1. Introduction

1.1. The importance of soil phosphorus availability

Phosphorus (P) is an essential element for all life, serving as a structural component of cells, being integral in energy transfer, and a component of genes and enzymes (Campbell and Reece, 2002; Schachtman et al., 1998). More than other nutrients, P is held tightly by the soil, so only low concentrations relative to plant requirements are in the soil solution (Holford, 1997). In alkaline soils, it is generally accepted that P is retained in the soil as calcium phosphate (CaP) minerals, limiting plant growth and agricultural production (Conyers and Moody, 2009; Holford, 1997). This research investigates factors that influence the supply of P to the soil solution of alkaline Vertosols, focusing on pH and the concentration of P itself and calcium (Ca) in the solution.

1.2. Soil and study region

Vertosols (Isbell, 2002), also known as Vertisols in both the World Reference Base (IUSS Working Group WRB, 2014) and Soil Taxonomy (Soil Survey Staff, 2014), are a major soil type used for agricultural production globally, with the largest distributions in Africa, Australia, India and the Americas (Hubble, 1984). Vertosols are characterised by high clay content and shrink-swell behaviour related to wetting and drying cycles (Isbell, 2002; IUSS Working Group WRB, 2014). The soil type is common in the northern grains region (NGR) of eastern Australia, an agricultural region of 4 M ha in northern New South Wales (NSW) and southern to central Queensland (Anon., 2004; Dang et al., 2006). Seventy five percent of the NGR is used for dryland cropping and Vertosols are the most commonly cropped soil type (Dang et al., 2010). The Vertosols in the NGR are commonly alkaline, with pH increasing from the topsoil to the upper subsoil (50 cm depth) (Northcote et al., 1961-1964). Cropping has been sustained on the more fertile of these Vertosols with little to no P inputs (Bell et al., 2013a; Schwenke, 2002). However, even on the fertile soils, responses to P fertiliser are increasingly common after net removal of P in agricultural produce from the soil for two decades or more (Bell et al., 2012; Bell et al., 2013a; Schwenke, 2002). The responses to P fertiliser can be variable, and uncertainty regarding the availability of soil P and its contribution to plant nutrition can lead to the application of more of fertiliser than required for adequate plant growth (Dorahy et al., 2004; McLaren et al., 2014a).

In alkaline soils the concentration of readily available P, or labile-P, that rapidly replenishes the soil solution (Pierzynski et al., 2005) has been estimated using the bicarbonate extraction methods of Olsen et al. (1954) or Colwell (1963), with the latter more common in Australia. However, in these soils plants access acid soluble pools of P not extracted by bicarbonate (Chan et al., 1988; Lester et al., 2003; Wang et al., 2007). Accordingly, a more recent approach to estimating their P fertility has been proposed, i.e. extract with bicarbonate for readily available P (the method of Colwell (1963)), and with dilute acid to include mineral P (the method of Kerr and von Stieglitz (1938); also known as the Bureau of Sugar Experiment Stations soil P test, BSES-P). The additional P that is generally extracted using the acid is thought of as slowly available, reserve-P (McLaren et al., 2014a); yet reserve-P is poorly correlated with Colwell-P (Moody et al., 2013). The 16 h BSES procedure acidifies the soil to approximately pH 3, causing CaP minerals to dissolve as well as changing P sorption properties (Truog, 1930). Such a non-specific procedure cannot be expected to represent the replenishment of labile P by the gradual dissolution of various CaP minerals differing solubility in response to the depletion of P from solution or moderate rhizosphere acidification. Clearly there is more to learn about P behaviour in these soils in the interests of understanding P kinetics, agricultural production and P fertiliser use efficiency.

1.3. Structure of this thesis

Chapter 2 reviews the importance of P for plant growth and plant mechanisms for P uptake. The partitioning of P in soil and the processes that affect P mobility between soil P pools are also examined. Various methods used to characterise and extract P, which aim to estimate the concentration of P available to plants, are then discussed. Focusing on alkaline Vertosols, the literature review identifies mobilisation of acid soluble P following agricultural production, mobilisation which may contribute to P nutrition directly via rhizosphere acidification, or which may slowly buffer bicarbonate-extractable pools. The review identifies a critical gap in the understanding of the partitioning of P in alkaline Vertosols.

Chapter 3 is an empirical examination of the solubility of P during incremental acidification. The technique involves the release of P with acidification in conjunction with removing P from solution using exchange membranes, or by solution interchange. The chapter aims to measure the effects of acidification and P removal on the supply of acid soluble P to solution. I hypothesise that acid soluble P will be solubilised more readily in the presence of a phosphate sink and test the hypothesis by using incremental acidification, with/without anion exchange membranes (AEM) in the suspensions.

In Chapter 4, a similar approach of incremental extraction is used, but keeping the pH steady at the initial level (~pH 8), or by acidifying then holding the reaction at pH 6.5 or pH 5.5. In one treatment, the released P was extracted from solution with a P sink, and in a second treatment with P and cation sinks. This study aims to identify the release of reserve-P during co-removal of P and Ca from solution using AEM and cation exchange membranes (CEM), while maintaining pH within defined ranges. From the results in chapter 3, we expect that the release of reserve-P increases as the solution pH is lowered. In addition, I hypothesise that: 1) the removal of both Ca and P from the solution at each pH level will solubilise more reserve-P than removing P alone; and 2) at each pH level the rate of P release will be relatively constant.

In Chapter 5, bulk P K-edge X-ray absorption near edge structure (XANES) spectroscopy is conducted on the sediments retained after the incremental extraction of P at static pH levels to identify the source of the P extracted. I hypothesise that bulk P K-edge XANES spectroscopy will show that: 1) several forms of both CaP and sorbed-P species are present in each soil; 2) sorbed forms are preferentially depleted at the initial soil pH; and 3) the more soluble CaP phases are preferentially depleted from a soil solution maintained at pH 6.5.

In Chapter 6, the fate of P in the alkaline soils equilibrated at lower pH levels (i.e. without extracting P) is investigated. With bulk P K-edge XANES, geochemical modelling, and measures of extractable P during acidification and equilibration, I investigate repartitioning of P between phases. I hypothesise that XANES will show that: 1) acidified equilibrations of P will result in repartitioning from mineral to sorbed (due to 1:5 dilution) forms; and 2) the resultant P phases will yield increased extractable Colwell-P concentrations.

The conclusion of this thesis draws together the information gained during the experimental chapters to identify implications for soil testing, and provide potential practical applications, and highlight potential avenues for further improve the understanding and management of P in similar alkaline soils.

2. Literature review

2.1. Introduction

Phosphorus is an essential element for all life, serving as a structural component of cells, being integral in energy transfer, and a component of genes and enzymes (Campbell and Reece, 2002). The solid phases of P in soil are stable, so generally only low concentrations relative to plant requirements are present in the soil solution (Holford, 1997). Phosphorus is absorbed by plants from the soil solution primarily as orthophosphate ($H_2PO_4^-$ or HPO_4^{2-}) (Gaxiola et al., 2011), though a range of organic and mineral P compounds may be taken up by plants (Armstrong, 1988).

The availability of P to plants is limited by the rate of release to solution, rather than the total concentration in the soil (Abdu, 2006). The low concentrations of P in soil water in the rhizosphere would need to be replenished 20 to 50 times per day to maintain adequate levels for plant growth (Marschner, 1995). The concentration of P in solution is a balance of processes including adsorption and desorption, precipitation and dissolution, and microbial immobilisation and mineralisation (Holford, 1997). Key variables also include pH and, indirectly, the redox potential (Pierzynski et al., 2005). Due to the low solubility of P minerals, the high reactivity of P with Al, Fe and Ca ions and minerals, and competitive uptake by other soil organisms, the concentration in soil solution can be rapidly depleted and often limit plant growth (Holford, 1997). The availability of P is crucial early in the growth cycle of plants (Grant et al., 2005; Römer and Schilling, 1986). This is particularly so for short season plants, while perennial plants have more time to accrue a larger component of their P requirements from less soluble sources (Conyers, 1999). Regardless, P deficiency may occur at any stage of the growing season so the rate of replenishment of P into solution is of great importance (Skinner and Matthews, 1989).

This chapter reviews the importance of P for plant growth and how plants source P, the various pools of soil P and factors influencing the mobility of P between these pools. I then review extraction methods used to estimate the availability of P to plants. Spectroscopic and modelling techniques used to characterise P forms are then reviewed. Reflecting the importance of P, large amounts of literature exist on these topics; this review focusses on research relevant to the mobility and availability of P in alkaline Vertosols. In particular, these soils occupy a large proportion of the highly productive NGR of northern NSW and southern Queensland, Australia (Dang et al., 2006). Traditionally, cropping has been sustained on the more fertile of the Vertosols in the NGR with little to no P fertiliser (Bell et al., 2013a). However, removal of P in agricultural produce from the soil at rates greater than replacement for periods of two decades or more has resulted in increasing reports of yield responses to P fertiliser (Bell et al., 2012; Bell et al., 2013a). These and other similarly alkaline soils have been the focus of a body of research investigating the management, availability and mobility of soil P (Chan et al., 1988; Dalal and Mayer, 1986; Guo et al., 2000; Hinsinger and Gilkes, 1995; Lester et al., 2003; McLaren et al., 2014a; Pundarikakshudu, 1989; Solis and Torrent, 1989a; Wang et al., 2007), however questions remain regarding the circumstances and mechanisms of P mobility.

2.2. Plant P nutrition

Phosphorus is used in the metabolic processes of energy transfer, respiration and photosynthesis and is a structural component of nucleic acids and of many coenzymes, phosphoproteins and phospholipids (Campbell and Reece, 2002; Grant et al., 2001). The importance of P for energy transfer is reflected in legumes requiring higher concentrations of P to fix N_2 (Israel, 1987; Smyth and Cravo, 1990). When P supply is adequate, most P in the plant is stored as orthophosphate in the vacuole or in storage compounds such as polyphosphate or phytate, reserves which can be used if P uptake becomes limited (Grant et al., 2001). The redistribution of phosphorus within the plant may therefore mediate short term uptake deficiencies (Veneklaas et al., 2012), though persistent low P availability will reduce productivity (Schachtman et al., 1998).

Phosphorus deficiency can delay leaf emergence, slow the expansion of leaves, decrease the final surface area (Colomb et al., 2000), cause earlier leaf senescence (Batten and Wardlaw, 1987; Grabau et al., 1986), and result in higher root:shoot ratios (Mollier and Pellerin, 1999). Such effects decrease photosynthesis (Grant et al., 2001) and the production of carbohydrates (Colomb et al., 2000; Mollier and Pellerin, 1999), slowing rates of growth and development (Batten and Wardlaw, 1987; Grabau et al., 1986). Examples of the impacts of P deficiency include decreased yields due to fewer fertile ears and grains per ear in wheat (Römer and Schilling, 1986), and decreased pod retention and seed size in soybean (Grabau et al., 1986). These effects can decrease apparent water use efficiency, with increased evaporative loss and less productive transpiration (Grant et al., 2001).

2.2.1. P acquisition by plants

Phosphorus uptake is greatest between pH 5 and 6, when the dominant P species is $H_2PO_4^-$ (Schachtman et al., 1998). Monovalent $H_2PO_4^-$ is preferentially absorbed over HPO_4^{2-}, even in alkaline soils (Hinsinger et al., 2003; Kovar and Classens, 2005). Even in a fertilised soil, the majority of P that a plant absorbs is cycled from solid phases (Mclaughlin et al., 1988b). The majority (>90%) of P that reaches the root moves by diffusion through the soil solution, along a concentration gradient generated by uptake (Barber, 1995; Schachtman et al., 1998). Diffusion is slow (Hedley and McLaughlin, 2005), though proportional to the concentration of P in solution (Moody et al., 1990).

The active uptake of phosphate maintains cellular P concentrations of 1-10 mM, up to four orders of magnitude greater than in the soil solution (Rausch and Bucher, 2002). The high P concentration in the cytoplasm, and the negative membrane potential of plant cells, indicate active inorganic P (Pi) uptake and accumulation via high affinity Pi transporters (Liu et al., 1998; Schachtman et al., 1998). The co-uptake of Ca also appears to be important in P uptake by decreasing the sorption of P to clays (Devau et al., 2013; Devau et al., 2010).

When P uptake is limited, plant responses include more root growth, and more effective associations with mycorrhizae (Schachtman et al., 1998). Within the plant, Pi stored in the vacuole can be mobilised from stems and older leaves to younger leaves, growing shoots and to the grain (Schachtman et al., 1998). During periods when P uptake exceeds demand it can be stored in organic compounds (e.g. phytate) (Schachtman et al., 1998). Grain yield can be supported by moving P from the leaves and stems to the grain and in some cases by ongoing uptake after anthesis (Miller et al., 1994; Mohamed and Marshall, 1979; Rose et al., 2007; Sutton et al., 1983). If high concentrations of P are available, the rate of uptake may be lowered and P may even be exuded (up to 70% of the influx), to prevent the accumulation of toxic Pi concentrations (Schachtman et al., 1998).

2.2.2. Root morphology

Phosphorus uptake by plants varies widely between species due to differences in maximum uptake rate, the minimum solution concentration at which uptake occurs, root surface area (through branching or root hairs), and rhizosphere modification (Moody and Bolland, 1999; Richardson et al., 2009). Larger root systems have a greater capacity for P uptake (Lynch, 1995), though increases in P uptake rate are not necessarily proportional to increases in the size of the root system (Krannitz et al., 1991). Finer root systems with higher ratios of surface area to volume, such as in many grasses, more effectively utilize a volume of soil and so have greater P uptake (Conyers and Moody, 2009; Lynch, 1995), though thick roots can overcome physical constraints that limit access to soil P (Conyers, 1999).

Important aspects of the root systems are architecture and plasticity (Hinsinger et al., 2011; Lynch, 2007; Niu et al., 2013). Only a small volume of the soil is explored by roots, estimated for annual crops by Barber (1995) as approximately 1% of the topsoil volume. The ability to change rooting pattern (be plastic) to P rich zones in the soil enables more efficient use of C resources to obtain nutrients (Lynch and Ho, 2005). Plasticity may be observed as a greater concentration of root hairs (Liu et al., 2006), more branching, longer laterals (Flavel et al., 2014), or the formation of cluster (proteoid) or dauciform roots (Gardner et al., 1982; Niu et al., 2013; Shane et al., 2006). These adaptations can increase plant growth by better utilizing P rich regions (e.g. by proliferation of lateral roots and root hairs) or by better exploiting recalcitrant forms of P by concentrating exudates as done by proteoid roots (Marschner, 1995; Niu et al., 2013).

A further adaptation to the low availability of P and other nutrients are the symbiotic associations with mycorrhizal fungi formed by 90% of terrestrial plants (Schachtman et al., 1998). These fungi depend on plants for their C source (Hause and Fester, 2005) and supply nutrients, particularly P, to the plants (Smith and Read, 1997). Mycorrhizal hyphae increase the volume of soil explored (Bolan, 1991; Hause and Fester, 2005). They also increase the rate of uptake of P, and lower the concentration of P in solution more than the plant is able to (Bolan, 1991). Using phosphatases, mycorrhizae acquire P from organic sources that are not available directly to the plant (Hayman, 1983; Jayachandran et al., 1992; Schachtman et al., 1998) and dissolve CaP minerals (Rosling et al., 2007). Mycorrhizal associations can be isolated to regions of low P in the root zone (Lu et al., 1994), and tend to be less effective in soils with adequate P (Schachtman et al., 1998; Smith et al., 2003).

2.2.3. Plant physiology

The complex processes by which root exudation and uptake influence rhizosphere conditions is beyond the scope of this review: see Vance et al. (2003), Hinsinger et al. (2003) and Richardson et al. (2009) for more extensive reviews. Briefly, in addition to forming mycorrhizal associations and altering rooting patterns, plants can overcome low P availability by exuding phosphatases, chelating compounds, organic acids/anions, protons and hydroxyls, by expression of P transporters and by inducing hypoxic conditions in the rhizosphere. The P uptake efficiency of many plants increases under P stress, with high affinity P transporters activated at low cellular P concentration (Liu et al., 1998). Plants may use combinations of these processes to increase the uptake of P. Lastly, internal redistribution of P can also ameliorate the effects of low concentrations of available P (Schachtman et al., 1998).

