmite was more abundant than gibbsite. Below 20 mm, rounded to subrounded particles dominate (Fig. 3), with a fairly consistent mineralogy and morphology consisting of a hematite and maghemite interior and a variable width (mainly < 1 mm) rind that increases with size (Table 1). The rind was dominated by fine-grained gibbsite often heavily impregnated with medium to fine grained angular quartz. These particles are often characterized by a concentric structure, even when lacking a hematite interior. Radial structures, such as veins or cracks are present but subordinate overall.

The SEM analysis was consistent with optical mineralogy and showed that aluminium and silicon oxides were more dominant in rinds whilst iron oxides dominated the interior (Fig. 4).

Colwell P values, whether for ground or intact untreated materials, for any size fraction of the soil were below the limits of reporting (<2 mg P kg⁻¹) and were not significantly different. PBI and PRI of ground materials for any untreated size fraction was significantly greater than the intact < 2 mm fraction of the soil. Ground PRI and PBI values increased with increasing size, particularly in the transition from < 2 mm to > 2 mm size fractions, and again from the < 20 mm fraction to those > 20 mm. Intact PRI of the < 2 mm fraction was about 6% of the ground PRI for the < 2 mm fraction, whilst the intact PRI of the > 2 mm fractions was < 0.1% of the PRI for the ground > 2 mm fractions. Intact PBI of the < 2 mm fraction was 29% of the ground PBI for the < 2 mm fraction, whilst the intact PBI of the > 2 mm fractions was 1–2% of the PBI for the ground > 2 mm fractions. For the < 2 mm fraction, Total P was significantly greater in the ground material than intact material

Table 1
Particle size distribution, surface area, rind thickness, mineralogy and analysis of the untreated fractions.

Size Fraction (mm)	Proportion (%)	Texture class	%	¹ Physical surface area (m ² /g)	N ₂ BET Surface Area (m ² /g)	Rind Thickness (range mm)	² Mineralogy	Sample Pre-processing	PBI	Colwell P (mg/kg)	PRI	Total P (mg/kg)
<2	19	Coarse sand (200–2000 μm)	61	104	31.2	0.0–0.1	Q, K, H, Gi, Go, M, i, t	Ground	156.3	<2	279.4	43
		Fine sand (20–200 μm)	28									
		Silt (2–20 μm)	4									
		Clay (<2 μm)	7									
2–4	10		0.59	26.3	0.3–0.5	Q, H, Gi, <u>M</u> , K, Go, R	Ground Intact	468 10.6	<2 <2	2677 1.8	54	
4–6	14		0.33	22.9	0.1–1.0	Q, H, <u>M</u> , <u>Gi</u> , K, R, Go, c	Ground Intact	411 5.1	<2 <2	2354 1.3	45	
6–8	16		0.28	20.0	0.2–1.0	Q, H, <u>M</u> , <u>Gi</u> , K, C, i	Ground Intact	430 4.7	<2 <2	2357 1.0	46	
8–10	15		0.18	16.4	0.1–1.0	Q, H, <u>Gi</u> , K, B, A, Go, C	Ground Intact	394 5.3	<2 <2	3535 1.2	46	
10–20	21		0.11	ND	1.0–2.0	Q, H, Gi, <u>M</u> , K, R, Go, B, mu	Ground	401	<2	4137	37	
20–31.5	3		0.06	ND		Q, Gi, H, B, a, k, go	Ground	710	<2	10,232	55	
31.5–40	2		0.05	ND		Q, B, H, <u>Gi</u> , <u>M</u> , K, A						
40–50	1		0.04	ND		B, M, <u>Q</u> , K, a, gi						

ND = not determined.

Q = quartz, H = hematite, Gi = gibbsite, M = maghemite, K = kaolinite, Go = goethite, B = boehmite, A = anatase, I = Ilmenite, Mu = muscovite, C = corundum, T = titanium oxides.

¹ Physical surface area estimated from mass-volume relationships based on median size and sphericity of unground particles (Pennell, 2016).

² Mineralogy: Dominant > 50%; bold, Major 20–50%; plain, Minor 10–20%; underline, Accessory 1–10%; italic, Trace < 1%; lowercase.