Root exudates can account for approximately 10–50% of photosynthate, which has a large effect on rhizosphere conditions (Richardson et al., 2009). Respiration from microbial decomposition of exudates and locally associated organic matter, and respiration by plant roots, can increase the partial pressure of CO_2 in the rhizosphere and acidify alkaline soils (Gras (1974), cited in Hinsinger et al. (2003)). This intense microbial activity can induce reducing conditions near the growing root tip due to rapid oxygen consumption (Marschner et al., 1986a).

An important group of exudates are phosphatases that can mineralise organic P (Nuruzzaman et al., 2006). This process is particularly valuable for species such as cotton, where other strategies, such as acidification are not effectively deployed (Wang et al., 2011). Different plants excrete a wide range and concentration of organic acids, e.g. citric, oxalic and malic acids. The acids may be excreted in concentrations great enough to acidify the rhizosphere (Hinsinger et al., 2003; Marschner et al., 1986a). Excreted as organic anions, they may buffer rhizosphere pH, indirectly acidify soil by being counterbalanced by OH^- influx or H^+ efflux, or have nil effect on pH if excreted with accompanying cations e.g. K^+ (Hinsinger et al., 2003). The anions, e.g. citrate, can also chelate Al and Fe, releasing bound P thus increasing the concentration of P in solution (Marschner et al., 1986a).

A direct source of rhizosphere acidification, particularly in non-proteoid species, occurs due to the excretion of H^+ to balance the net greater uptake of cations than anions (Hedley et al., 1982a; Hinsinger et al., 2003). Legumes in particular excrete large amounts of protons (Hinsinger and Gilkes, 1995; Tang et al., 1997). Acidification of the rhizosphere in neutral and alkaline soils can dissolve CaP (Hinsinger and Gilkes, 1995; Lehr and Brown, 1958). However, as this process is energy expensive, a high soil pH buffer capacity, or CaP in less soluble forms, may put this mechanism beyond the capability of some individual plants, genotypes or species (Gollany and Schumacher, 1993; Lynch and Ho, 2005; Schubert et al., 1990; Zoysa et al., 1998).

2.3. Phosphorus pools in soil

The typical concentration of total P (Pt) in soils is 500 – 2000 mg kg^{-1}, with extremes of 35 – 8000 mg kg^{-1} (Frossard et al., 2000; Hesterberg, 2010; McLaren et al., 2015a; Vance et al., 2003). Like many other nutrients, P is concentrated near the soil surface due to plant acquisition from depth, retention by the soil, and fertiliser application (Hesterberg, 2010).

More than 170 P minerals have been identified in soil (Holford, 1997). The majority of soil P is in various solid phase compounds which are in dynamic equilibrium with a much smaller quantity in the soil solution (Pierzynski et al., 2005). The solid phase of Pt comprises organic P (Po) and Pi species.

Phosphorus cycling and its availability to plants are influenced by the amounts and forms of Pi and Po, soil solution chemistry (redox, pH, ionic strength), microbial activity, moisture (Pierzynski et al., 2005). In alkaline/calcareous soils, the main groups of P are labile P, P sorbed to Al or Fe oxy/hydroxides, CaP minerals, and occluded P (Adhami et al., 2007). Manganese can be more active than Fe in P cycling in anaerobic sediments (White et al., 2008), though information on manganese phosphates in alkaline soils is limited (Adhami et al., 2007).

The solubility of the mineral forms vary depending on the soil pH, mineral substitution, and surface area (Pierzynski et al., 2005). In relatively young, unweathered alkaline soils, CaP tend to comprise the major pool of soil P. With time, the total Pt generally decreases, and the proportion of occluded and organic forms increases (Prietzel et al., 2013; Richardson et al., 2004; Walker and Syers, 1976).

2.3.1. Solution P

Typical concentrations of P in solution are from <1 to-10 µM (Conyers and Moody, 2009; McLaughlin et al., 1999), but may be as great as 250 µM in fertilised soils (Pierzynski et al., 2005). The predominant form of P in the soil solution is the orthophosphate ion $H_2PO_4^-$ (for pH 4-7.2) and HPO_4^{2-} (for pH >7.2) (Pierzynski et al., 2005). The concentration of P in solution is maintained at a low level by microbial uptake and by surface reactions with clay minerals, aluminium and iron oxides, and calcium and magnesium minerals, while soil organic matter (SOM), depending on form, may increase or decrease sorption (Debicka et al., 2015; Guppy et al., 2005; Mclaughlin et al., 1988a; Pierzynski et al., 2005). These reactions are the process of buffering of the soil solution concentration. The removal of P from solution causes buffering firstly from labile pools, and subsequently from more recalcitrant pools (Pierzynski et al., 2005). Conversely, addition of P through mineralization of organic matter or fertiliser addition induces a buffering to solid phases. Initial sorption reactions may be followed by absorption into solid phases or occlusion (Kadlac and Wallace, 2009), and precipitates may transform to less soluble species (Hedley and McLaughlin, 2005; Lindsay, 1979).

Phosphate is relatively immobile in most soils, with movement primarily by diffusion (Schachtman et al., 1998). Phosphate can also move by mass flow in soils where macropore flow occurs, such as sandy soils, cracking clays and highly organic soils, particularly when high quantities of fertiliser or manures have been applied (Grant et al., 2005; Pierzynski et al., 2005). Glæsner et al. (2011) found substantial particulate P leaching during irrigation, though little dissolved Pi or Po was leached.

2.3.2. Mineral P

Apatite ($Ca_{10}(X)(PO_4)_6$, where X is F^-, Cl^-, OH^- or CO_3^{2-} , is the primary source of P in soil (Pierzynski et al., 2005). Calcium phosphate minerals form a large pool of P in alkaline soils (Fixen et al., 1983; Lindsay, 1979), particularly in those soils which have undergone limited weathering, such as some Vertosols in the NGR (Cross and Schlesinger, 1995; Walker and Syers, 1976). The various CaP minerals are increasingly soluble below pH 8; although the rate of dissolution varies with species (Lindsay, 1979), surface area, co-precipitation and substitution (Pierzynski et al., 2005). Common CaP minerals in soil, in order of decreasing solubility, are brushite (or dicalcium phosphate dihydrate, DCPD, $CaHPO_4 \cdot 2H_2O$), monetite (or dicalcium phosphate, DCP, $CaHPO_4$), octacalcium phosphate (OCP, $Ca_8H(PO_4)_6 \cdot 5H_2O$), β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), and the apatites hydroxyapatite (HAp, $Ca_5(PO_4)_3OH$) and fluorapatite (FP, $Ca_5(PO_4)_3F$). Strengite and variscite (Fe and Al phosphates) are more stable at acidic pH levels (Lindsay, 1979; Sato et al., 2005; Wright and Peech, 1960).

Calcium phosphate minerals in the soil may be native, and include precipitates on calcite (Lindsay, 1979; Pierzynski et al., 2005). A portion of P applied in fertilisers may initially react with the soil to precipitate as CaP minerals, and these products are more likely to comprise the CaP minerals found in non-alkaline soils (Hedley and McLaughlin, 2005). A greater proportion of P tends to precipitate when applied to alkaline/calcareous soils in solid granular form compared to liquid fertilisers (Lombi et al., 2006). Calcium phosphate minerals have been identified by synchrotron based spectroscopy, and inferred via acidic extractions, in moderately acidic soils: examples of acidic soils containing CaP minerals include those that have had recent additions of P fertiliser or manures (Beauchemin et al., 2003; Liu et al., 2015; Sato et al., 2005), but also some that have not had P fertiliser applied for 15 years (Liu et al., 2015). A further example of moderately acidic soils containing CaP minerals was reported by Delgado and Torrent (2000), who used a sequential fractionation procedure to infer the presence of CaP minerals in a soil limed to ameliorate acidity.

Relatively soluble mineral phosphates in soil are either depleted or transformed to more stable forms over time. Transformation from more to less soluble CaP forms tends to increase over time (Alvarez et al., 2004; Bell and Black, 1970b; Lindsay, 1979; Lombi et al., 2006; Sato et al., 2005). The process of transformation can be relatively slow, with intermediate forms that are available to plants persisting for months to years (Delgado and Torrent, 2000; Havlin and Westfall, 1984; Strong and Racz, 1970). Organic matter, e.g. humic substances, can slow the transformation of Ca-P minerals to more stable forms (Alvarez et al., 2004; Song et al., 2006). The slower transformation may be due to the formation of less crystalline species that persist for longer than the intermediate species that form in their absence, or slowed crystal growth due to adsorption of the organic ligand onto the seed crystal (Alvarez et al., 2004; Inskeep and Silvertooth, 1988).

Whilst the solubility products of mineral species may ultimately control the solution P concentration (Lindsay, 1979), their influence is affected by sorption and desorption reactions, the slow kinetics of mineral equilibria, and the differing solubilites of pure minerals, amorphous precipitates and minerals with isomorphous substitution (Fixen et al., 1983; Havlin and Westfall, 1984; Pierzynski et al., 2005). In addition, sorption may have a stronger influence on the concentration of P in solution depending on pH. Murrmann and Peech (1969b) reported on the concentration of P in solution of two soils that had a history of high P fertiliser application. They manipulated the pH both up and down from the initial value and found that the concentration of P in solution near pH 8 fitted the OCP isotherm and below pH 6 was less than that in equilibrium with hydroxyapatite. That is, at low pH the concentration in solution was controlled by sorption not mineral solubility. Similarly, (Devau et al., 2009) reported that in soils with a low degree of P saturation (i.e. the ratio between concentration oxalate-extractable P to the concentration of co-extracted Al and Fe), sorption controlled the concentration of P in solution.

2.3.3. Sorbed P

Compared to the buffering of solution P by mineral precipitation/dissolution, the rate of sorption processes are rapid (Froelich, 1988; Wang et al., 2013). The equilibration of P in the soil solution involves sorption and desorption reactions with many types of surfaces that provide anion exchange capacity. These surfaces include hydrous Al and Fe oxide minerals and coatings on other surfaces, highly weathered kaolin clay minerals (at low pH), the edges of clay micelles, clays with structural Fe, carbonates, and organic matter (Froelich, 1988; Kizewski et al., 2011; Singh and Gilkes, 1992). Surface complexes of P on Fe and Al oxy/hydroxides, and clay minerals, by ligand exchange of surface OH_2 or OH^- groups with phosphate initially forms a relatively weak monodentate bond from which P may readily desorb (Rájan and Fox, 1972; Sato and Comerford, 2005).

Subsequent rearrangement of monodentate bonds can yield stronger bidentate-binuclear bonds, decreasing P mobility (Borggaard, 1983; Khare et al., 2007; Rájan and Fox, 1972; Sato and Comerford, 2005; Schwertmann, 2008). Alternatively, Wang et al. (2013) found that inner sphere sorption onto ferrihydrite, goethite and hematite was mainly binuclear bidentate. Sorption onto the Fe oxyhydr/oxides was preferentially via exchange with two $Fe\text{-}OH_2^{1/2+}$ groups, and secondly with a $Fe\text{-}OH_2^{1/2+}$ and $Fe\text{-}OH^{1/2}$ (Wang et al., 2013). The initial sorption reactions are thought to occur within minutes to hours (Froelich, 1988), then slows as the specific adsorption of P makes the surface more negative (Rajan, 1976). The reactions occur over a wide range of pH (Holford and Mattingly, 1975; Solis and Torrent, 1989b), but are favoured at low pH due to charge characteristics and the lower solubility of Al and Fe oxy/hydroxides compared with more crystalline mineral forms in acidic environments (Goldberg and Sposito, 1984a). Phosphate can sorb to carbonates, followed by growth of CaP precipitates (Freeman and Rowell, 1981; Wang et al., 2012; Weng et al., 2012). With the growth of precipitates, occlusion by growth of oxide phases, or diffusion into Fe oxides, more stable sorption develops over days and months to years (Barrow, 1983b; Bolan et al., 1985; Castro and Torrent, 1998; Froelich, 1988; Khare et al., 2005).

The strength of sorption by electrostatic retention tends to decrease as saturation increases due to decreased binding energy as the distance from the sorption surface of subsequent orthophosphate ions increases (Barrow and Debnath, 2014; Guppy et al., 2005). Electrostatic sorption to Al and Fe oxy/ hydroxides in soils may be mediated by the presence of sorbed Ca, which can have a large influence of P sorption at high pH (Weng et al., 2011). Whereas P sorption to oxy/hydroxides increases as pH decreases, in soil the decreasing sorption of Ca to oxyhydroxides at lower pH leads to less P sorption than at higher pH (Rietra et al., 2001; Weng et al., 2011).

It is increasingly considered that clays play an important P role in P sorption, though the extent of their influence is debated. For example, re-analysis of historic data indicates that surface complexation on clays may be as important to P sorption as that on metal oxy/hydroxides, influenced by structural Fe in the clays and surface area (Devau et al., 2009; Devau et al., 2013; Gérard, 2016; Lumsdon, 2012; Weng et al., 2011).

Organic matter variously increases, decreases or does not affect P sorption, and the effects are sometimes confounded by the inclusion of P in added organic matter (Guppy et al., 2005). Humic substances may be bound to Fe/Al surfaces blocking phosphate binding sites and thereby decreasing P adsorption (Moshi et al., 1974; Weng et al., 2012). The magnitude of the decreased adsorption is dependent on pH (Sibanda and Young, 1986), and is likely restricted to the rhizosphere as exudates are ephemeral (Guppy et al., 2005). Conversely, humic substances may inhibit the crystallization of Al and Fe oxy/hydroxides (Schwertmann, 1966) which maintains greater sorption capacity (Borggaard et al., 1990; Wang et al., 2013). The formation of ternary complexes of humus-iron-orthophosphate greatly increases the P adsorption capacity of humus, and the sorption ratio of P:Fe is greater with humus than as amorphous Fe(III) hydroxides (Gerke and Hermann, 1992). The electrostatic influence of Ca on P sorption was also observed by Gerke and Hermann (1992), who observed that the greater sorption by ternary complexes was enhanced by Ca in solution at pH 6.2 but not at pH 5.2.

2.3.4. Organic P

The proportion of organic P tends to be greater in soils that are relatively more weathered (Walker and Syers, 1976). Organic P is contained in plant residues and the microbial biomass, as part of humic molecules, phytate, and a range of other compounds including phospholipids, DNA and a range of phosphomono- and di- esters (Hesterberg, 2010;

McLaren et al., 2015c; Pierzynski et al., 2005). Phytate has long been considered to comprise a large proportion of Po, though recent analyses and interpretation of NMR spectra suggests that phytate has been overestimated (Doolette et al., 2010; Doolette et al., 2011b; McLaren et al., 2015c).

Up to 75% of P in freshly added organic matter is Pi, and is expected to remain as Pi until rapid incorporation into Po by soil microbes when there is sufficient soil moisture (Mclaughlin et al., 1988a). The majority of Po has likely been processed by and released from microbes rather than being direct plant residues (Kirkby et al., 2013; Mclaughlin et al., 1988a). Organic P must be mineralised by microbes or and enzymatic hydrolysis to become available to plants (Guppy and McLaughlin, 2009). In alkaline Vertosols, McLaren et al. (2014b) found that most of the organic P is not plant available over the growing season, and that inorganic P was of more importance to P management.

2.4. Processes influencing P mobility between pools

2.4.1. Phosphorus buffering capacity

Phosphorus buffering capacity is the ability of a soil to maintain a stable concentration of P in solution as P is added or removed (Holford, 1997). Buffering is a dynamic process where desorption or dissolution from the solid phase occurs in response to the removal of P from solution, while sorption, precipitation or immobilisation occurs as P is added to solution (Pierzynski et al., 2005). Phosphorus buffering is the reason for the widely observed relatively inefficient uptake of fertilisers (McLaughlin et al., 2011), although it can also minimise P leaching (Djodjic et al., 2004).

Desorption is a more important process to plants, and it occurs more slowly than sorption (Pierzynski et al., 2005; Sato and Comerford, 2005). Hysteresis develops between sorption and desorption as P accumulates in more recalcitrant sorbed and mineral pools over time

(Barrow, 1983b). Initial desorption may be relatively rapid in a soil with a high proportion of labile or weakly held P, but decreases as this pool becomes depleted (Guppy et al., 2005; Koopmans et al., 2004; Nafiu, 2009). Plants adapt their root morphology and can alter the soil in the rhizosphere, though highly buffering soils present a clear challenge to plant growth. When the rate of plant uptake is greater than desorption, dissolution of mineral species can become an important source of P (Holford, 1997). Holford (1997) argued that desorption hysteresis observed in between adsorption and desorption in batch experiments is not so relevant in the soil environment due to rhizosphere modification, such as exudates or acidification (Marschner et al., 1986a; Richardson et al., 2009).

Desorption from oxy/hydroxides in soil is slow and partly irreversible due to the strength of specific sorption bonds and occlusion (Cornell and Schwertmann, 2003; Wang et al., 2013) due to micropores and the formation of binuclear bonds. However, Barrow (1983a) considered that even the more strongly held P can move into solution if a low enough solution concentration is maintained.

Changes in the concentration of Ca in solution affect the buffering of P from sorbed and mineral pools. With sufficient Ca in solution, the addition of P can result in precipitation of CaP minerals (Tunesi et al., 1999). Conversely, a decrease in the concentration of Ca by exchange, complexation or uptake, can induce CaP mineral dissolution, as reviewed by Hinsinger (2001).

Langmuir and Freundlich equations are commonly fitted to sorption isotherm data. There is some disagreement over the fitting of these alternative curves. The parameters of the Langmuir equation are used to interpret sorption properties, but the relationships do not necessarily reflect real phenomena. In addition, the Langmuir equations (single or double surface) indicate a constant affinity for sorption though this is not observed in practice

(Barrow, 2008). For better data fitting and conceptual reasons, Barrow (2008) preferred the Freundlich equation.

2.4.2. Fluctuations between reducing and oxidising conditions

Fluctuations between reducing and oxidizing conditions in the soil are important because plant uptake of P ceases soon after the onset of waterlogging, with significant yield penalties if waterlogging occurs at sensitive growth stages (e.g. anthesis) (de San Celedonio et al., 2014; DeLaune et al., 1999; Dodd et al., 2013). Reducing conditions develop in soils when O_2 supply does not meet the biological oxygen demand. This begins to occur within hours of waterlogging due to slow diffusion of O_2, which is more than 10,000 times slower in soil than through air (Ponnamperuma, 1972; Vepraskas and Sprecher, 1994). The occurrence and rate of development of reduced conditions is heterogeneous within a soil, and is influenced by microbial activity, and the concentration and lability of organic matter (Grunth et al., 2008), soil porosity and related factors such as sodicity (Dodd et al., 2013). As O_2 is depleted, a wide range of fungi and bacteria (Lovley, 1991) can reduce NO_3, Mn, Fe, SO_4 or CO_2, occurring sequentially in that order (Shahandeh et al., 2003; Vepraskas and Sprecher, 1994). In acidic soils, pH rises in anaerobic conditions as NO_3, Mn(IV) and Fe(III) are reduced, whilst in calcareous soils, pH falls as CO_2 in the soil water reacts to form H^+ and HCO_3^- (Hesterberg, 2010; Kovar and Classens, 2005). Near the growing root tip, reducing conditions generated due to cellular respiration and microbial decomposition of organic matter can also occur (Marschner et al., 1986b).

Hydrologic equilibration can be slow as the rate of water flow in fine soil pores is very slow. The solum may therefore contain aerated macropores or cracks within a reduced matrix (Jacob et al., 1997; Page et al., 2002). Vertosols have dynamic porosity characteristics, particularly in cracking clay soils, where permeability may vary by over two orders of magnitude across short distances (Wells et al., 2007).

Although P is not directly involved in reduction processes (Scalenghe et al., 2002), the concentration of P in solution generally increases as soils become reduced due to reductive dissolution of Fe(III) and associated P, the release of P from microbial biomass and P-iron-humus complexes, and the trend toward pH neutrality (Gächter et al., 1988; Hutchison and Hesterberg, 2004; Kovar and Classens, 2005; Paige et al., 1997; Stumm and Sulzberger, 1992). The greater the Fe content reduced, and the greater the degree of P saturation of Fe sites, the more P is released into solution (Pierzynski et al., 2005; Scalenghe et al., 2002; Shao et al., 2006). When (pe+pH) <12, redox potential increases the solubility of P and Fe (Lindsay, 1979), although this varies between soils (Lefroy et al., 1993) Indirectly, hydrogen sulfide produced by microbial reduction of sulfate may also contribute to an increase in the concentration of P in solution by converting the iron phosphate to ferrous sulfide (Welp et al. (1983); cited in Lefroy et al. (1993)).

Phosphorus released during Fe reduction may be removed from solution, for example by Al (Murray and Hesterberg, 2006) or Fe(II) minerals (Barber, 2002). As wet soils dry out and oxidizing conditions return, Fe(III) oxy/hydroxides form and resorb P (Willett, 1989; Willett et al., 1978), and Fe(III) phosphates precipitate (Abdu, 2006). However, the aging of oxy/hydroxides (e.g. transformation of the high surface area ferrihydrite to minerals with lower surface area, e.g. goethite or hematite (Schwertmann, 2008), gradually diminishes P sorption capacity (Parfitt, 1989).

Reducing conditions have been considered to be not important in alkaline soils due to a lack of reductant-soluble P (Reddy and Patrick, 1983). However, as Adhami et al. (2012) found, more substantial proportions of applied P were transformed into Al- and Fe-P fractions in highly calcareous soils, than previously reported, indicating that reducing conditions may influence P mobility. Iron compounds may not be a dominant P sink in the Vertosols of the NGR, however an increase in sorption may contribute to lowering the P concentration in solution. Soils waterlogged for relatively short time periods, and that contain low concentrations of organic matter, would undergo lesser changes to sorption properties (Willett and Higgins, 1978), particularly at neutral to alkaline pH (Willett, 1989).

2.4.3. Acidification

As pH decreases below 8, CaP minerals become increasing unstable, the dissolution of CaP minerals may directly replenish solution P (Lindsay, 1979; Marschner et al., 1986a). This potential replenishment applies equally to acidification of the solum and to microsites within it, which is a potential mechanism for the depletion of acid soluble P by agricultural production (Dalal, 1997; Wang et al., 2007).

Rhizosphere acidification by 2 pH units (Grinsted et al., 1982; Hinsinger and Gilkes, 1995; Youssef and Chino, 1989) or as much as 2.7 pH units (Dinkelaker et al., 1989) – has been measured in neutral and alkaline soils for various species of brassicas, cereals and legumes, with the latter generally most effective at decreasing the pH of the rhizosphere (Gollany and Schumacher, 1993). With acidification, the presence of Ca:P ratios in the soil solution close to those of CaP minerals may also indicate dissolution of CaP minerals (Bell and Mika, 1979; Lindsay, 1979; Nezat et al., 2008). Rhizosphere acidification has been associated with plant uptake of P both from solution (Dinkelaker et al., 1989; Hinsinger and Gilkes, 1995) and directly from CaP (Blum et al., 2002; Lehr and Brown, 1958). Rhizosphere acidification, therefore, may be the process behind the depletion of acid soluble reserve-P in the Vertosols of the NGR (Chan et al., 1988; Dalal, 1997; Wang et al., 2007) and elsewhere (Pundarikakshudu, 1989; Solis and Torrent, 1989a).

The degree of acidification is affected by the soil pH buffer capacity, which is influenced by clay type and content (Volk and Jackson, 1963), organic matter (Ritchie and Dolling, 1985), and mineral components such as calcite (Lund et al., 1975) and dolomite (Ebeling et al., 2008) as well as the form and concentration of CaP (Hinsinger, 2001; Hinsinger and Gilkes, 1995). The availability of CaP minerals to plants is therefore likely to differ between species and genotypes in proportion to their capacity to acidify the rhizosphere and decrease the concentration of P in the soil solution (Conyers and Moody, 2009; Fageria and Stone, 2006; Gollany and Schumacher, 1993; Grinsted et al., 1982; Hinsinger, 2001; Hinsinger and Gilkes, 1995; Marschner et al., 1986a; Schachtman et al., 1998). However, rhizosphere acidification is energy expensive for plants, and if the pH buffer capacity of the soil is large, the acidification capability of some plant species or genotypes may be insufficient to access acid soluble P (Lynch and Ho, 2005; Schubert et al., 1990). Rhizosphere acidification need be sustained only long enough to release P in the localised parts of the root zone actively taking up nutrients. This would minimise the energy cost (Gollany and Schumacher, 1993; Marschner et al., 1986a).

The potential availability of sorbed P or mineral CaP phases by acidification has been exploited by the application of elemental sulfur (S^0) or sulfuric acid (H_2SO_4). The acidity generated by microbial oxidation of S^0 may increase plant available P from rock P and soil apatite, though effects are generally confined to the surface where S^0 is applied (Jaggi et al., 2005; Modaihsh et al., 1989). In a greenhouse trial, the co-application of S^0 with rock phosphate increased P uptake from the rock phosphate and doubled the yield of maize (Matamwa et al., 2015). With the application of H_2SO_4 to alkaline soils, Khorsandi (1994) found increased bicarbonate-extractable P, P uptake and sorghum yields before pH buffered. In addition to causing the dissolution of CaP minerals, soil acidification has increased solution P concentrations in neutral and acidic soils (Barrow, 1984; Devau et al., 2009; Weng et al., 2011). In these cases Ca^{2+} may be desorbed from the surfaces, and the subsequent increase in their net negative charge increases the electrostatic repulsion of orthophosphate anions (Weng et al., 2011).

2.5. Soil phosphorus testing

The predictive strength of soil P testing is crucial for fertility management. The definition of critical P levels in soil tests is complicated by the effects on P uptake of diverse soil, plant and environmental factors. These factors include: P diffusion, soil type, soil physicochemical and biological factors, season (including rainfall amount and distribution), and crop physiology (McLaughlin et al., 1999; Moody and Bolland, 1999). In addition, the processes of grinding, sieving and mixing in preparation for analysis can create artefacts in the behaviour of soil P in the laboratory (McLaughlin et al., 1999).

Given the complexity of P behaviour in soils and of plant/soil interactions described above, it would be naïve to expect a chemical extraction to be strongly predictive of P uptake by a wide range of plants on a wide range of soils. The large range of test methods proposed for the purpose is testament to this prediction. At best a P test provides a relative estimate of P availability (Sibbesen, 1983), and its effectiveness increases the better it correlates with plant uptake (McLaughlin et al., 1999). In practice, reliability is therefore often limited to particular conditions (Myers et al., 2005). Further, the 'critical value' of the most suitable test for a soil can vary between plant species which have different rates of demand for P (Moody et al., 1997; Moody et al., 1990). Given this high degree of complexity, Holford and Doyle (1992) considered the development of a universal measure for labile P to be unlikely. Nonetheless, correlations between test values and plant uptake or fertiliser requirement can be improved by accounting for different soil properties which affect P availability (Colwell and Donnelly, 1971).

Soil P tests can be grouped into five types: 1. dissolution in water, dilute salt solutions or acidic solutions; 2. adding anionic sinks to the water or salt extractions; 3. desorption and ion exchange; 4. isotopic exchange (Chardon et al., 1996); and 5. measures of P buffering capacity (Barrow, 2000; Bolland and Windsor, 2007; Bowman and Olsen, 1985; Sibbesen, 1983).

2.5.1. Type 1 P tests: dissolution in water, dilute salt solutions or acidic solutions

The water, dilute salt solutions (e.g. 0.005-0.01 M $CaCl_2$ (Rayment and Lyons, 2011), dilute KCl (Holford and Doyle, 1992)) and acid methods of Type 1 provide a measure of the P in the soil solution (Bache and Williams, 1971). Acid extractants of various concentrations, such as dilute H_2SO_4 (Kerr and von Stieglitz, 1938; Truog, 1930), Mehlich 1 (0.05 N HCl and 0.025 N H_2SO_4) (Mehlich, 1953) and HCl (Barber, 1958; Warren and Cooke, 1965), can be well suited to acidic, low cation exchange capacity soils. The method of Kerr and von Stieglitz (1938), commonly known in Australia as the Bureau of Sugar Experimental Stations (BSES) was modified from the Truog (1930) procedure for acidic soils under sugar cane in Australia. In alkaline soils, however, the acidic extractants may overestimate available P by dissolving more P (i.e. CaP minerals) than is available to plants in a growing season (Tiessen and Moir, 2008). Acidic extractions may also operate partly as Type 3 tests, desorbing P from Al and Fe oxyhydroxides. Acidic extractions have also been used in fractionation schemes or to estimate mineral or reserve supplies of P (Guppy et al., 2000; Hedley et al., 1982b; McLaren et al., 2014a).

2.5.2. Type 2 P tests: anionic sinks to the water or salt extractions

Type 2 methods include anion exchange resins (AER) or AEM, iron oxide impregnated paper strips (FeO) and diffuse gradients in thin films (DGT). The FeO and DGT have a similar sink (ferrihydrite), as generally do the AEM and AER (Amer et al., 1955; Chardon et al., 1996; Guo et al., 1996; Mason et al., 2010; Myers et al., 2005; Skogley and Dobermann, 1996). In contrast to other test methods in which P accumulates in the extracting solution, these procedures remove P from solution. For P extraction, the AEM, AER and FeO are generally tumbled in a soil suspension, and the DGT are commonly placed on the surface of moist soil, though all may be used both *in situ* and in suspension (Mason et al., 2010; Menon et al., 1990; Qian and Schoenau, 2002; Santner et al., 2015). The development of AEM removed much of the difficulty of managing separate particles of resin (Saunders, 1964) and AEM have replaced AER use. The AEM are generally saturated with HCO_3^- or Cl^- as the counter-ion (Mclaughlin et al., 1994; Myers et al., 2005).

The type 2 tests are considered to measure P obtained from solution, desorption and dissolution (Moody et al., 2013), and as such provide an indication of the concentration and rate of P released to solution (Tiessen and Moir, 2008). They mimic the plant root by acting as a P sink, and supposedly do not react with the soil (Mason et al., 2010; Menon et al., 1989; Tiessen and Moir, 2008). However, the pH of the soil suspension can be affected by using HCO_3^- as the counter-ion instead of Cl^- (Myers et al., 2005). The FeO can acidify the soil solution (Myers et al., 2005), and the DGT sink may have a similar acidifying effect. In addition, possible contamination with fine sediment on the FeO impregnated paper may give elevated results if the sediment is not carefully removed prior to elution (Chardon et al., 1996; Lookman et al., 1995). The ferrihydrite gel used in the

DGT test is more specific to P sorption than the AER or AEM (Mason et al., 2010), so may be more representative of the selective uptake of P by plants (Schachtman et al., 1998). The thin diffusion barrier used in DGT is designed to control the rate of P sorption, to more closely mimic P uptake by plant roots, relative to the otherwise uncontrolled rate of sorption by resins or FeO in direct contact with the solution (Mason et al., 2010).

2.5.3. Type 3 P tests: desorption and ion exchange

Type 3 methods attempt to extract a measure of labile P that replenishes the soil solution during a growing season (Bache and Williams, 1971), using various exchange ions in solutions of differing pH. Many tests have been developed around the world. Examples of acidic methods include the Mehlich 2, and 3 (Mehlich, 1984) and Bray-1 and Bray-2 tests (Bray and Kurtz, 1945). The Mehlich-3 extractant (0.2 N CH_3COOH + 0.25 N NH_4N0_3 + 0.015 N NH_4F + 0.013 N HNO_3 + 0.001 M EDTA) was developed to be applicable for a wide range of nutrients and be less corrosive to laboratory equipment than earlier versions. The weakly acidic Bray-1 (0.025 M HCl + 0.03 M NH_4F) and more strongly acidic Bray-2 (0.1 M HCl + 0.03 M NH_4F) more closely reflect labile P , use NH_4F intended to extract mainly sorbed Al-P and HCl dissolving CaP minerals (Tandon et al., 1967). However the acids can be neutralised in calcareous soils, and even in neutral soils for Bray 1, giving variable results depending on soil pH buffer capacity (Holford and Doyle, 1992). Low Bray-P values can also result from poor extraction due to the F exchanging anion precipitating with Ca (Fixen and Grove, 1990). The neutralisation of Bray-1 in alkaline soils may be primarily due to calcite more so than dolomite as the latter does not dissolve quickly enough to neutralise the acid in the short extraction period (Ebeling et al., 2008). The search for more broadly applicable and multi-nutrient extractions led to the development of the Kewlona extraction (0.25 N HOAc + 0.015 N NH_4F, and versions modified with acetic acid) used in Canada (van Lierop, 1988).