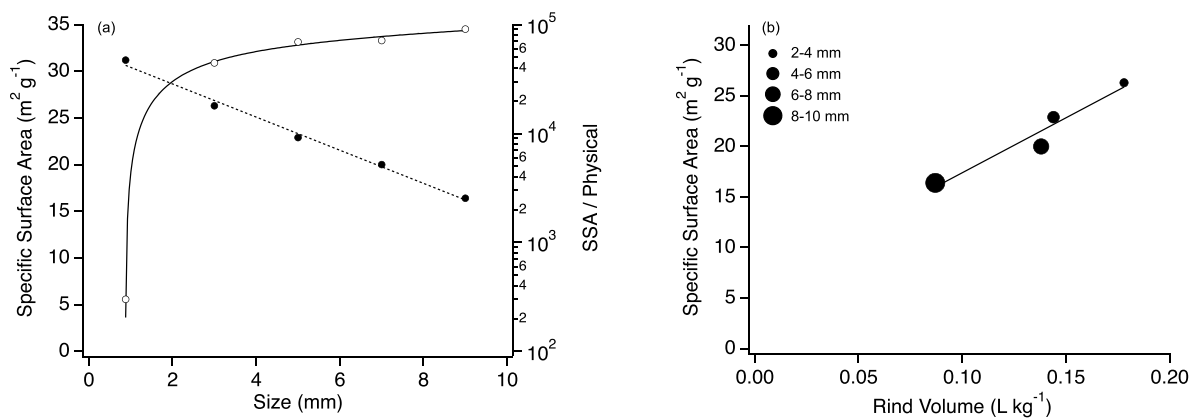


Fig. 2. (a) Specific surface area (left y axis ●, dashed line, $SSA = 32.19 - 1.77 \times Size; r^2 = 0.99$) and the ratio of SSA to physical surface area (right y axis ○, solid line, $\frac{SSA}{physical\ surface\ area} = 1.69 \times 10^5 - 3.80 \times 10^4 \times \exp\left(\frac{-(Size-0.88)}{1.35}\right) - 1.31 \times 10^5 \times \exp\left(\frac{-(Size-0.88)}{16.89}\right); r^2 = 0.97$) as a function of particle size. Midpoint of size range used for fractions > 2 mm. Size for < 2 mm fraction based on proportions in textural classes. (b) Specific surface area as a function of rind volume estimated from midpoint of particle size range and rind thickness. $SSA = 6.53 + 108.73 \times Rind\ Volume; r^2 = 0.94$. Symbol size reflects particle size.

(Table 1).

Phosphorus adsorption determined from incubations 2 and 4 was described well by the Freundlich equation and increased with decreasing particle size (Fig. 5a). At the same initial P concentration, the 2–4, 4–6, 6–8 and 8–10 mm fractions adsorbed 80%, 55%, 47% and 12% respectively of the P adsorbed by the < 2 mm fraction. When expressed per unit area (Fig. 5b), P adsorption was well described by the Freundlich equation and increased with decreasing particle size. There was less variation in the amount of P sorbed when expressed on a unit area basis (Fig. 5b) than on a mass basis (Fig. 5a).

Colwell P of the < 2 mm fraction was more than three times that of the Colwell P attained by the > 2 mm fractions when incubated at the same initial P concentration (Fig. 6a). Colwell P for the < 2 mm fraction

ranged up to 128 mg P kg⁻¹ whilst the Colwell P of the > 2 mm fractions decreased with increasing size, ranging up to 40 mg P kg⁻¹ for the 2–4 mm fraction, and 18 mg P kg⁻¹ for the 8–10 mm fraction. Colwell P of intact < 2 mm and > 2 mm fractions was linearly correlated to the Colwell P of ground < 2 mm and > 2 mm fractions, and followed a 1:1 relationship (Fig. 6b). The slope of the fitted line was 1, and the intercept was not significantly different than 0, hence Colwell P intact = Colwell P ground.

The relationship between the PRI of P enriched and untreated ground and intact fractions was distinctly different for the < 2 mm and > 2 mm fractions (Fig. 7a). The PRI of the intact < 2 mm fraction ranged between 2.4 and 17, whilst in the ground state PRI varied between 36 and 578. The PRI of the ground > 2 mm fractions was much higher than the