Oxalate extractable-P is used as an estimate of sorbed P, and to provide a measure of the degree of saturation of sorption sites (e.g. Devau et al., 2009; Maguire and Sims, 2002; Pautler and Sims, 2000). Oxalate extractable P may overestimate available P (van der Zee et al., 1987), and is not applicable to soils containing CaP minerals as they are dissolved by the acidic extractant (Uusitalo and Tuhkanen, 2000). The degree of P saturation of sorption sites may be estimated using sorption isotherms, or as the proportion of oxalate extracted P of the sum of the co-extracted Al and Fe (Börling et al., 2001; Freese et al., 1992), or oxalate extractable Al and pH in neutral – alkaline soils (Renneson et al., 2015).

The 0.5 M sodium bicarbonate solution used in the Olsen-P method was designed for neutral to alkaline and calcareous soils (Olsen et al., 1954). The procedure desorbs P from Fe oxides and carbonates, and by decreasing the activity of Al and Ca, minimises precipitation of P and enhances Ca-P mineral dissolution (Olsen et al., 1954; Samadi and Gilkes, 1998; Tiessen and Moir, 2008). The Colwell P test (Colwell-P) is a modification of the Olsen test, and performed using a greater ratio of solution to soil and a longer extraction period (Colwell, 1963) it extracts a greater quantity of P (Tiessen and Moir, 2008). Colwell-P has been correlated with sorbed P (Barrow, 2000), though a portion of mineral P is also extracted (Bertrand et al., 2003; Holford and Doyle, 1992). The bicarbonate extracts typically include non-orthophosphate P, particularly extracts that have a yellow colour that indicates organic matter (Coventry et al., 2001; Tiessen and Moir, 2008). This can be more pronounced in Olsen extracts (Rayment and Lyons, 2011). The greater dilution in the Colwell method compared to the Olsen method increases the solubilisation of less labile forms which may not represent plant available P (Bertrand et al., 2003; Mason et al., 2010). Phosphorus buffer capacity affects the concentration of P extracted in the bicarbonate procedures, so their reliability is improved by use in conjunction with a measure of P buffer capacity (Burkitt et al., 2002).

2.5.4. Type 4 P tests: isotopic exchange

The Type 4 methods may be considered a variant of Type 3 methods, with the exchange anion being identical to natural orthophosphate except that it is labelled with ^{32}P or ^{33}P. Measures of isotopically exchangeable P are the *E* value and *L* value. The *E* value is measured on soil solutions equilibrated for a certain period. Short periods represent Pi exchanged on soil surfaces, and longer periods can be correlated to bicarbonate-P and plant uptake (Di et al., 1997). The *L* value assumes equilibrium of labelled P and labile P, though this may not hold in practice (Di et al., 1997). Isotopic methods can indicate rates and concentrations of P uptake from the soil, the mineralisation of organic matter, and the fate of applied fertiliser (Mclaughlin et al., 1988a; Mclaughlin et al., 1988b; Mclaughlin et al., 1988c). Isotope studies provide valuable information on the cycling between pools of P applied in organic residues or fertiliser in the short term, but the short life of ^{32}P and ^{33}P isotopes prevents studies of the fate of residual P over the longer term (Mclaughlin et al., 1988a).

2.5.5. Type 5 P tests: buffering capacity

Type 5 tests measure aspects of P buffering, which involves sorption-desorption and dissolution-precipitation processes. These methods include the addition of increasing concentrations of P, or multiple desorption steps, to establish sorption isotherms. Sorption isotherms are curvilinear relationships between the concentration of P remaining in solution and the concentration added or removed (Barrow, 2008; Holford, 1982). A range of single or double point sorption indices have been developed to avoid the time consuming requirement of multiple measurements (e.g. Bache and Williams, 1971; Bolland et al., 1996; Börling et al., 2001; Simard et al., 1994; Willett et al., 1978).

The usefulness of P adsorption buffer capacity to assess P availability depends on how closely it matches desorption, and the comparison shows that desorption exhibits hysteresis (Moody et al., 1988). Adsorption measures remain more frequently used than desorption measures as they are easier to establish, even though (Moody et al., 1988) found that more of the variance in P uptake by maize was described when Colwell-P was combined with a P desorption measure. Ozanne and Shaw (1967) developed the phosphorus buffering capacity (PBC) to guide fertiliser requirement in low P soils in Western Australia. This measure was widely used in Australia to adjust critical Colwell values (Bolland and Gilkes, 2004; Helyar and Spencer, 1977). The PBC is the amount of P sorbed to increase the P concentration remaining in solution from 0.25 to 0.35 mg/L, with these values selected to represent a fertile soil P concentration. Due to the requirement for multiple P additions to establish the PBC, and limitations of earlier single point indices, Burkitt et al. (2002) developed another single point estimate of the PBC, termed the phosphorus buffering index (PBI). The PBI is calculated from the concentration of P remaining in solution after adding a solution containing 1000 mg P kg^{-1} soil using a Freundlich equation, and may include the value of bicarbonate extractable P to account for P already sorbed by the soil (Barrow, 2000; Burkitt et al., 2002; Burkitt et al., 2008). The PBI is now used to adjust critical Colwell and Olsen benchmarks between soils and to guide fertiliser applications in Australia (Bell et al., 2013b; Moody, 2007).

Buffer capacity isotherms or indices are sometimes used to estimate total sorption capacity. The sorption capacity is used to assess the lability of sorbed P, and of the degree of P saturation, both of which are important factors in managing fertiliser application and minimising off-site impacts (Barrow, 1983a; Barrow and Debnath, 2014). Methods to estimate sorption capacity include using the P sorption isotherm (Holford, 1997), P sorbed in single saturating additions or soil properties such as the concentration of oxalate-extractable Al and Fe (van der Zee and van Riemsdijk, 1988) and pH (Renneson et al., 2015), Mehlich-3 extractable Al, Fe or Ca and clay (Kleinman and Sharpley, 2002). The accuracy of the oxalate extractable Fe and Al to provide a quantity measure of buffer capacity is limited due to the oxalate being correlated with poorly crystalline minerals, but not specific to them, as well as the extract not assessing the P sorption of more crystalline minerals (Schwertmann, 1973) or other surfaces (Gérard, 2016). In neutral to alkaline soils, the use of oxalate extractable Al with pH (Renneson et al., 2015), or Mehlich-3 extractable Ca with Mg (Ige et al., 2005) or clay (Kleinman and Sharpley, 2002) are suitable methods to estimate P sorption capacity.

2.5.6. Use of soil P tests for plant nutrition management

Development of the above tests, and many more besides, reflects the difficulty in correlating a test value with a plant response, and even worse, with a fertiliser requirement (Devau et al., 2009; Tiessen and Moir, 2008). Many studies have reported on the efficacy of tests for various locations, soils and plant responses, fundamentally attempting to describe labile P for particular soil, plant and seasonal circumstances (Holford, 1997). Many of the tests have been found to apply in certain circumstances, but results can be inconsistent or not broadly applicable. Tests may also fail to find universal acceptance because of the work required to calibrate test values against plant responses from deficient through adequate to luxury levels, so that critical ranges can be estimated (McLaughlin et al., 1999).

The concentrations measured in the water and dilute salt extracts of Type 1 are low in air dried soils and fluctuate with plant uptake and soil processes (Holford, 1997). Due to this variability, they are not commonly used for agronomic management in Australia (Holford, 1997). In addition the better relationships of $CaCl_2$-P with plant uptake and yield compared to Colwell-P previously observed (e.g. Moody et al., 1988; Moody et al., 1990;

Moody et al., 1983) have been superseded by using measures of P buffer capacity to adjust critical Colwell-P values (Moody, 2007; Speirs et al., 2013).

There are myriad reports of the application of soil P test procedures to production, and a sample of these applicable to alkaline soils follows. Indiati et al. (2002) found AEM to be better correlated to P uptake by maize ($r^2 = 0.88$) than Olsen ($r^2 = 0.77$), FeO ($r^2 = 0.74$), and Mehlich-3 ($r^2 = 0.75$) in neutral to alkaline soils. Used together with a cation exchange resin, the extraction of P by AEM may better mimic plant uptake of nutrients from the soil (Dalal, 1985); however the combined sinks may also extract P that is not available to plants (Delgado and Torrent, 2000; Warren and Sahrawat, 1993). Dry matter production of maize was equally correlated with FeO-P and Olsen-P ($r^2 = 0.96$) on calcareous soils (Menon et al., 1991). Bertrand et al. (2003) found that AEM-P was better correlated with isotopically exchangeable P ($r^2 = 0.6$) than Colwell-P ($r^2 = 0.44$). Mason et al. (2010) found that the DGT correctly predicted yield response in 18 of 20 cases, compared to 14 and 11 cases for AEM and Colwell (adjusted for PBI), respectively. The DGT P values may relate more closely to plant available P than do P extracted using FeO or AEM (Guo et al., 1996; Six et al., 2012), though the main benefit of DGT over other soil test methods in Australia appears to be on calcareous soils (Speirs et al., 2013). Tiessen and Moir (2008) suggested the use of P sinks was appropriate to assess the amounts and rates of P release to solution. Multiple sink extractions, with either AEM or AER (Bache and Ireland, 1980; Delgado and Torrent, 2000; Nafiu, 2009; Roboredo and Coutinho, 2006; Sato and Comerford, 2006; Uusitalo and Tuhkanen, 2000) or FeO (Chardon et al., 1996; Lookman et al., 1995; McLaren et al., 2014a) have been used to investigate P desorption or the replenishment of labile pools. These multiple extraction studies generally report progressively diminishing concentrations of P as the remaining P is more tightly retained.

The following sample of reports indicates the suitability of these and other tests on a wider range of soils. Lin et al. (1991) found P uptake by wheat was better correlated with AEM ($r^2 = 0.84$) and FeO ($r^2 = 0.83$) than with Olsen-P ($r^2 = 0.75$), while Mehlich-1 and Bray-1 were not correlated across a wide range of soils with Olsen-P < 55 mg kg^{-1}. Mallarino and Atia (2005) found that the soil P test value between the Mehlich-3, AEM (HCO_3^- form), Olsen-P across a range of soil types were correlated ($r^2 > 0.84$), and equally effective at predicting a critical range for corn yield (mean relative yield response > 92%). However, others have been found Mehlich-3 to extract large amounts of non-labile P and be poorly correlated with yield in a range of soils (n.s. Holford (1980b), r = 0.39 Speirs et al. (2013)). Bray-1 has been recommended over other acidic extracts and Olsen for rice culture (Anh and Phung, 2004), and broadly for soils low in calcite (Ebeling et al., 2008). In a review of three studies comparing the effectiveness of various tests including the bicarbonate and Bray methods on acidic to alkaline calcareous soils, Holford (1997) reported on the correlation with yield on a range of soil types varying in pH for the Bray-2 compared to Colwell-P and Olsen-P in three different trials. Relative wheat yield from field trials on soils with pH ranging from 5.5 to 8.1 were better correlated to Bray-2 than Olsen and Colwell ($r^2 = 0.62$, 0.51 and 0.4, respectively) but slightly worse after adjusting for P buffering ($r^2 = 0.65$, 0.74 and 0.72) (Holford, 1980a). In a glasshouse experiment with soils ranging from pH 5.4 to 8.1, relative yield of clover was slightly better correlated with Bray-2 than Olsen and Colwell (r = 0.94, 0.92 and 0.83 , respectively) (Holford, 1980b). In the third instance, wheat yield on soils ranging in pH from 4.8 to 7.7 was better correlated over 4 years with Bray-2 than Olsen and Colwell (Bray-2 $r^2 = 0.47$ to 0.59; Olsen-P and Colwell-P $r^2 < 0.29$, and were not improved by measures of sorptivity) (Holford and Doyle, 1992). In the review, (Holford, 1997) also found the correlations were better for the soil tests less correlated with exchangeable P (i.e Bray-2 and lactate-P compared to Olsen-P and Colwell-P), which he interpreted as indicating that nonexchangeable pools are an important source of plant available P . The Kewlona soil test, used on soils with a wide range of pH in Canada, correlate with bicarbonate extracts and may better predict relative yield (e.g. r = 0.71 cf 0.6) (Ashworth and Mrazek, 1995; Soon, 1990; van Lierop, 1988).

It is an article of faith that isotopically exchangeable P equates with labile P (Guppy et al., 2005); however, the review by Holford (1997) suggested that mineral P may contribute to P uptake by crops. Wang et al. (2007) found that HCl-soluble P was contributing to the replenishment of labile pools over the medium term (years to decades) in the NGR, and similar trends have been reported in the region (Dalal, 1997) and elsewhere (Guo et al., 2000; Pundarikakshudu, 1989; Shailaja and Sahrawat, 1990). The BSES method, while developed for acidic soils, has recently been used to indicate acid-soluble reserve-P that may slowly replenish Colwell-P (McLaren et al., 2014a; Moody et al., 2013). The difficulty in estimating the supply of reserve-P to labile-P is illustrated by the weaker correlation between BSES-P and both Colwell-P and Olsen-P in soils with substantial reserve-P compared to those with low reserve-P (Moody et al., 2013). McLaren et al. (2014a) proposed that reserve-P can contribute to the slow replenishment of the soil solution above that of Colwell-P when the Ca:P in the BSES extract is less than 74:1 on a mass basis, or 57:1 on a molar basis.

Moody (1991) argued that it is imperative that measures of labile P, the intensity of P in solution, and P buffer capacity be measured. The value of Colwell-P/PBI can be correlated with the solution intensity of P (estimated as $CaCl_2$-P or and FeO-P) (Moody, 2011; Moody et al., 2013). Further, by using the PBI, critical Colwell-P values can be refined, and fertiliser P requirements predicted (Burkitt et al., 2002; Moody, 2007; Speirs et al., 2013), and as an environmental risk assessment of P in runoff (Dougherty et al., 2011). As well as being used to complement Colwell values, a measure of P buffering capacity has also been found to improve yield correlations for Olsen (Burkitt et al., 2002), BSES (Hurney et al., 2010), solution P (Holford and Mattingly, 1979), Bray-1 and exchangeable-P (Holford, 1997).

Difficulty still exists with bicarbonate procedures due to the possible extraction of non-orthophosphate P that may not be plant available (Coventry et al., 2001), and the extraction of P that is not available to plants in calcareous soils compared to limed acidic soils (Delgado and Torrent, 2000). While the PBI adjustment improves the reliability of Colwell-P for fertility management, factors such as other soil properties, environment, management practices and species still need to be considered (Bolland and Gilkes, 2004; Speirs et al., 2013). It has been considered that the existing sorbed P be accounted for when calculating the PBI (Barrow, 2000), for example by subtracting the Colwell-P value (Burkitt et al., 2002); however the author subsequently recommended that this adjustment not be done as it can mask changes that occur in sorption capacity after fertiliser application Burkitt et al. (2008).

In the alkaline Vertosols in the NGR, the pool of acid soluble reserve-P appears to be an important source of P nutrition (Wang et al., 2007). However, Moody et al. (2013) did not find evidence to suggest that reserve-P contributes to the concentration of P in solution, and (Moody, 2007) recommended that PBI and Colwell be used throughout Australia for agronomic management as a pragmatic option to capture the quantity of labile-P and buffer capacity. Recent reviews of Australian data and testing of archived samples supported this recommendation, except for calcareous soils where the DGT was most suitable (Speirs et al., 2013), though the wide confidence intervals for critical values indicate that there remains potential to improve the understanding of P mobility and agronomic management. The finding of (McLaren et al., 2014a) that the quantity of reserve-P may slowly replenish Colwell-P given certain thresholds (BSES-P > 61 mg kg^{-1}

and molar Ca:P < 57) suggests that closer examination of soil properties is warranted. In addition, acid soluble P has been considered a labile pool of P in alkaline soils (Guo et al., 2000; McKenzie et al., 1992; Pundarikakshudu, 1989; Truog, 1930). Considering the processes of rhizosphere acidification and the incremental, ongoing uptake of P from solution by plants, a fresh look at soil properties and P extraction with existing tests may be useful.

2.6. Soil phosphorus characterisation

Most of the soil P tests described are used for agronomic management. More involved techniques are used to research the relationships of P to other soil constituents, partitioning based on extractability, and repartitioning of P over the longer term. Broadly, these techniques are fractionation schemes using a series of different extractants, sophisticated spectroscopy, and modelling techniques. Studies that use a combination of techniques provide important insights into P speciation and mobility.

2.6.1. Phosphorus fractionation schemes

Phosphorus fractionation schemes are used to estimate the proportions of soil P in pools of different solubility. The schemes are designed to sequentially extract P from increasingly resistant pools, using increasingly strong extractants. Many different schemes have been developed to investigate P transformations in different soils and sediments (see Condron and Newman, 2011). Perhaps the most well-known and widely used are the Hedley et al. (1982b), and Chang and Jackson (1957) schemes or subsequent derivations. By using various extractants that can solubilise P from synthesised P compounds, and alternatively not dissolve other compounds, the concentration of P extracted at each step is inferred to be primarily associated with particular components in the soil, e.g. labile, Al-sorbed, Fe-sorbed, CaP minerals and resistant pools (Adhami et al., 2007; Tiessen and Moir, 2008).

Limitations of the schemes to assign extracted P to a particular pool are profound and include: a lack of selectivity for the proposed fractions; that Po is not as well defined as Pi; and that each step can affect the remaining forms (O'Halloran and Cade-Menun, 2008; Schwertmann, 1973; Stewart and Tiessen, 1987; Tiessen and Moir, 2008).

Despite the limitations of fractionation schemes, when selected and used with consideration of their limitations, they can provide valuable information on a range of soil P processes (Condron and Newman, 2011). Examples include investigations on: the repartitioning of P due to waterlogging (Adhami et al., 2012); transformation of P after the application of fertiliser or manures (Delgado and Torrent, 2000; Kashem et al., 2004; Liu et al., 2015; Vu et al., 2010); the forms of P depleted during agricultural production (Wang et al., 2007); and the transformation of P during pedogenesis (Sato et al., 2009).

The classification of P is greatly improved when used in conjunction with solid state speciation, such as ^{31}P NMR or XANES (Condron and Newman, 2011). Importantly, the restrictions of access and cost of these technologies mean that fractionation schemes alone rather than in conjunction with solid state speciation remain a commonly used technique to characterise soil P.

2.6.2. Spectroscopic identification

Direct techniques such as nuclear magnetic resonance, X-ray diffraction, and infrared or Raman spectroscopy can complement indirect techniques; however, speciation or quantification is limited by high detection limits, interference from other soil constituents, or a lack of identifiable features (Bell and Black, 1970a; Kizewski et al., 2011; McDowell et al., 2003a; McDowell et al., 2003b; Pierzynski et al., 1990b; Pierzynski et al., 2005; Xu et al., 2014).

^{31}P NMR has provided valuable insights into the composition of soil P, particularly organic P (Doolette et al., 2011a; McLaren et al., 2015c). However, variable extraction of soil P and possible transformation of species during extracted with sodium hydroxide–ethylenediaminetetra-acetic acid (NaOH-EDTA) for solution ^{31}P NMR leaves a still incomplete picture (Kizewski et al., 2011; Kruse et al., 2015). Despite paramagnetic interference from Fe, solid state NMR also provides valuable insights on P mobility and speciation, however only 10-20% of the P atoms in a sample are detected (Kizewski et al., 2011). Insights from NMR include the identification of CaP mineral and sorbed species contributing to P mobility (Maguire and Sims, 2002), clarification of the abundance and stability of Po forms (McLaren et al., 2015c), notably phytate (Doolette et al., 2010; Doolette et al., 2011a) and the fate of P fertiliser (McLaren et al., 2015b).

The increasing use of XANES over the last two decades has enabled different mineral and sorbed P species to be identified, and their concentrations estimated, using linear combination fitting (LCF) of standard spectra (Ajiboye et al., 2007b; Hesterberg, 2010). Linear combination fitting is less reliable when minerals are less crystalline and contain more impurities in soil compared with synthesized or geological minerals (Hesterberg, 2010). In addition, the spectra are generally only adequately resolved to allow identification of three or four species (Kizewski et al., 2011), and still the statistical fitting can give ambiguous results (Kelly et al., 2008; Kruse et al., 2015). Sorbed species may present similar spectra in XANES, but be better resolved with X-ray absorption fine edge spectroscopy (EXAFS) (Kelly et al., 2008). A further limitation is that the spectra of organic P species are similar and lacking in features when measured with P K-edge XANES (the technique most commonly used) ; consequently, organic P species are generally only broadly classified (Hesterberg, 2010). Nonetheless, XANES investigations have identified P associated with Ca, Fe and Al in mineral and sorbed phases of various soils (e.g. Beauchemin et al., 2003; Lombi et al., 2006; Sato et al., 2005), including

Vertosols (Ajiboye et al., 2008). Most investigations have been conducted on soils with relatively high P concentrations (e.g. > 800 mg P kg^{-1}) or upon the addition of P fertiliser or P-rich amendments, as the similar spectral features of CaP species and the poor spectral quality at P concentrations close to the detection limit of the beamline limits the accuracy of LCF (Liu et al., 2015; Oxmann, 2013). Recently, Klysubun et al. (2012) reported P K–edge XANES spectra collected at low total P concentrations (~50 mg kg^{-1}) at beamline BL8 of the Synchrotron Light Research Institute (SLRI, Thailand). This enabled identification of P species in a catena (Prietzel et al., 2013), and P K–edge XANES may be well suited to identifying CaP in at relatively low concentrations.

Spectra of XANES and the P $L_{2,3}$ edge have more spectral features than the P K-edge, not only mineral species including CaP minerals, but also organic P species (Kruse et al., 2009), however the higher detection limit restricts it broader use with soils. Finer scale micro- or nano- P K-edge XANES has also been used to characterise P species in soil samples. This has the benefit over bulk XANES of enabling better identification of P species and associations in regions of high concentrations (Lombi et al., 2006; Schefe et al., 2011). However, observing differences between treatments is more difficult (Schefe et al., 2011).

2.6.3. Speciation modelling

Solution chemistry may be used to compare the status of a system with standard solubility products to indicate the degree of saturation with respect to mineral phases (Gustafsson, 2015). The model outputs are commonly used to support other analytical data, and indicate the equilibrium status of a system. Data that do not fit known solubility products can indicate a system not in equilibrium and/or the influence of other processes, e.g. sorption (Devau et al., 2009; Murrmann and Peech, 1969a; Weng et al., 2011).

The complexity of clay minerals, non-crystalline minerals, oxy/hydroxides, and highly varied range organic compounds in soils complicates the investigation of the rates of chemical reactions (Sparks, 1986). Major limitations to modelling include: soil heterogeneity and slow kinetics responding to P addition, plant uptake and water movement; non-equilibrium of solution with the solid phase; limited analyses for model parameters, and uncertainty of organic compounds (Pierzynski et al., 2005; Schwab, 2011). These types of uncertainties can lead to differing interpretation of the processes driving P mobility, e.g. (Devau et al., 2013; Lumsdon, 2012; Weng et al., 2011). Nonetheless, modelling provides new interpretations of P kinetics, e.g. in a re-analysis of historic data, Gérard (2016) established that the interpretation of sorption surfaces are dependent on the data and parameters used in a model. His reinterpretation found that the clays can be as or more important than oxy/hydroxides to P sorption.

2.7. Scope for research

There is a need to improve the understanding of P mobility, and the potential sources of P that contribute to plant uptake in alkaline soils. This may provide an opportunity to improve the agricultural production and P fertiliser use efficiency. The following research will focus on Vertosols from the NGR that contain concentrations of P acid soluble P that McLaren et al. (2014a) suggested replenish Colwell-P. Using indicators provided in the literature review, i.e. manipulation of pH, analysis of extracted solutions, and solid state analysis of the soil, the aim of the following research is to elucidate the circumstances and processes by which acid soluble reserve-P contributes to the soil solution through techniques that:

- Identify the P phases in the soil.
- Assess the effects of acidification on the supply of P to solution.
- Assess the effect of Ca and P on the supply of P to solution.

- Identify the contribution of each phase to solution P.

I plan to use a combination of existing techniques in a novel way. Primarily, I plan to incrementally manipulate soil suspension pH while extracting P or Ca from solution, rather than acidifying the suspension in a single extraction. Conversely, I will also acidify soil suspensions and then test the change in P extractability after a period of equilibration. Solid state analyses (will then be performed in the soil sediments.

Using these approaches, the hypotheses that I will test in this thesis are that:

- acid soluble P will be solubilised more readily in the presence of a phosphate sink by using incremental acidification.
- the removal of both Ca and P from the solution at each pH level will solubilise more reserve-P than removing P alone.
- the rate of P release will be relatively constant at a maintained pH level.
- X-ray absorption near edge structure (XANES) spectroscopy will identify different forms of P (mineral and sorbed) that are preferentially depleted as the suspension is acidified.
- equilibration after acidification will result in some P repartitioning that changes its extractability.

3. Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils

The work contained in this chapter has been published in *Geoderma*.

Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J., McLaren, T.I., 2015. Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils. *Geoderma* 259-260, 35-44. DOI: http://dx.doi.org/10.1016/j.geoderma.2015.05.001

Andersson, K. O., Tighe, M. K., Guppy, C. N., Milham, P. J. & McLaren, T. I. (2015). Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils. *Geoderma, 259-260*, 35-44.

http://dx.doi.org/10.1016/j.geoderma.2015.05.001

4. The release of phosphorus in alkaline vertic soils as influenced by pH and by anion and cation sinks

The work contained in this chapter has been published in *Geoderma*.

Andersson, K. O.; Tighe, M. K.; Guppy, C. N.; Milham, P. J.; McLaren, T. I., 2016. The release of phosphorus in alkaline vertic soils as influenced by pH and by anion and cation sinks. *Geoderma*. 264, *Part A*, 17-27. DOI: 10.1016/j.geoderma.2015.10.001.

Three of the six soils studied in Chapter 3 are studied further. Note that soil 6 as published in Ch 3 is hereafter soil 3.

Andersson, K. O., Tighe, M. K., Guppy, C. N., Milham, P. J. & McLaren, T. I. (2016). The release of phosphorus in alkaline vertic soils as influenced by pH and by anion and cation sinks. *Geoderma, 264*, Part A, 17-27.

http://dx.doi.org/10.1016/j.geoderma.2015.10.001

5. XANES demonstrates the release of calcium phosphates from alkaline Vertosols to moderately acidified solution

The work contained in this chapter has been published in *Environmental Science and Technology*.

Andersson, K. O.; Tighe, M. K.; Guppy, C. N.; Milham, P. J.; McLaren, T. I., 2016. XANES demonstrates the release of calcium phosphates from alkaline Vertisols to moderately acidified solution. *Environmental Science and Technology* 50 (8), 4229–4237. DOI: 10.1021/acs.est.5b04814.

Andersson, K. O., Tighe, M. K., Guppy, C. N., Milham, P. J., McLaren, T. I., Schefe, C. R. & Lombi, E. (2016). XANES demonstrates the release of calcium phosphates from alkaline Vertisols to moderately acidified solution. *Environmental Science and Technology, 50*(8), 4229–4237.

http://dx.doi.org/10.1021/acs.est.5b04814

6. The transformation of calcium phosphates in alkaline Vertosols during equilibration experiments

The work contained in this chapter is has been submitted to the *Soil Science Society of America Journal*.

Andersson, K. O.; Tighe, M. K.; Guppy, C. N.; Milham, P. J.; McLaren, T. I. The transformation of calcium phosphates in alkaline Vertisols during equilibration experiments. *Soil Science Society of America Journal*, submitted.

7. Conclusions, implications and future research directions

This research identified the circumstances under which acid-soluble P sources, including CaP minerals, supply P to solution. Using exchange membranes to mimic plant uptake, and manipulating the pH of soil suspensions, the results indicate the conditions under which CaP minerals may directly supply P to plants and replenish the bicarbonate extractable pools in alkaline Vertosols. They also provide a mechanism for the observed depletion of acid soluble reserve-P in the Vertosols of the NGR, and alkaline soils elsewhere. The findings may apply to other alkaline soils, vertic and non-vertic worldwide.

I have shown that acidification of alkaline Vertosols typically caused a large release of reserve-P in a narrow, moderately acidic pH range. The threshold pH at which the large release occurred was higher by 0.7–1.0 pH units when P was removed from solution than when it was allowed to accumulate. The narrow pH range of the increase, and the Ca:P ratios in the extractions approaching those of CaP minerals, were indicative of the dissolution of CaP minerals.

Further examination revealed that the soils contained several pools differing in solubility. Following the removal of readily extractable P, the low extractability of P at the initial soil pH was confirmed by the relatively low levels of P extracted when the pH was maintained at the initial levels. When the pH was maintained at levels above and below the identified threshold, the release of P indicated the presence of two more pools. Whether or not these pools were mineral or sorbed could not be confirmed by the incremental depletion method. However, the influence of soil Ca on P extractability was confirmed as greater concentrations of P were extracted when Ca was removed from suspension.

Bulk P K-edge XANES the importance of both mineral CaP and sorbed P phases in the soils. The spectra of soil samples depleted of P under controlled conditions elucidated the nature of P speciation and mobilisation. As hypothesised, Incremental extraction of P over. The XANES analyses also showed that sorbed P, in various guises, was an important pool of P, and ongoing contributor to acid-soluble P.

However, when acidification occurs without concurrent plant uptake, it appears that repartitioning to sorbed phases of lower extractability may compromise the ability of plants to exploit acid-soluble P, particularly CaP minerals.

The findings suggest that a likely mechanism by which acid-soluble reserve-P is accessed in the alkaline Vertosols in the NGR, and more broadly in neutral-alkaline agricultural soils around the world, is by rhizosphere acidification and plant uptake of nutrients. This has implications for the ongoing availability of P in soils containing CaP minerals, either native or fertiliser reaction products. For instance, the mobilisation of reserve-P in a soil with a high proportion of relatively soluble CaP minerals will be maintained more readily for a longer period than in a soil with a similar concentration of reserve-P but a greater proportion of less labile CaP minerals. In addition, as the relatively labile reserve-P is depleted, the supply of reserve-P to solution is likely to be greatly diminished. The mobilisation of the reserve-P will be further governed by the capacity of plants to acidify the rhizosphere, and the pH buffer capacity of the soil. Importantly, the identification of sorbed P phases contributing to acid-soluble P highlights the complexity of P forms in soils. This complexity of mineral and sorbed phases shows that a combination of desorption, slow dissolution, and repartitioning are all important factors influencing the mobilisation of P and its potential availability to plants. By understanding in greater detail the interaction of these factors, there is the potential to improve fertiliser P efficiency by tailoring applications according to the concentration of P in more labile phases, the soil pH buffer capacity, and the selection of plants for acidification capacity.

The key results of the extractability of acid-soluble reserve-P at moderately acidic pH, the influence of Ca, and the possible repartitioning to less available forms provides several avenues for further research, including soil testing, plant interactions, the effect of reducing conditions, and solid state investigations.

Firstly, a combination of relatively simple soil test procedures may improve the assessment of the availability of P to plants. To wit, a short-term (overnight) extraction with an AEM buffered to pH 6.5, and a measure of pH buffer capacity. The two measures may differentiate the relative accessibility, via acidification, of the potentially more labile acid-soluble P. This approach would also require the understanding of plant related factors. These factors include the potential of different plants to overcome pH buffer capacity and acidify the soil, the variability of pH buffer capacity in soil (e.g. as influenced by discrete calcite concretions), and the potentially confounding influence of low molecular weight organic acids on mineral dissolution/precipitation. The aim of the suggested approach is to provide a quantitative estimate of the labile portion of acid-soluble P to plants that can acidify their rhizosphere. The greater depletion of acid-soluble P relative to bicarbonate-extractable P in similar soils after cropping, e.g. as reported by Wang et al. (2007) and Dalal (1997), indicates that the pools should not necessarily be considered ‘stable’. I have shown that the proportion of reserve-P that is extractable after moderate acidification varies between similar soils. Gaining a quantitative appreciation of the more labile portions should enable a producer to anticipate the longevity of labile, compared stable, portions of reserve-P supplies as they monitor the removal of P in produce. This should apply as well to soils with high extractable P concentrations, similar to those studied here, as to soils with lower concentrations.

The importance of these plant interactions leads to the second area of further research. Plant based studies are required to examine if the extractability of soil P reported here is available to plants. Studies would include P depletion experiments, manipulated rhizosphere pH, the role of cation depletion, and isotope experiments. Depletion experiments could determine the rate of supply of P from different pools, while manipulating the rhizosphere pH with ammonium-N (acidifying effect) or nitrate-N (alkalising effect) could assess the effect of rhizosphere pH on P supply. Investigations using plants with high rates of Ca uptake (e.g. legumes) may show the effect of co-uptake of Ca on P solubilisation. The relative uptake of P from these alkaline soils compared to fertiliser or applied residues may be investigated with labelled fertiliser and residues. Studying soil and plant interactions at the micro-scale with planar electrodes is a promising avenue to discover mobilisation of reserve P under acidification, and reducing, conditions in the rhizosphere.