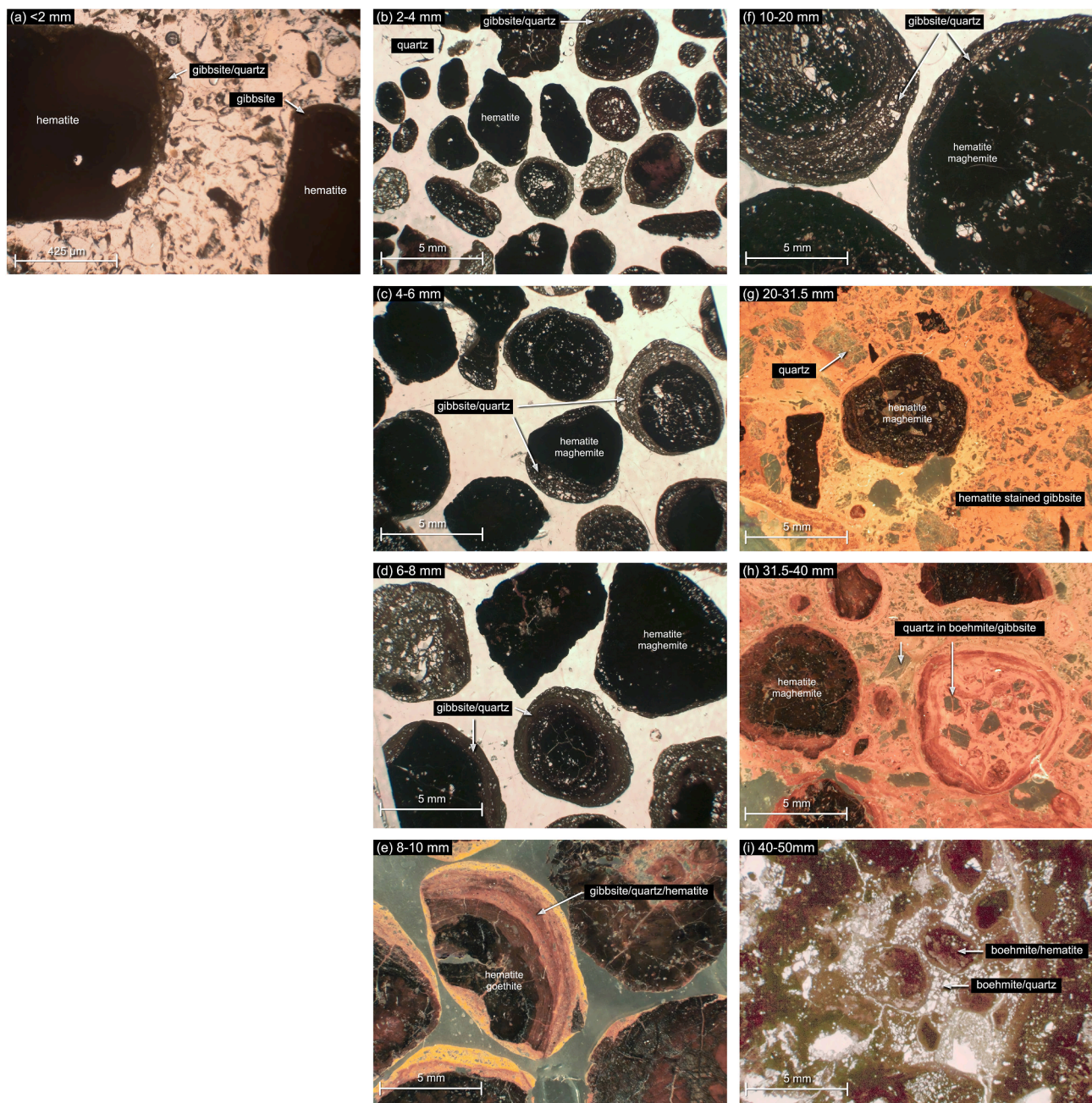


Fig. 3. Optical mineralogy of (a) < 2 mm, (b) 2–4 mm, (c) 4–6 mm, (d) 6–8 mm, (e) 8–10 mm, (f) 10–20 mm, (g) 20–31.5 mm, (h) 31.5–40 mm and (i) 40–50 mm fractions. All at the same scale except < 2 mm fraction which is shown at higher magnification.

ground < 2 mm fractions, ranging from 214 to 5600. However, the PRI of the intact > 2 mm fractions was in a very narrow range from -0.78 to 1.97 . All of the P enriched intact fractions showed an exponential decline in PRI with increasing amounts of P applied (Fig. 7b). The PRI of the intact < 2 mm fraction fell by 85% when up to $1000 \text{ mg P kg}^{-1}$ was applied. The PRI of the intact > 2 mm fractions also fell by 86%, 104%, 138% and 154% for the 2–4, 4–6, 6–8 and 8–10 mm fractions respectively when up to $1000 \text{ mg P kg}^{-1}$ was applied. PRI was negative when up to $1000 \text{ mg P kg}^{-1}$ was applied to the 4–6, 6–8 and 8–10 mm fractions.

Soil PRI increased by as much as 38% when the percentage of the 2–4 mm fraction increased for incubation occurring in an end over end shaker. In contrast, PRI decreased by > 50% as the percentage of the 2–4 mm fraction increased for incubation occurring quiescently (Fig. 8a). Incubating solutions for samples with 100% gravel from the

end over end shaker were cloudy and showed evidence of abrasion at the end of the incubation, with around 3.8% of the original mass > 2 mm observed as < 2 mm fine material. $\Delta \text{NaF pH}$ increased with decreasing soil gravel content (Fig. 8b). Soil gravel mixes with 0% 2–4 mm fraction had a PRI of 10.8 compared to 100% 2–4 mm fraction which had a PRI of 5. Mixes with 0% 2–4 mm fraction had a $\Delta \text{NaF pH}$ of 1.92, whilst mixes comprised of 100% 2–4 mm fraction had a $\Delta \text{NaF pH}$ of 0.72.

4. Discussion

In support of hypothesis 3, the 1:1 correlation between ground Colwell P of the < 2 mm and > 2 mm fractions and intact counterparts (Fig. 6b) indicates that P fertility measurement of the > 2 mm fraction is possible in a laboratory setting by grinding the sample. Whilst the < 2 mm and > 2 mm fractions were examined for Colwell P separately, this

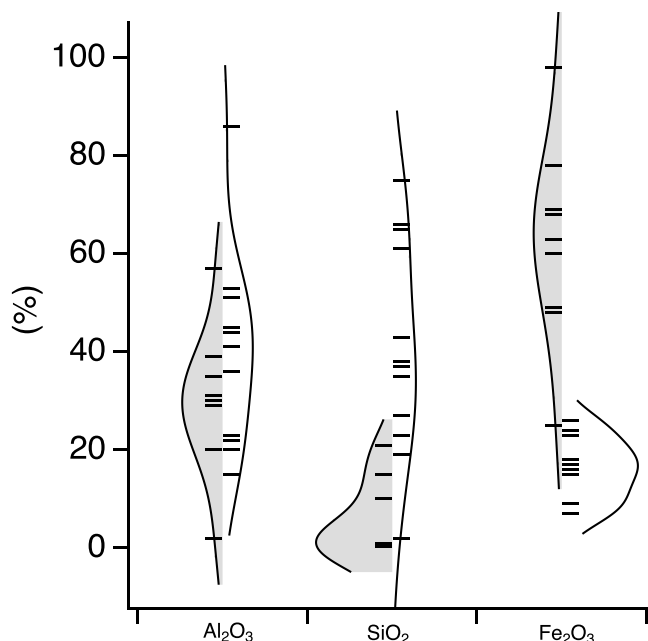


Fig. 4. Asymmetric violin plots of Al, Si and Fe composition of interior (grey shading) and rinds (white shading) of the > 2 mm fraction from SEM/EDS.