The indirect effects of waterlogging on the mobilisation of acid soluble reserve-P in alkaline soils containing phases of CaP minerals and P sorbed to clays as well as Al-, Fe-(oxy/hydr)oxides is a third area of investigation. The science may be advanced via lab incubation studies of soil x fertiliser form x wetting/drying cycles using soils that have a range of P characteristics (based on the size and extractability of their P pools). Soil test characterisation could assist in the assessment of changes in extractability and the distribution of P in various soil pools influenced by soil wetting/drying cycles. Subsequent plant based studies would assess the effect of the treatments on P availability.

Lastly, further solid state investigations are warranted to fully elucidate the nature of the acid soluble P in these soils. These investigations should supplement other techniques, and be conducted on untreated soils and samples exposed to the aforementioned treatments. Bulk P K-edge XANES may identify treatment effects, while μ-XANES and mapping can provide greater detail on the presence of minor components. ^{31}P NMR is an important technique that can be used in conjunction with XANES to identify organic P compounds.

References

Abdu, N., 2006. Soil-phosphorus extraction methodologies: A review. African Journal of Agricultural Research 1(5), 159-161. DOI:

Adhami, E., Memarian, H.R., Rassaei, F., Mahdavi, E., Maftoun, M., Ronaghi, A., Fasaei, R.G., 2007. Relationship between phosphorus fractions and properties of highly calcareous soils. Soil Res. 45(4), 255-261. DOI: http://dx.doi.org/10.1071/SR06118

Adhami, E., Ronaghi, A., Karimian, N., Molavi, R., 2012. Transformation of phosphorus in highly calcareous soils under field capacity and waterlogged conditions. Soil Res. 50(3), 249-255. DOI: http://dx.doi.org/10.1071/SR11250

Agbenin, J.O., 1994. Adsorbed phosphorus partitioning in some benchmark soils from Northeast Brazil. Fertilizer Res. 40(3), 185-191. DOI: 10.1007/bf00750464

Agbenin, J.O., van Raij, B., 2001. Kinetics and energetics of phosphate release from tropical soils determined by mixed ion-exchange resins. Soil Sci. Soc. Am. J. 65(4), 1108-1114. DOI: 10.2136/sssaj2001.6541108x

Ahmed, N., 1983. Vertisols. In: L.P. Wilding, G.P. Hall, N.E. Smeck (Eds.), Pedogenesis and soil taxonomy: The soil orders. Elsevier Science Publishers, Amsterdam, pp. 91-123

Aitken, R.L., Moody, P.W., 1994. The effect of valence and ionic strength on the measurement of pH buffer capacity. Soil Res. 32(5), 975-984. DOI: http://dx.doi.org/10.1071/SR9940975

Ajiboye, B., Akinremi, O.O., Hu, Y., Flaten, D.N., 2007a. Phosphorus speciation of sequential extracts of organic amendments using nuclear magnetic resonance and x-ray absorption near-edge structure spectroscopies. J. Environ. Qual. 36(6), 1563-1576. DOI: 10.2134/jeq2006.0541

Ajiboye, B., Akinremi, O.O., Hu, Y., Jürgensen, A., 2008. XANES speciation of phosphorus in organically amended and fertilized Vertisol and Mollisol. Soil Sci. Soc. Am. J. 72(5), 1256-1262. DOI: 10.2136/sssaj2007.0078

Ajiboye, B., Akinremi, O.O., Jürgensen, A., 2007b. Experimental validation of quantitative XANES analysis for phosphorus speciation. Soil Sci. Soc. Am. J. 71(4), 1288-1291. DOI: 10.2136/sssaj2007.0007

Alvarez, R., Evans, L.A., Milham, P.J., Wilson, M.A., 2004. Effects of humic material on the precipitation of calcium phosphate. Geoderma 118(3–4), 245-260. DOI: 10.1016/s0016-7061(03)00207-6

Amer, F., Bouldin, D.R., Black, C.A., Duke, F.R., 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P32-equilibration. Plant Soil 6(4), 391-408. DOI: 10.1007/bf01343648

Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J., McLaren, T.I., 2015. Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils. Geoderma 259-260, 35-44. DOI: http://dx.doi.org/10.1016/j.geoderma.2015.05.001

Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J., McLaren, T.I., 2016. The release of phosphorus in alkaline vertic soils as influenced by pH and by anion and cation sinks. Geoderma 264, 17-27. DOI: 10.1016/j.geoderma.2015.10.001

Andersson, K.O., Tighe, M.K., Guppy, C.N., Milham, P.J., McLaren, T.I., Schefe, C.R., Lombi, E., under review. XANES demonstrates the release of calcium phosphates from alkaline Vertisols to moderately acidified solution. Environ. Sci. Technol. DOI:

Anh, T.T.N., Phung, C.V., 2004. Soil phosphorus availability tests for irrigated lowland rice in Cantho, Vietnam. Omonrice 12(58-68). DOI:

Anon., 2004. AgSTATs 2001. In: Australian Bureau of Statistics (Ed.), Canberra.

Armstrong, R.D., 1988. The phosphorus nutrition of mulga pasture grasses with reference to the invasion of *Aristida armata*, Griffith University, Brisbane.

Ashworth, J., Mrazek, K., 1995. “Modified Kelowna” test for available phosphorus and potassium in soil. Commun. Soil Sci. Plant Anal. 26(5-6), 731-739. DOI: 10.1080/00103629509369331

Bache, B.W., Ireland, C., 1980. Desorption of phosphate from soils using anion exchange resins. J. Soil Sci. 31(2), 297-306. DOI: 10.1111/j.1365-2389.1980.tb02082.x

Bache, B.W., Williams, E.G., 1971. A phosphate sorption index for soils. J. Soil Sci. 22(3), 289-301. DOI:

Barber, S.A., 1958. Prediction of the residual effect of phosphate applications. In: R.A. Laubengayer (Ed.), Proceedings of the Indiana Academy of Science, Crawfordsville, Indiana, pp. 330-336.

Barber, S.A., 1995. Soil nutrient bioavailability: a mechanistic approach. 2 ed. John Wiley, New York, USA.

Barber, T.M., 2002. Phosphate adsorption by mixed and reduced iron phases in static and dynamic systems. M.Sc Thesis, Stanford University.

Barrow, N.J., 1974. Effect of previous additions of phosphate on phosphate adsorption by soils. Soil Sci. 118(2), 82-89. DOI:

Barrow, N.J., 1983a. A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. 34(4), 733-750. DOI: 10.1111/j.1365-2389.1983.tb01068.x

Barrow, N.J., 1983b. On the reversibility of phosphate sorption by soils. J. Soil Sci. 34(4), 751-758. DOI: 10.1111/j.1365-2389.1983.tb01069.x

Barrow, N.J., 1984. Modelling the effects of pH on phosphate sorption by soils. J. Soil Sci. 35(2), 283-297. DOI: 10.1111/j.1365-2389.1984.tb00283.x

Barrow, N.J., 2000. Towards a single-point method for measuring phosphate sorption by soils. Soil Res. 38(6), 1099-1113. DOI: http://dx.doi.org/10.1071/SR99135

Barrow, N.J., 2008. The description of sorption curves. Eur. J. Soil Sci. 59(5), 900-910. DOI: 10.1111/j.1365-2389.2008.01041.x

Barrow, N.J., Debnath, A., 2014. Effect of phosphate status on the sorption and desorption properties of some soils of northern India. Plant Soil 378(1-2), 383-395. DOI: 10.1007/s11104-014-2042-8

Barrow, N.J., Shaw, T.C., 1975. The slow reactions between soil and anions: 5. effects of period of prior contact on the desorption of phosphate from soils. Soil Sci. 119(4), 311-320. DOI:

Barrow, N.J., Shaw, T.C., 1977. Factors affecting the amount of phosphate extracted from soil by anion exchange resin. Geoderma 18(4), 309-323. DOI: http://dx.doi.org/10.1016/0016-7061(77)90039-8

Batten, G.D., Wardlaw, I.F., 1987. Senescence of the flag leaf and grain yield following late foliar and root applications of phosphate on plants of differing phosphorus status. Journal of Plant Nutrition 10(7), 735-748. DOI: 10.1080/01904168709363605

Beauchemin, S., Hesterberg, D., Chou, J., Beauchemin, M., Simard, R.R., Sayers, D.E., 2003. Speciation of phosphorus in phosphorus-enriched agricultural soils using X-Ray absorption near-edge structure spectroscopy and chemical fractionation. J. Environ. Qual. 32(5), 1809-1819. DOI: 10.2134/jeq2003.1809

Bell, L.C., Black, C.A., 1970a. Comparison of methods for identifying crystalline phosphates produced by interaction of orthophosphate fertilizers with soils. Soil Sci. Soc. Am. J. 34(4), 579-582. DOI: 10.2136/sssaj1970.03615995003400040013x

Bell, L.C., Black, C.A., 1970b. Crystalline phosphates produced by interaction of orthophosphate fertilizers with slightly acid and alkaline soils. Soil Sci. Soc. Am. J. 34(5), 735-740. DOI: 10.2136/sssaj1970.03615995003400050020x

Bell, L.C., Mika, H., 1979. The pH dependence of the surface concentrations of calcium and phosphorus on hydroxyapatite in aqueous solutions. J. Soil Sci. 30(2), 247-258. DOI: 10.1111/j.1365-2389.1979.tb00982.x

Bell, M., Lester, D., Smith, L., Want, P., 2012. Increasing complexity in nutrient management on clay soils in the northern grain belt – nutrient stratification and multiple nutrient limitations. In: I. Yunusa (Ed.), Proceedings of the 16th Australian Agronomy Conference. Australian Society of Agronomy/The Regional Institute, Armidale, NSW.

Bell, M.J., Moody, P.W., Anderson, G.C., Strong, W., 2013a. Soil phosphorus–crop response calibration relationships and criteria for oilseeds, grain legumes and summer cereal crops grown in Australia. Crop Pasture Sci. 64(5), 499-513. DOI: http://dx.doi.org/10.1071/CP12428

Bell, R., Reuter, D., Scott, B., Sparrow, L., Strong, W., Chen, W., 2013b. Soil phosphorus–crop response calibration relationships and criteria for winter cereal crops grown in Australia. Crop Pasture Sci. 64(5), 480-498. DOI: http://dx.doi.org/10.1071/CP13016

Bertrand, I., Holloway, R.E., Armstrong, R.D., McLaughlin, M.J., 2003. Chemical characteristics of phosphorus in alkaline soils from southern Australia. Soil Res. 41(1), 61-76. DOI: http://dx.doi.org/10.1071/SR02021

Blum, J.D., Klaue, A., Nezat, C.A., Driscoll, C.T., Johnson, C.E., Siccama, T.G., Eagar, C., Fahey, T.J., Likens, G.E., 2002. Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. Nature 417(6890), 729-731. DOI: 10.1038/nature00793

Bolan, N.S., 1991. A critical review on the role of mycorrhizal fungi in the uptake of phosphorus by plants. Plant Soil 134(2), 189-207. DOI: 10.1007/bf00012037

Bolan, N.S., Barrow, N.J., Posner, A.M., 1985. Describing the effect of time on sorption of phosphate by iron and aluminium hydroxides. J. Soil Sci. 36(2), 187-197. DOI: 10.1111/j.1365-2389.1985.tb00323.x

Bolan, N.S., Robson, A.D., Barrow, N.J., Aylmore, L.A.G., 1984. Specific activity of phosphorus in mycorrhizal and non-mycorrhizal plants in relation to the availability of phosphorus to plants. Soil Biol. Biochem. 16(4), 299-304. DOI: http://dx.doi.org/10.1016/0038-0717(84)90023-3

Bolland, M.D.A., Gilkes, R.J., 2004. The systematic effect of soil P buffer capacity on Colwell soil P test v. plant response calibration exists only when field experiments are adjacent. Soil Res. 42(7), 763-766. DOI: http://dx.doi.org/10.1071/SR04022

Bolland, M.D.A., Gilkes, R.J., Brennan, R.F., Allen, D.G., 1996. Comparison of seven phosphorus sorption indices. Soil Res. 34(1), 81-89. DOI: http://dx.doi.org/10.1071/SR9960081

Bolland, M.D.A., Windsor, D.P., 2007. Converting reactive iron, reactive aluminium, and phosphorus retention index (PRI) to the phosphorus buffering index (PBI) for sandy soils of south-western Australia. Soil Res. 45(4), 262-265. DOI: http://dx.doi.org/10.1071/SR07026

Borggaard, O.K., 1983. Effect of surface area and mineralogy of iron oxides on their surface charge and anion-adsorption. Clays Clay Miner. 31(3), 230-232. DOI: 10.1346/CCMN.1983.0310309

Borggaard, O.K., Jorgensen, S.S., Moberg, J.P., Raben-Lange, B., 1990. Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. J. Soil Sci. 41(3), 443-449. DOI: 10.1111/j.1365-2389.1990.tb00078.x

Börling, K., Otabbong, E., Barberis, E., 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. Nutrient Cycling in Agroecosystems 59(1), 39-46. DOI: 10.1023/a:1009888707349

Bowman, R.A., Olsen, S.R., 1985. Assessment of phosphate-buffering capacity: 1. Laboratory methods. Soil Sci. 140(4), 287-291. DOI:

Bramley, R.G.V., Barrow, N.J., 1992. The reaction between phosphate and dry soil. II. The effect of time, temperature and moisture status during incubation on the amount of plant available P. J. Soil Sci. 43(4), 759-766. DOI: 10.1111/j.1365-2389.1992.tb00175.x

Brandes, J.A., Ingall, E., Paterson, D., 2007. Characterization of minerals and organic phosphorus species in marine sediments using soft X-ray fluorescence spectromicroscopy. Mar. Chem. 103(3–4), 250-265. DOI: http://dx.doi.org/10.1016/j.marchem.2006.09.004

Bray, R.H., Kurtz, L.T., 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. 59(1), 39-45. DOI:

Brookins, D.G., 1988. Eh-pH diagrams for geochemistry. Springer-Verlag, Berlin. DOI:10.1007/978-3-642-73093-1

Bruce, R.C., Rayment, G.E., 1982. Analytical methods and interpretations used by the Agricultural Chemistry Branch for soil and land use surveys. Queensland Department of Primary Industries Bulletin QB 82004.

Burkitt, L.L., Gourley, C.J.P., Sale, P.W.G., Uren, N.C., Hannah, M.C., 2001. Factors affecting the change in extractable phosphorus following the application of phosphatic fertiliser on pasture soils in southern Victoria. Soil Res. 39(4), 759-771. DOI: http://dx.doi.org/10.1071/SR00069

Burkitt, L.L., Moody, P.W., Gourley, C.J.P., Hannah, M.C., 2002. A simple phosphorus buffering index for Australian soils. Soil Res. 40(3), 497-513. DOI: http://dx.doi.org/10.1071/SR01050

Burkitt, L.L., Sale, P.W.G., Gourley, C.J.P., 2008. Soil phosphorus buffering measures should not be adjusted for current phosphorus fertility. Soil Res. 46(8), 676-685. DOI: http://dx.doi.org/10.1071/SR06126

Campbell, N.A., Reece, J.B., 2002. Biology. 7 ed. Benjamin Cummings, San Francisco, CA.