result implies that if a representative sample of the soil including the > 2 mm fraction can be collected, subsampled, and ground, that ground entire unsieved soil Colwell P could be determined. Additional steps such as grinding would need to be included in traditional laboratory methods, however, this is likely to be less of a barrier than scaling up traditional methods by increasing sample weights and extractant volumes. The action of grinding the > 2 mm fraction likely distributes and homogenises the P-enriched rind with the highly P retentive > 2 mm fraction interior (Table 1, Fig. 7). This idea is consistent with previous reports that identified that P adsorption onto the > 2 mm fraction of ironstone gravels was predominantly on the surface (Weaver et al., 1992), most likely associated with the rind (Fig. 3). Grinding of a representative sample containing the < 2 mm and > 2 mm fractions prior to analysis is likely to offer a solution to the assessment of P fertility of soils containing ironstone gravels, however this does require some additional experimentation using field-based soils that have been P

enriched in an agricultural setting.

The measurement of Colwell P in the > 2 mm fraction of up to 41 mg P kg⁻¹ for the 2–4 mm fraction and 18 mg P kg⁻¹ for the 8–10 mm fraction suggests that the > 2 mm fraction will contribute P to pastures and crops. The Colwell P values for the > 2 mm fraction is similar to the critical values and ranges reported to achieve 90% relative yield for winter cereal crops in Australia (Bell et al., 2013a; Bell et al., 2013b). The contribution of the > 2 mm fraction to P retention and Colwell P of the entire unsieved soil will depend on the relative quantities, size distribution, and chemical reactivity of the > 2 mm fraction compared to the < 2 mm fraction. For example, a gravel soil with particle size distribution and P retention characteristics as shown in Table 1, and where the < 2 mm fraction has a Colwell P of 2 mg P kg⁻¹, or 7% of the Colwell P required to achieve 95% relative yield in pastures (Gourley et al., 2019; Rogers et al., 2021), and the > 2 mm fraction is comprised of P enriched ironstone gravels that contribute 80% of the soil mass, would result in an estimated Colwell P for the entire unsieved soil of 33, 24, 16 and 15 mg P kg⁻¹ if the ironstone gravel was enriched to the maximum levels shown in Fig. 6a (2–4 mm: 41 mg P kg⁻¹, 4–6 mm: 30 mg P kg⁻¹, 6–8 mm: 19 mg P kg⁻¹, 8–10 mm: 18 mg P kg⁻¹) and the size of the ironstone gravel was 2–4, 4–6, 6–8 and 8–10 mm respectively. In this example the percentage contribution to the entire soil Colwell P is 99%, 98%, 97% and 97% from 2–4, 4–6, 6–8 and 8–10 mm ironstone gravels respectively. Conversely, if the < 2 mm and > 2 mm fractions were enriched to the maximum Colwell P levels shown in Fig. 6a (<2 mm: 124 mg P kg⁻¹, 2–4 mm: 41 mg P kg⁻¹, 4–6 mm: 30 mg P kg⁻¹, 6–8 mm: 19 mg P kg⁻¹, 8–10 mm: 18 mg P kg⁻¹), and the > 2 mm fraction contributed 80% of the soil mass, the resulting Colwell P for the entire unsieved soil is estimated to be 58, 49, 40 and 39 mg P kg⁻¹ if the size of the ironstone gravel was 2–4, 4–6, 6–8 and 8–10 mm respectively. In this example the percentage contribution to the entire soil Colwell P is 57%, 49%, 38% and 37% from 2–4, 4–6, 6–8 and 8–10 mm ironstone gravels respectively. In the former example the Colwell P of the > 2 mm fraction may be diluted by the < 2 mm fraction and contribute most of the plant available P, whilst in the latter the Colwell P for the < 2 mm fraction may be diluted by the > 2 mm fraction because of the relative Colwell P concentrations of each fraction, and their contribution to the soil mass. In general, > 2 mm ironstone gravels will provide a greater contribution to entire unsieved soil Colwell P than the < 2 mm fraction when the weighted Colwell P of the > 2 mm fraction is greater than that of the < 2 mm fraction. Conversely, > 2 mm ironstone gravels will provide a smaller contribution to entire unsieved soil Colwell P than the < 2 mm

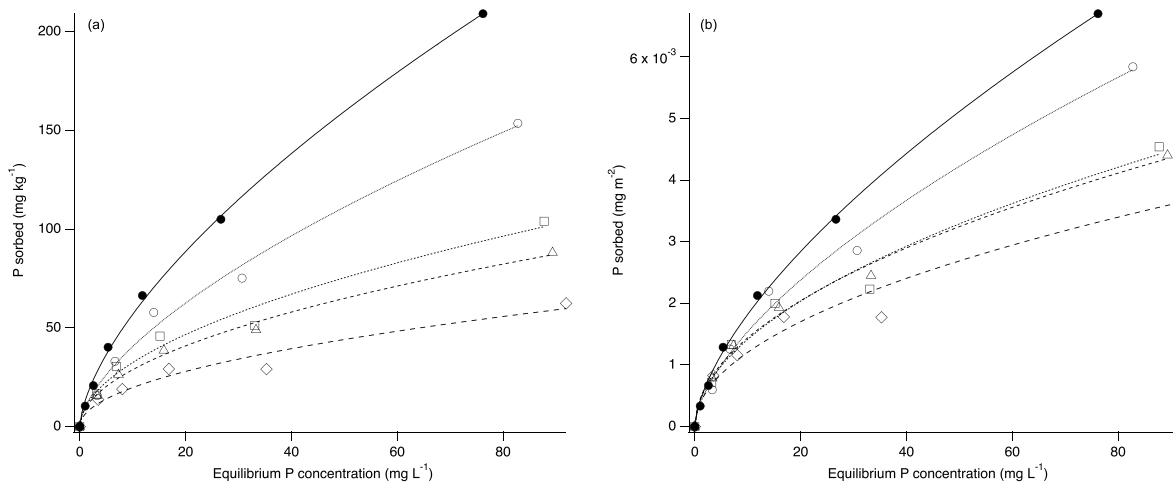


Fig. 5. P sorption isotherms with fitted Freundlich curves ($y = A \times X^b$). Symbols in parenthesis followed by Freundlich coefficients and r^2 (A, b, r^2) on a (a) mass basis for < 2 mm (●, 12.97, 0.64, 0.99), 2–4 mm (○, 9.58, 0.63, 0.99), 4–6 mm (□, 9.69, 0.52, 0.98), 6–8 mm (△, 9.01, 0.50, 0.99) and 8–10 mm (◇, 6.23, 0.50, 0.95) fractions, and (b) unit area basis for < 2 mm (●, 0.00042, 0.64, 0.99), 2–4 mm (○, 0.00036, 0.63, 0.99), 4–6 mm (□, 0.00042, 0.52, 0.98), 6–8 mm (△, 0.00045, 0.50, 0.99) and 8–10 mm (◇, 0.00038, 0.50, 0.96) fractions. Data from incubations 2 and 4.

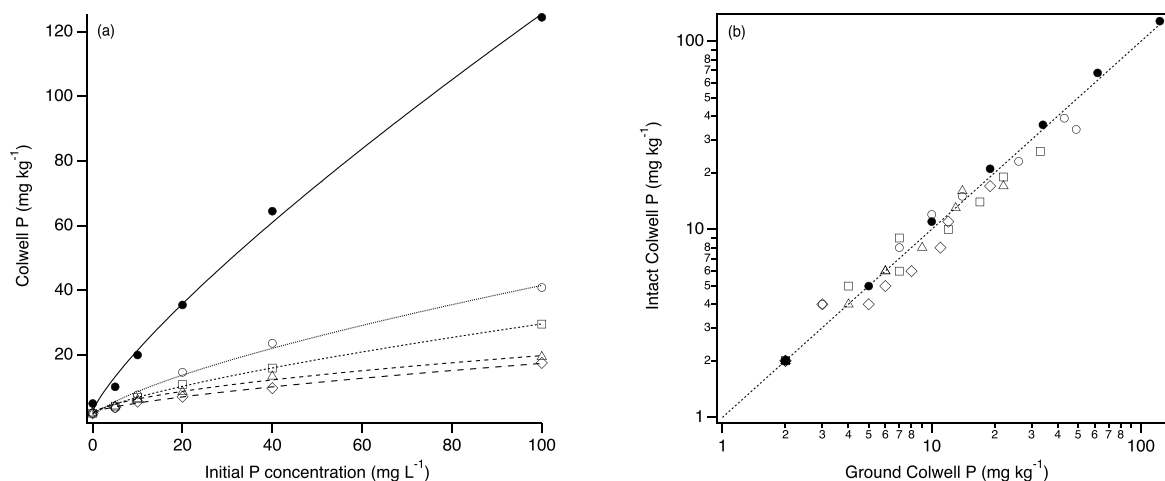


Fig. 6. (a) Mean Colwell P as a function of incubation with different initial P concentrations and fitted power curves ($y = a + b \times X^c$). Symbols in parenthesis followed by coefficients and r^2 (a, b, c, r^2) for the < 2 mm (●, 2.44, 2.95, 0.81, 0.99), 2–4 mm (○, 0.69, 1.58, 0.71, 0.99), 4–6 mm (□, 1.72, 0.97, 0.73, 0.99), 6–8 mm (△, 1.64, 1.25, 0.58, 0.99) and 8–10 mm (◇, 2.11, 0.60, 0.70, 0.99) fractions. (b) Median intact Colwell P as a function of median ground Colwell P for < 2 mm (●), 2–4 mm (○), 4–6 mm (□), 6–8 mm (△) and 8–10 mm (◇) fractions. $\log_{10} \text{Intact Colwell P} = 0.96 \times \log_{10} \text{Ground Colwell P} + 0.03$; $r^2 = 0.98$.

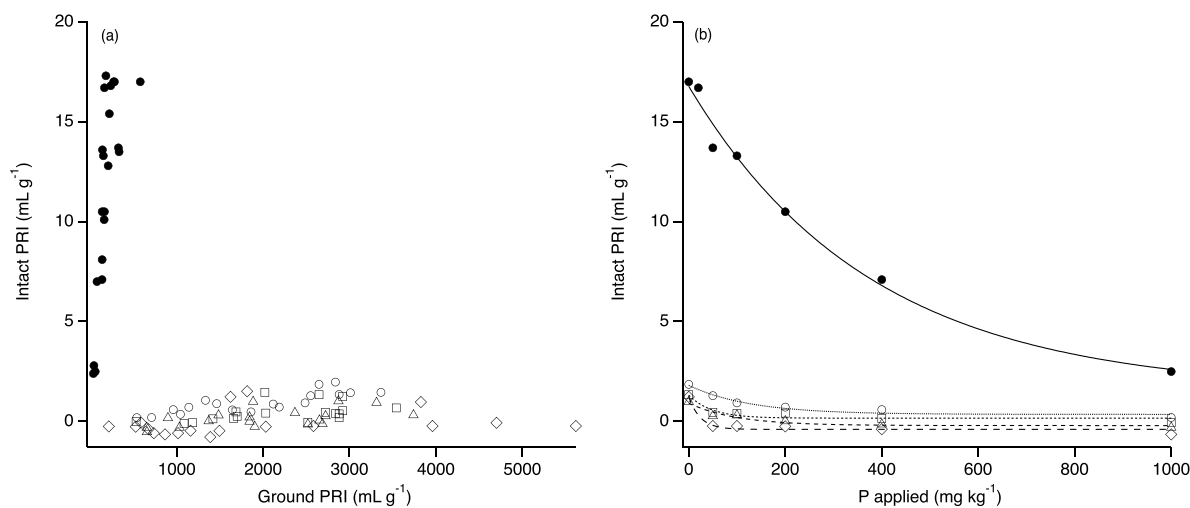


Fig. 7. (a) Intact PRI as a function of ground PRI for < 2 mm (●), 2–4 mm (○), 4–6 mm (□), 6–8 mm (△) and 8–10 mm (◇) fractions. (b) Median intact PRI variation with increasing amount of P applied with fitted exponential curves ($y = a + b \times \exp(-c \times X)$). Symbols in parenthesis followed by coefficients and r^2 (a, b, c, r^2) for < 2 mm (●, 1.53, 15.25, 0.003, 0.98), 2–4 mm (○, 0.35, 1.46, 0.008, 0.93), 4–6 mm (□, 0.17, 1.15, 0.021, 0.88), 6–8 mm (△, -0.20, 1.12, 0.010, 0.93) and 8–10 mm (◇, -0.39, 1.62, 0.041, 0.95) fractions.

fraction when the weighted Colwell P of the > 2 mm fraction is less than that of the < 2 mm fraction.

Further studies to examine plant growth in the presence of P enriched and untreated < 2 mm and > 2 mm fractions, and the steady-state gradient in P concentration that occurs between the two size fractions, would assist to increase understanding and develop empirical rules for P decisions on these soils. Additional factors outside the scope of this study will also influence the ability of plant roots to interact with and access P associated with the > 2 mm fraction. These factors include soil biology and soil moisture.

In support of hypothesis 4, grinding of samples, in particular the > 2 mm fraction leads to large increases in single point P sorption measures such as PRI (Fig. 7a), an analogue of PBI (Burkitt et al., 2002). The action of grinding exposes large amounts of material, largely hematite (Fig. 3, Table 1) from the interior of the > 2 mm fraction that significantly increases P retention. This is undesirable since critical values of Colwell P can be dependent on P sorption measures such as PBI (Gourley et al., 2019; Moody, 2007) for interpretation and fertiliser recommendation.

The very high PRI and PBI of ground fractions > 2 mm in size (Table 1) suggests that even a small quantity of these materials would increase the PRI or PBI of the < 2 mm fraction. Given that critical Colwell P values are PBI dependent (Gourley et al., 2019; Moody, 2007), increases in PBI measured in the < 2 mm fraction would result in higher P fertiliser recommendations than is necessary. The increase in P retention from grinding suggests that a more accurate estimate of plant-available P will be obtained by using sampling methods that minimise damage to the coarse fraction in ironstone gravel soils.

Traditional approaches using end over end shakers to determine single point P sorption measures also resulted in increases in PRI as the > 2 mm content increased compared to quiescent adsorption (Fig. 8a). This suggests that the surface of the > 2 mm fraction was abraded in the incubation process, leading to elevated PRI and an undesirable result compared to quiescent adsorption where PRI would be expected to decrease with increasing > 2 mm content. These findings support hypothesis 5. Alternative approaches such as the use of $\Delta \text{NaF pH}$ show promise as indirect measures of P sorption, as identified by the positive

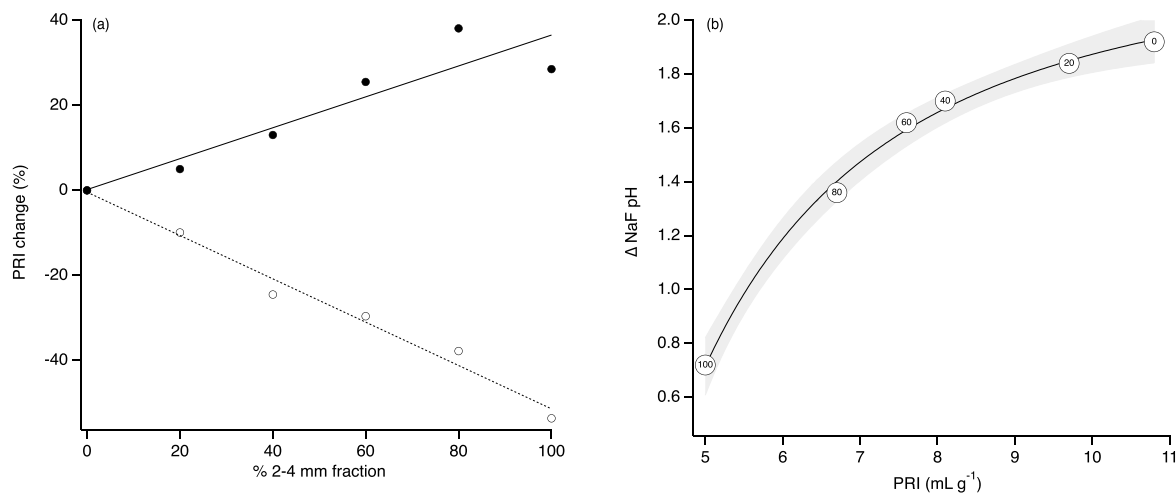


Fig. 8. (a) Change in PRI (%) with increasing percentage 2–4 mm fraction with linear fits ($y = a + b \times X$). Symbols in parenthesis followed by coefficients and r^2 (a, b, r^2) for sample incubation by end over end shaker (●; 0.193, 0.363, 0.85) or quiescently (○; -0.414, -0.510, 0.98). (b) Change in NaF pH as a function of PRI for mixes of < 2 mm and 2–4 mm fractions. Symbol label shows 2–4 mm fraction (% by weight). $\Delta \text{NaFpH} = 2.251 - 40.007 \times \text{PRI}^{-2.025}$; $r^2 = 0.94$

correlation between PRI and Δ NaF pH as the percentage of < 2 mm fraction increased (Fig. 8b). These findings are in support of hypothesis 6. The use of Δ NaF pH does however require additional experimentation across a range of soils with varying PBI or PRI and > 2 mm fraction content to develop pedo-transfer functions for wider use of the method (Summers et al., 2020). In addition, the effects of previously adsorbed P on Δ NaF pH was not examined here, but was shown to decrease PRI for all size fractions (Fig. 7b). Previously adsorbed P is usually accounted for as Colwell P when reporting PBI so that P sorption estimates mimic those of the soil prior to the addition of P (Rayment and Lyons, 2011).

In support of hypothesis 1, SSA decreased with increasing particle size. Specific surface area was much higher than expected for the > 2 mm fraction when compared to the < 2 mm fraction according to the SSA/physical surface area ratio (Fig. 2). In addition, the ratio of SSA to physical surface area suggests that the thickness of rinds, rind volume and rind mineralogy may contribute to SSA. Whilst the rind thickness and volume for an individual 8–10 mm particle may be greater than for a 2–4 mm particle, the number of smaller particles contributing to the same mass as large particles results in a larger rind volume for the same mass of smaller particles. Rind volume per unit mass doubles when particles decrease in size from 8–10 mm to 2–4 mm, whilst SSA increases 1.6 fold (Fig. 2b). This similarity in degree of change in rind volume and SSA, along with previous evidence using autoradiography of the retention of P to the surface of similar particles > 2 mm in size (Weaver et al., 1992) suggests that the rind thickness and volume, and mineralogy are all likely contributors to the SSA of the > 2 mm fraction. When compared to the very limited citations of SSA for the > 2 mm fraction, the SSA of the > 2 mm fraction examined here ($16\text{--}26 \text{ m}^2 \text{ g}^{-1}$) seems realistic compared to $6.8 \text{ m}^2 \text{ g}^{-1}$ (Drizo et al., 1999) for similar bauxitic materials of an ill-defined but likely larger particle size range (97% by weight > 6.8 mm). The other reported SSA measurements (Tokunaga et al., 2003) were for 2–6 mm gravels derived from basalt. In this case, the SSA values were 27 and $22 \text{ m}^2 \text{ g}^{-1}$ for a water based SSA, and 11.7 and $11.3 \text{ m}^2 \text{ g}^{-1}$ when using less reactive gases for 2 and 6 mm basaltic gravels respectively. The surface area of the > 2 mm fraction examined here is therefore not insignificant, particularly when compared to reported values of 10, 32 and $65 \text{ m}^2 \text{ g}^{-1}$ for kaolinite, montmorillonite and bentonite respectively (Pennell, 2016), and when the contribution to the soil mass and rind volume made by the > 2 mm fraction is considered. The > 2 mm fraction is therefore likely to contribute significantly to P sorption and plant P dynamics. Further examination of the surface topography of rinds, along with the porosity and connectivity of pores would increase knowledge of potential for water and solute exchange

with plant roots.

The < 2 mm fraction adsorbed more P than the > 2 mm fractions on a mass basis and the amount adsorbed systematically increased with decreasing size and surface area, supporting hypothesis 2 (Fig. 5). The decrease in the variation of the amount of P adsorbed when expressed on a unit area basis suggests that SSA is one factor influencing P retention, however all the variation is not removed suggesting other factors are at play. These other factors may include differences in mineralogy, surface microtopography, porosity and pore connectivity. Phosphorus adsorption by similar ironstone gravel soils has been previously demonstrated (Weaver et al., 1992), however these previous studies have some differences. The > 2 mm fraction size distributions were reconstructed for entire unsieved soil and > 2 mm P sorption studies, whilst specific size ranges were used here to better understand and isolate the effects of particle size. The demonstration of P sorption by the > 2 mm fraction belies its physical size, and along with the low contribution of the < 2 mm fraction to the soil mass would result in the > 2 mm fraction contributing significantly to the P retained by the whole soil. For example, in a soil with 80% of the mass in the > 2 mm fraction and 20% in the < 2 mm fraction (Table 1), and with the P retention characteristics described in Fig. 5 for the highest rate of P addition, it is estimated that the > 2 mm fraction contributes to 75%, 67%, 63% and 54% of the P retained by the entire unsieved soil when the > 2 mm fraction is comprised of 2–4 mm, 4–6 mm, 6–8 mm and 8–10 mm size fractions respectively. These fractional contributions from the > 2 mm fraction will increase, or decrease, when the < 2 mm fraction is less or more P retentive respectively than the < 2 mm fraction examined here, and when the relative contributions from the < 2 mm and > 2 mm fractions to soil mass varies. For soils where the P retention of the < 2 mm fraction is around 5% of the example above, it is estimated that the > 2 mm fraction contributes 96–98% of the P retained by the entire unsieved soil. In addition, the lower surface area of the > 2 mm fraction, along with lower P retention capacity indicates that the > 2 mm fraction will saturate with P more quickly than the < 2 mm fraction. This is further reinforced by the effect of decreasing PRI with increasing P applied (Fig. 7b), the effect of which has the greatest proportional reduction with increasing particle size. Therefore the > 2 mm fraction cannot be ignored in relation to soil P and plant P dynamics.

Overall, the mineralogy of the soil used in this study was consistent with previous descriptions of common ironstone gravel soils of the Darling Range in south west WA (Anand and Butt, 2003). These soils are dominated by quartz, gibbsite, kaolinite, goethite, hematite and maghemite in the near surface layers. Cornelius et al. (2006) and Gilkes

et al. (1973) describe rounded or subrounded > 2 mm particles with dark hematitic interiors, and often lighter coloured material comprised of gibbsite and goethite as an outer coating or rind, varying in thickness up to 3 mm. Quartz grains were often embedded in or protruded the rind. This is very similar to the > 2 mm fractions seen in Fig. 3.

Whilst it is common to see morphologically distinct features of the > 2 mm fraction such as a hematitic core and gibbsite quartz rinds in fractions > 2 mm (Anand and Gilkes, 1987), the < 2 mm fraction of the soil examined here also contained particles (Fig. 3a) of similar concentric morphology (pisolites) and mineralogy as observed in the > 2 mm fraction. The dominance of quartz in the < 2 mm fraction and the relatively low clay content (Table 1) suggests that pisolites < 2 mm in size may provide an important role in soil P dynamics.

The interior of the > 2 mm fraction was compositionally distinct from the rind, composed of quartz with an impregnated cement of clays, silicates and iron oxides (Fig. 3, Fig. 4). Even though the < 2 mm fraction was dominated by quartz, it had the highest surface area and contained similar soil minerals capable of retaining P as the > 2 mm fraction. The higher surface area and P retentive minerals of the < 2 mm fraction result in higher PRI and PBI values of intact materials (Table 1). The rinds of the > 2 mm fractions were dominated by Al minerals capable of P retention (Fig. 4) and could retain P to a level that belies their physical size (Fig. 5ab).

The mineralogy of the ironstone gravel particles in this study are typical of those described in the south-west corner of the agricultural region in SWWA (Anand and Butt, 2003; Anand and Gilkes, 1987; Cornelius et al., 2006; Gilkes et al., 1973; Leopold et al., 2018); however, there is a strong geographic pattern in the geochemistry of ironstone gravels in the agricultural region of WA. A spatial analysis of the silica, iron and aluminium oxide percentages in ironstone gravels (Griffin et al., 2016) based on the survey by Cornelius et al. (2006) shows that silica dominates ironstone gravel composition in the inland areas, iron dominates where metasediments and ultrabasic rocks are the parent materials, and aluminium is most abundant in areas with historically higher rainfall, which is consistent with modelling showing that > 1200 mm annual rainfall is probably required for bauxite formation (Price et al., 1997). The impact of different mineralogy observed throughout this region on the relative adsorption and supply capacity of the < 2 mm and > 2 mm fractions requires investigation to determine whether it is possible to develop a single approach to predict whole soil P supply to crops.

In light of these findings, soil sampling techniques for situations where ironstone gravels are present need to consider how both representative and intact soil samples can be collected. In addition, analysis of soils for plant available P will need to consider including the > 2 mm fraction either through sample grinding if standard techniques of bicarbonate extractable P are used, or through the use of alternative non-destructive techniques such as DGT (Mason et al., 2013). Where measures of P retention are used in conjunction with measures of bicarbonate extractable P to support interpretation of soil analysis for fertiliser recommendation (Gourley et al., 2019), consideration will need to be given to the use of alternative measures of P retention that can retain sample integrity, for example sodium fluoride pH.

5. Conclusions

Phosphorus adsorbed onto the surface of ironstone gravels can be measured as Colwell P at concentrations capable of supporting 90% of relative yield of winter cereal crops in Australia. The 1:1 correlation of Colwell P in ground materials and intact counterparts suggests there is potential to use a similar approach for the entire unsieved soil, assuming a representative sample can be obtained and ground. Grinding of samples for the measurement of P retention measures such as PRI or PBI is not supported, neither is the use of end over end shakers due to surface abrasion of the > 2 mm fraction, however the use of Δ NaF pH offers some potential. Phosphorus adsorption by the > 2 mm fraction was less

than the < 2 mm fraction, but is likely significant in the context of the entire unsieved soil, and was influenced by SSA. Specific surface area measurements suggest greater SSA for the > 2 mm fraction than their physical size would imply, possibly influenced by the thickness and mineralogy of rinds. Factors other than SSA are likely to be important in P adsorption. Soil sampling methods that have potential to fracture or grind ironstone gravels may lead to overestimates of PBI in the < 2 mm fraction, and higher P fertilisation rates than is necessary. The P environment in the soil-solution used for analysis in the laboratory will differ to the soil-solution environment that plants have access to.

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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.

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