Castro, B., Torrent, J., 1998. Phosphate sorption by calcareous Vertisols and Inceptisols as evaluated from extended P-sorption curves. Eur. J. Soil Sci. 49(4), 661-667. DOI: 10.1046/j.1365-2389.1998.4940661.x

Chan, K.Y., Bellotti, W.D., Roberts, W.P., 1988. Changes in surface soil properties of vertisols under dryland cropping in a semiarid environment. Soil Res. 26(3), 509-518. DOI: http://dx.doi.org/10.1071/SR9880509

Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84(2), 133-144. DOI:

Chardon, W.J., Menon, R.G., Chien, S.H., 1996. Iron oxide-impregnated filter paper (Pi test): a review of its development and methodological research. Nutrient Cycling in Agroecosystems 46, 41-51. DOI: 10.1007/BF00210223

Cheesman, A.W., Turner, B.L., Reddy, K.R., 2010. Interaction of phosphorus compounds with anion-exchange membranes: implications for soil analysis. Soil Sci. Soc. Am. J. 74(5), 1607-1612. DOI: 10.2136/sssaj2009.0295

Christoffersen, M.R., Christoffersen, J., Kibalczyc, W., 1990. Apparent solubilities of two amorphous calcium phosphates and of octacalcium phosphate in the temperature range 30–42°C. J. Cryst. Growth 106(2–3), 349-354. DOI: http://dx.doi.org/10.1016/0022-0248(90)90079-Z

Cole, C.V., Olsen, S.R., Scott, C.O., 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Am. J. 17(4), 352-356. DOI: 10.2136/sssaj1953.03615995001700040013x

Colomb, B., Kiniry, J.R., Debaeke, P., 2000. Effect of soil phosphorus on leaf development and senescence dynamics of field-grown maize. Agron. J. 92(3), 428-435. DOI: 10.2134/agronj2000.923428x

Colwell, J.D., 1963. The estimation of the phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis. Aust. J. Exp. Ag. 3(10), 190-197. DOI: http://dx.doi.org/10.1071/EA9630190

Colwell, J.D., Donnelly, J.D., 1971. Effects of soil composition on the relationships between soil test values for phosphorus fertilizer requirements. Soil Res. 9(1), 43-54. DOI: http://dx.doi.org/10.1071/SR9710043

Condron, L.M., Moir, J.O., Tiessen, H., Stewart, J.W.B., 1990. Critical evaluation of methods for determining total organic phosphorus in tropical soils. Soil Sci. Soc. Am. J. 54(5), 1261-1266. DOI: 10.2136/sssaj1990.03615995005400050010x

Condron, L.M., Newman, S., 2011. Revisiting the fundamentals of phosphorus fractionation of sediments and soils. J. Soils Sed. 11(5), 830-840. DOI: 10.1007/s11368-011-0363-2

Conyers, M.K., 1999. Factors affecting soil test interpretation. In: K.I. Peverill, L.A. Sparrow, D.J. Reuter (Eds.), Soil analysis: an interpretation manual. CSIRO, Collingwood, Victoria, pp. 23-34

Conyers, M.K., Moody, P.W., 2009. A conceptual framework for improving the P efficiency of organic farming without inputs of soluble P fertiliser. Crop Pasture Sci. 60(2), 100-104. DOI: http://dx.doi.org/10.1071/CP06327

Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides. Wiley-VCH Verlag GmbH & Co. KGaA. DOI:10.1002/3527602097.fmatter

Coughlan, K., Loch, R., 1984. The relationship between aggregation and other soil properties in cracking clay soils. Soil Res. 22(1), 59-69. DOI: http://dx.doi.org/10.1071/SR9840059

Coventry, J.L., Halliwell, D.J., Nash, D.M., 2001. The orthophosphate content of bicarbonate soil extracts. Soil Res. 39(2), 415-421. DOI: http://dx.doi.org/10.1071/SR99140

Crews, T.E., 1996. The supply of phosphorus from native, inorganic phosphorus pools in continuously cultivated Mexican agroecosystems. Agriculture, Ecosystems & Environment 57(2–3), 197-208. DOI: http://dx.doi.org/10.1016/0167-8809(95)01013-0

Cross, A.F., Schlesinger, W.H., 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64(3–4), 197-214. DOI: http://dx.doi.org/10.1016/0016-7061(94)00023-4

Cross, A.F., Schlesinger, W.H., 2001. Biological and geochemical controls on phosphorus fractions in semiarid soils. Biogeochemistry 52(2), 155-172. DOI: 10.2307/1469449

Curtin, D., McCallum, F.M., Williams, P.H., 2003. Phosphorus in light fraction organic matter separated from soils receiving long-term applications of superphosphate. Biology and Fertility of Soils 37(5), 280-287. DOI: 10.1007/s00374-003-0598-1

Dalal, R.C., 1985. Comparative prediction of yield response and phosphorus uptake from soil using anion- and cation-anion-exchange resins. Soil Sci. 139(3), 227-231. DOI:

Dalal, R.C., 1997. Long-term phosphorus trends in Vertisols under continuous cereal cropping. Soil Res. 35(2), 327-340. DOI: http://dx.doi.org/10.1071/S96052

Dalal, R.C., Mayer, R.J., 1986. Long term trends in fertility of soils under continuous cultivation and cereal cropping in southern Queensland. I. Overall changes in soil properties and trends in winter cereal yields. Soil Res. 24(2), 265-279. DOI: http://dx.doi.org/10.1071/SR9860265

Dalal, R.C., Probert, M.E., 1997. Soil nutrient depletion. In: A.L. Clarke, P.B. Wylie (Eds.), Sustainable crop production in the sub-tropics. Queensland Department of Primary Industries, Brisbane, pp. 42–63

Dang, Y.P., Dalal, R.C., Buck, S.R., Harms, B., Kelly, R., Hochman, Z., Schwenke, G.D., Biggs, A.J.W., Ferguson, N.J., Norrish, S., Routley, R., McDonald, M., Hall, C., Singh, D.K., Daniells, I.G., Farquharson, R., Manning, W., Speirs, S., Grewal, H.S., Cornish, P., Bodapati, N., Orange, D., 2010. Diagnosis, extent, impacts, and management of subsoil constraints in the northern grains cropping region of Australia. Soil Res. 48(2), 105-119. DOI: http://dx.doi.org/10.1071/SR09074

Dang, Y.P., Dalal, R.C., Routley, R., Schwenke, G.D., Daniells, I., 2006. Subsoil constraints to grain production in the cropping soils of the north-eastern region of Australia: an overview. Aust. J. Exp. Ag. 46(1), 19-35. DOI: http://dx.doi.org/10.1071/EA04079

Day, P.R., 1965. Particle fractionation and particle-size analysis. In: C.A. Black (Ed.), Methods of soil analysis, Part 1. American Society of Agronomy, Inc., Madison, Wisconsin, pp. 545-567

de San Celedonio, R.P., Abeledo, L.G., Miralles, D.J., 2014. Identifying the critical period for waterlogging on yield and its components in wheat and barley. Plant Soil 378(1-2), 265-277. DOI: 10.1007/s11104-014-2028-6

Debicka, M., Kocowicz, A., Weber, J., Jamroz, E., 2015. Organic matter effects on phosphorus sorption in sandy soils. Archives of Agronomy and Soil Science, 1-16. DOI: 10.1080/03650340.2015.1083981

DeLaune, R.D., Jugsujinda, A., Reddy, K.R., 1999. Effect of root oxygen stress on phosphorus uptake by cattail. Journal of Plant Nutrition 22(3), 459-466. DOI:

Delgado, A., Torrent, J., 2000. Phosphorus forms and desorption patterns in heavily fertilized calcareous and limed acid soils. Soil Sci. Soc. Am. J. 64(6), 2031-2037. DOI: 10.2136/sssaj2000.6462031x

Devau, N., Cadre, E.L., Hinsinger, P., Jaillard, B., Gérard, F., 2009. Soil pH controls the environmental availability of phosphorus: Experimental and mechanistic modelling approaches. Appl. Geochem. 24(11), 2163-2174. DOI: http://dx.doi.org/10.1016/j.apgeochem.2009.09.020

Devau, N., Hinsinger, P., Le Cadre, E., Colomb, B., Gérard, F., 2011. Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils. Geochim. Cosmochim. Acta 75(10), 2980-2996. DOI: http://dx.doi.org/10.1016/j.gca.2011.02.034

Devau, N., Hinsinger, P., Le Cadre, E., Colomb, B., Gérard, F., 2013. Reply to the Comment by D.G. Lumsdon on "Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils" by N. Devau, P. Hinsinger, E. Le Cadre, B. Colomb and F. Gérard. Geochim. Cosmochim. Acta 124, 410-417. DOI: http://dx.doi.org/10.1016/j.gca.2013.03.044

Devau, N., Le Cadre, E., Hinsinger, P., Gérard, F., 2010. A mechanistic model for understanding root-induced chemical changes controlling phosphorus availability. Ann. Bot. 105(7), 1183-1197. DOI: 10.1093/aob/mcq098

Di, H.J., Condron, L.M., Frossard, E., 1997. Isotope techniques to study phosphorus cycling in agricultural and forest soils: a review. Biology and Fertility of Soils 24(1), 1-12. DOI: 10.1007/bf01420213

Dinkelaker, B., Römheld, V., Marschner, H., 1989. Citric acid excretion and precipitation of calcium citrate in the rhizosphere of white lupin (Lupinus albus L.). Plant, Cell Environ. 12(3), 285-292. DOI: 10.1111/j.1365-3040.1989.tb01942.x

Djodjic, F., Börling, K., Bergström, L., 2004. Phosphorus leaching in relation to soil type and soil phosphorus content. J. Environ. Qual. 33(2), 678-684. DOI: 10.2134/jeq2004.6780

Dodd, K., Guppy, C.N., Lockwood, P.V., Rochester, I.J., 2013. Impact of waterlogging on the nutrition of cotton (Gossypium hirsutum L.) produced in sodic soils. Crop Pasture Sci. 64(8), 816-824. DOI: http://dx.doi.org/10.1071/CP13093

Doolette, A.L., Smernik, R.J., Dougherty, W.J., 2010. Rapid decomposition of phytate applied to a calcareous soil demonstrated by a solution ^{31}P NMR study. Eur. J. Soil Sci. 61, 563-575. DOI:

Doolette, A.L., Smernik, R.J., Dougherty, W.J., 2011a. Overestimation of the importance of phytate in NaOH–EDTA soil extracts as assessed by 31P NMR analyses. Org. Geochem. 42(8), 955-964. DOI: http://dx.doi.org/10.1016/j.orggeochem.2011.04.004

Doolette, A.L., Smernik, R.J., Dougherty, W.J., 2011b. A quantitative assessment of phosphorus forms in some Australian soils. Soil Res. 49(2), 152-165. DOI: http://dx.doi.org/10.1071/SR10092

Dorahy, C.G., Rochester, I.J., Blair, G.J., 2004. Response of field-grown cotton (Gossypium hirsutum L.) to phosphorus fertilisation on alkaline soils in eastern Australia. Soil Res. 42(8), 913-920. DOI: http://dx.doi.org/10.1071/SR04037

Dougherty, W.J., Mason, S.D., Burkitt, L.L., Milham, P.J., 2011. Relationship between phosphorus concentration in surface runoff and a novel soil phosphorus test procedure (DGT) under simulated rainfall. Soil Res. 49(6), 523-528. DOI: http://dx.doi.org/10.1071/SR11151

Ebeling, A.M., Bundy, L.G., Kittell, A.W., Ebeling, D.D., 2008. Evaluating the Bray P1 test on alkaline, calcareous soils. Soil Sci. Soc. Am. J. 72(4), 985-991. DOI: 10.2136/sssaj2006.0347

Eveborn, D., Gustafsson, J.P., Hesterberg, D., Hillier, S., 2009. XANES speciation of P in environmental samples: an assessment of filter media for on-site wastewater treatment. Environ. Sci. Technol. 43(17), 6515-6521. DOI: 10.1021/es901084z

Fageria, N.K., Stone, L.F., 2006. Physical, chemical, and biological changes in the rhizosphere and nutrient availability. Journal of Plant Nutrition 29(7), 1327-1356. DOI: 10.1080/01904160600767682

Federer, A.C., Hornbeck, J.W., 1985. The buffer capacity of forest soils in New England. Water, Air, Soil Pollut. 26(2), 163-173. DOI: 10.1007/bf00292066

Fixen, P.E., Grove, J.H., 1990. Testing soil for phosphorus. In: R.L. Westerman (Ed.), Soil testing and plant analysis. Soil Sci. Soc. Am., Madison, WI., pp. 141-180

Fixen, P.E., Ludwick, A.E., Olsen, S.R., 1983. Phosphorus and potassium fertilization of irrigated alfalfa on calcareous soils: II. soil phosphorus solubility relationships. Soil Sci. Soc. Am. J. 47(1), 112-117. DOI: 10.2136/sssaj1983.03615995004700010023x

Flavel, R.J., Guppy, C.N., Tighe, M.K., Watt, M., Young, I.M., 2014. Quantifying the response of wheat (*Triticum aestivum* L) root system architecture to phosphorus in an Oxisol. Plant Soil 385(1-2), 303-310. DOI: 10.1007/s11104-014-2191-9

Freeman, J.S., Rowell, D.L., 1981. The adsorption and precipitation of phosphate onto calcite. J. Soil Sci. 32(1), 75-84. DOI: 10.1111/j.1365-2389.1981.tb01687.x

Freese, D., van der Zee, S.E.A.T.M., van Riemsdijk, W.H., 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils. J. Soil Sci. 43(4), 729-738. DOI: 10.1111/j.1365-2389.1992.tb00172.x

Froelich, P.N., 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnologya and Oceanography 33(4/2), 649-668. DOI:

Frossard, E., Condron, L.M., Oberson, A., Sinaj, S., Fardeau, J.C., 2000. Processes governing phosphorus availability in temperate soils. J Environ Qual 29(1), 15-23. DOI:

Gächter, R., Meyer, J.S., Mares, A., 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnol. Oceanogr. 33(6part2), 1542-1558. DOI: 10.4319/lo.1988.33.6part2.1542

Gardner, W.K., Parbery, D.G., Barber, D.A., 1982. The acquisition of phosphorus by *Lupinus albus* L. II. The effect of varying phosphorus supply and soil type on some characteristics of the soil/root interface. Plant Soil 68(1), 33-41. DOI: 10.1007/bf02374725

Gaxiola, R.A., Edwards, M., Elser, J.J., 2011. A transgenic approach to enhance phosphorus use efficiency in crops as part of a comprehensive strategy for sustainable agriculture. Chemosphere 84, 840-845. DOI:

Gérard, F., 2016. Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils — A myth revisited. Geoderma 262, 213-226. DOI: http://dx.doi.org/10.1016/j.geoderma.2015.08.036

Gerke, J., Hermann, R., 1992. Adsorption of orthophosphate to humic-Fe-complexes and to amorphous Fe-oxide. Zeitschrift für Pflanzenernährung und Bodenkunde 155(3), 233-236. DOI: 10.1002/jpln.19921550313

Glæsner, N., Kjaergaard, C., Rubæk, G.H., Magid, J., 2011. Effect of irrigation regimes on mobilization of nonreactive tracers and dissolved and particulate phosphorus in slurry-injected soils. Water Resour. Res. 47(12), W12536. DOI: 10.1029/2011wr010769

Goldberg, S., Sposito, G., 1984a. A chemical model of phosphate adsorption by soils: I. Reference oxide minerals. Soil Sci. Soc. Am. J. 48(4), 772-778. DOI: 10.2136/sssaj1984.03615995004800040015x

Goldberg, S., Sposito, G., 1984b. A chemical model of phosphate adsorption by soils: II. noncalcareous soils. Soil Sci. Soc. Am. J. 48(4), 779-783. DOI: 10.2136/sssaj1984.03615995004800040016x

Gollany, H.T., Schumacher, T.E., 1993. Combined use of colorimetric and microelectrode methods for evaluating rhizosphere pH. Plant Soil 154(2), 151-159. DOI: 10.1007/bf00012520

Grabau, L.J., Blevins, D.G., Minor, H.C., 1986. P nutrition during seed development. Plant Physiol. 82(4), 1008-1012. DOI:

Grant, C., Bittman, S., Montreal, M., Plenchette, C., Morel, C., 2005. Soil and fertilizer phosphorus: Effects on plant P supply and mycorrhizal development. Canadian Journal of Plant Science 85, 3-14. DOI:

Grant, C.A., Flaten, D.N., Tomasiewicz, D.J., Sheppard, S.C., 2001. The importance of early season phosphorus nutrition. Canadian Journal of Plant Science 81, 211–224. DOI:

Gras, F., 1974. Une méthode expérimentale pour la détermination du pH et de la solubilité du carbonate de calcium en sols calcaires. Bull. Assoc. Fr. Etude Sol 1, 33–48. DOI:

Grinsted, M.J., Hedley, M.J., White, R.E., Nye, P.H., 1982. Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. I. pH change and the increase in P concentration in the soil solution. New Phytol. 91(1), 19-29. DOI: 10.2307/2434347

Grunth, N.L., Askaer, L., Eberling, B., 2008. Oxygen depletion and phosphorus release following flooding of a cultivated wetland area in Denmark. Danish Journal of Geography 108(2), 17-25. DOI:

Guo, F., Yost, R.S., Hue, N.V., Evensen, C.I., Silva, J.A., 2000. Changes in phosphorus fractions in soils under intensive plant growth. Soil Sci. Soc. Am. J. 64(5), 1681-1689. DOI: 10.2136/sssaj2000.6451681x

Guo, F., Yost, R.S., Jones, R.C., 1996. Evaluating iron impregnated paper strips for assessing available soil phosphorus. Commun. Soil Sci. Plant Anal. 27(11-12), 2561-2590. DOI: 10.1080/00103629609369723

Guppy, C.N., McLaughlin, M.J., 2009. Options for increasing the biological cycling of phosphorus in low-input and organic agricultural systems. Crop Pasture Sci. 60(2), 116-123. DOI: http://dx.doi.org/10.1071/CP07157

Guppy, C.N., Menzies, N.W., Moody, P.W., Blamey, F.P.C., 2005. Competitive sorption reactions between phosphorus and organic matter in soil: a review. Soil Res. 43(2), 189-202. DOI: http://dx.doi.org/10.1071/SR04049

Guppy, C.N., Menzies, N.W., Moody, P.W., Compton, B.L., Blamey, F.P.C., 2000. Analytical methods and quality assurance. Commun. Soil Sci. Plant Anal. 31(11-14), 1981-1991. DOI: 10.1080/00103620009370556

Gustafsson, J.P., 2015. Visual MINTEQ. V3.1 Version 3.1. Available at: http://vminteq.lwr.kth.se/. Date accessed: 16 July 2015

Harrison, R.B., Adams, F., 1987. Solubility characteristics of residual phosphate in a fertilized and limed Ultisol. Soil Sci. Soc. Am. J. 51(4), 963-969. DOI: 10.2136/sssaj1987.03615995005100040026x

Hause, B., Fester, T., 2005. Molecular and cell biology of arbuscular mycorrhizal symbiosis. Planta 221(2), 184-196. DOI: 10.1007/s00425-004-1436-x

Havlin, J.L., Westfall, D.G., 1984. Soil test phosphorus and solubility relationships in calcareous soils. Soil Sci. Soc. Am. J. 48(2), 327-330. DOI: 10.2136/sssaj1984.03615995004800020021x

Hayman, D.S., 1983. The physiology of vesicular–arbuscular endomycorrhizal symbiosis. Canadian Journal of Botany 61(3), 944-963. DOI: 10.1139/b83-105

Hedley, M., McLaughlin, M.J., 2005. Reactions of phosphate fertilizers and by-products in soils. In: J.T. Sims, A.N. Sharpley (Eds.), Phosphorus: agriculture and the environment. Agronomy Monograph. American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc, Madison, Wisconsin, USA, pp. 181-252

Hedley, M.J., Nye, P.H., White, R.E., 1982a. Plant-induced changes in the rhizosphere of rape (*Brassica nafus* var. Emerald) seedlings. II. Origin of the pH change. New Phytol. 91, 31-44. DOI:

Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982b. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sci. Soc. Am. J. 46, 960-976. DOI:

Hedley, M.J., White, R.E., Nye, P.H., 1982c. Plant-induced changes in the rhizosphere of rape (*Brassica nafus* var. Emerald) seedlings. III. Changes in L value, soil phosphate fractions and phosphatase activity. New Phytol. 91, 45-56. DOI:

Helyar, K.R., Spencer, K., 1977. Sodium bicarbonate soil test values and the phosphate buffering capacity of soils. Soil Res. 15(3), 263-273. DOI: http://dx.doi.org/10.1071/SR9770263

Hesterberg, D., 2010. Macro-scale chemical properties and x-ray absorption spectroscopy of soil phosphorus. In: B. Singh, M. Gräfe (Eds.), Synchrotron-based techniques in soils and sediments. Developments in Soil Science. Elsevier, Burlington, MA., pp. 313-356

Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. Plant Soil 237, 173-195. DOI: 10.1023/A:1013351617532

Hinsinger, P., Betencourt, E., Bernard, L., Brauman, A., Plassard, C., Shen, J., Tang, X., Zhang, F., 2011. P for two, sharing a scarce resource: soil phosphorus acquisition in the rhizosphere of intercropped species. Plant Physiol. 156(3), 1078-1086. DOI: http://dx.doi.org/10.1104/pp.111.175331

Hinsinger, P., Gilkes, R.J., 1995. Root-induced dissolution of phosphate rock in the rhizosphere of lupins grown in alkaline soil. Soil Res. 33(3), 477-489. DOI: http://dx.doi.org/10.1071/SR9950477

Hinsinger, P., Plassard, C., Tang, C., Jaillard, B., 2003. Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: A review. Plant Soil 248(1-2), 43-59. DOI: 10.1023/a:1022371130939

Holford, I.C.R., 1980a. Effects of phosphate buffer capacity on critical levels and relationships between soil tests and labile phosphate in wheat growing soils. Soil Res. 18(4), 405-414. DOI: http://dx.doi.org/10.1071/SR9800405

Holford, I.C.R., 1980b. Greenhouse evaluation of four phosphorus soil tests in relation to phosphate buffering and labile phosphate in soils. Soil Sci. Soc. Am. J. 44(3), 555-559. DOI: 10.2136/sssaj1980.03615995004400030024x

Holford, I.C.R., 1982. The comparative significance and utility of the Freundlich and Langmuir parameters for characterizing sorption and plant availability of phosphate in soils. Soil Res. 20(3), 233-242. DOI: http://dx.doi.org/10.1071/SR9820233

Holford, I.C.R., 1997. Soil phosphorus: its measurement, and its uptake by plants. Soil Res. 35(2), 227-240. DOI: http://dx.doi.org/10.1071/S96047

Holford, I.C.R., Doyle, A.D., 1992. Influence of intensity/quantity characteristics of soil phosphorus tests on their relationships to phosphorus responsiveness of wheat under field conditions. Soil Res. 30(3), 343-356. DOI: http://dx.doi.org/10.1071/SR9920343

Holford, I.C.R., Mattingly, G.E.G., 1975. The high- and low-energy phosphate assorbing surfaces in calcareous soils. J. Soil Sci. 26, 407-417. DOI: 10.1111/j.1365-2389.1975.tb01964.x

Holford, I.C.R., Mattingly, G.E.G., 1979. Effects of phosphate buffering on the extraction of labile phosphate by plants and by soil tests. Soil Res. 17(3), 511-514. DOI: http://dx.doi.org/10.1071/SR9790511

House, W.A., Donaldson, L., 1986. Adsorption and coprecipitation of phosphate on calcite. J. Colloid Interface Sci. 112(2), 309-324. DOI: http://dx.doi.org/10.1016/0021-9797(86)90101-3

Hubble, G.D., 1984. The cracking clay soils: Definition, distribution, nature, genesis and use. In: J.W. McGarity, E.H. Hoult, H.B. So (Eds.), The properties and utilisation of cracking clay soils, University of New England, Armidale, NSW, pp. 3-13.

Hurney, A.P., Schroeder, B.L., Skocaj, D.M., 2010. Phosphorus fertiliser requirements for soils with very high phosphorus sorption characteristics [Poster paper], Proceedings of the Australian Society of Sugar Cane Technologists, pp. 709.

Hutchison, K.J., Hesterberg, D., 2004. Dissolution of phosphate in a phosphorus-enriched Ultisol as affected by microbial reduction. J. Environ. Qual. 33(5), 1793-1802. DOI: 10.2134/jeq2004.1793

Ige, D.V., Akinremi, O.O., Flaten, D.N., 2005. Environmental index for estimating the risk of phosphorus loss in calcareous soils of manitoba. J. Environ. Qual. 34(6), 1944-1951. DOI: 10.2134/jeq2004.0468

Indiati, R., Diana, G., Figliolia, A., Perucchini, I., 2002. Comparison of conventional and innovative soil phosphorus tests in estimating plant-available phosphorus. Options Méditerranéennes A(50), 257-266. DOI:

Ingall, E.D., Brandes, J.A., Diaz, J.M., de Jonge, M.D., Paterson, D., McNulty, I., Elliott, W.C., Northrup, P., 2011. Phosphorus K-edge XANES spectroscopy of mineral standards. J. Synchrot. Radiat. 18(2), 189-197. DOI: 10.1107/s0909049510045322

Inskeep, W.P., Silvertooth, J.C., 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. Soil Sci. Soc. Am. J. 52(4), 941-946. DOI: 10.2136/sssaj1988.03615995005200040007x

Isbell, R.F., 2002. The Australian Soil Classification. Revised Edition. CSIRO Publishing, Melbourne.

Isbell, R.F., Thompson, C.H., Hubble, G.D., Beckman, G.D., Paton, T.R., 1967. Atlas of Australian Soils. Sheet 4, Brisbane - Charleville - Rockhampton - Clermont Area. CSIRO Division of Soils, Melbourne.

Israel, D.W., 1987. Investigation of the role of phosphorus in symbiotic dinitrogen fixation. Plant Physiol. 84(3), 835-840. DOI:

IUSS Working Group WRB, 2014. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps, FAO, Rome.

Jacob, J.S., Griffin, R.W., Miller, W.L., Wilding, L.R., 1997. Aquerts and aquertic soils: a querulous proposition. In: M.J. Vepraskas, S.W. Sprecher (Eds.), Aquic Conditions and Hydric Soils: The Problem Soils. SSSA Special Publication. Soil Science Society of America, Madison, WI, pp. 61-77. DOI:10.2136/sssaspecpub50.c4

Jaggi, R.C., Aulakh, M.S., Sharma, R., 2005. Impacts of elemental S applied under various temperature and moisture regimes on pH and available P in acidic, neutral and alkaline soils. Biology and Fertility of Soils 41(1), 52-58. DOI: 10.1007/s00374-004-0792-9

Jayachandran, K., Schwab, A.P., Hetricic, B.A.D., 1992. Mineralization of organic phosphorus by vesicular-arbuscular mycorrhizal fungi. Soil Biol. Biochem. 24(9), 897-903. DOI: 10.1016/0038-0717(92)90012-m

Johnston, A.E., Poulton, P.R., 1992. The role of phosphorus in crop production and soil fertility: 150 years of field experiments at Rothamsted, United Kingdom. In: J.J. Schultz (Ed.), Phosphate fertilizers and the environment. International Fertilizer Development Center, Muscle Shoals, Alabama, USA, pp. 45–64

Kadlac, R.H., Wallace, S.D., 2009. Treatment wetlands. 2 ed. CRC Press, Boca Raton, FL, USA.

Kashem, M.A., Akinremi, O.O., Racz, G.J., 2004. Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. Can. J. Soil Sci. 84(1), 83-90. DOI: 10.4141/s03-018

Kelly, S.D., Hesterberg, D., Ravel, B., 2008. Analysis of soils and minerals using x-ray absorption spectroscopy. In: A.L. Ulery, L.R. Drees (Eds.), Methods of soil analysis, Part 5. SSSA Book Series. Soil Science Society of America, Madison, Wisconsin, USA, pp. 387-464

Kerr, H.W., von Stieglitz, C.R., 1938. The laboratory determination of soil fertility, Technical Communication No. 9. Qld Sugar Experiment Stations.

Khare, N., Hesterberg, D., Martin, J.D., 2005. XANES investigation of phosphate sorption in single and binary systems of iron and aluminium oxide minerals. Environ. Sci. Technol. 39, 2152-2160. DOI:

Khare, N., Martin, J.D., Hesterberg, D., 2007. Phosphate bonding configuration on ferrihydrite based on molecular orbital calculations and XANES fingerprinting. Geochim. Cosmochim. Acta 71(18), 4405-4415. DOI: http://dx.doi.org/10.1016/j.gca.2007.07.008

Khasawneh, F.E., Doll, E.C., 1978. The use of phosphate rock for direct application to soils. Advances in Agronomy 30, 159-206. DOI: 10.1016/S0065-2113(08)60706-3

Khorsandi, F., 1994. Sulfuric acid effects on iron and phosphorus availability in two calcareous soils. Journal of Plant Nutrition 17(9), 1611-1623. DOI: 10.1080/01904169409364833

Kirkby, C.A., Richardson, A.E., Wade, L.J., Batten, G.D., Blanchard, C., Kirkegaard, J.A., 2013. Carbon-nutrient stoichiometry to increase soil carbon sequestration. Soil Biol. Biochem. 60(0), 77-86. DOI: http://dx.doi.org/10.1016/j.soilbio.2013.01.011

Kirkby, E.A., Pilbeam, D.J., 1984. Calcium as a plant nutrient. Plant, Cell Environ. 7(6), 397-405. DOI: 10.1111/j.1365-3040.1984.tb01429.x

Kissel, D.E., Sonon, L.S., Cabrera, M.L., 2012. Rapid measurement of soil pH buffering capacity. Soil Sci. Soc. Am. J. 76(2), 694-699. DOI: 10.2136/sssaj2011.0091

Kizewski, F.R., Liu, Y.-T., Morris, A., Hesterberg, D., 2011. Spectroscopic approaches for phosphorus speciation in soils and other environmental systems. J. Environ. Qual. 40(3), 751-766. DOI:

Kleinman, P.J.A., Sharpley, A.N., 2002. Estimating soil phosphorus sorption saturation from Mehlich-3 data. Commun. Soil Sci. Plant Anal. 33(11-12), 1825-1839. DOI: 10.1081/css-120004825

Klysubun, W., Sombunchoo, P., Deenan, W., Kongmark, C., 2012. Performance and status of beamline BL8 at SLRI for X-ray absorption spectroscopy. J. Synchrot. Radiat. 19(6), 930-936. DOI: doi:10.1107/S0909049512040381

Koopmans, G.F., Chardon, W.J., Ehlert, P.A.I., Dolfing, J., Suurs, R.A.A., Oenema, O., van Riemsdijk, W.H., 2004. Phosphorus availability for plant uptake in a phosphorus-enriched noncalcareous sandy soil. J. Environ. Qual. 33(3), 965-975. DOI: 10.2134/jeq2004.0965

Kovar, J.L., Classens, N., 2005. Soil-root interactions and phosphorus nutrition of plants. In: J.T. Sims, A.N. Sharpley (Eds.), Phosphorus: agriculture and the environment. Agronomy Monograph. American Societyof Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc, Madison, Wisconsin, USA

Krannitz, P.G., Aarssen, L.W., Lefebvre, D.D., 1991. Correction for non-linear relationships between root size and short term Pi uptake in genotype comparisons. Plant Soil 133(2), 157-167. DOI:

Kruse, J., Abraham, M., Amelung, W., Baum, C., Bol, R., Kühn, O., Lewandowski, H., Niederberger, J., Oelmann, Y., Rüger, C., Santner, J., Siebers, M., Siebers, N., Spohn, M., Vestergren, J., Vogts, A., Leinweber, P., 2015. Innovative methods in soil phosphorus research: A review. Journal of Plant Nutrition and Soil Science 178(1), 43-88. DOI: 10.1002/jpln.201400327

Kruse, J., Leinweber, P., Eckhardt, K.-U., Godlinski, F., Hu, Y., Zuin, L., 2009. Phosphorus L2,3-edge XANES: overview of reference compounds. J. Synchrot. Radiat. 16(2), 247-259. DOI: 10.1107/s0909049509000211

Lefroy, R.D.B., Samosir, S.S.R., Blair, G.J., 1993. The dynamics of sulfur, phosphorus and iron in flooded soils as affected by changes in Eh and pH. Soil Res. 31(4), 493-508. DOI: http://dx.doi.org/10.1071/SR9930493

Lehmann, J., Schroth, G., 2003. Nutrient Leaching. In: G. Schroth, F. Sinclair (Eds.), Trees, Crops and Soil Fertility. CABI Publishing, Wallingford, pp. 151-166

Lehr, J.R., Brown, W.E., 1958. Calcium phosphate fertilizers: II. A petrographic study of their alteration in soils. Soil Sci. Soc. Am. J. 22(1), 29-32. DOI: 10.2136/sssaj1958.03615995002200010009x

Lester, D.W., Dowling, C.W., Birch, C.J., 2003. Fertilizer N and P application on two vertosols of NE Australia: I Trends in bicarbonate extractable P. In: Z.Z. Rengel (Ed.), 2nd International Symposium on Phosphorus Dynamics in the Soil-Plant Continuum, Perth, Australia, pp. 204-205.

Lin, T.-H., Ho, S.-B., Houng, K.-H., 1991. The use of iron oxide-impregnated filter paper for the extraction of available phosphorus from Taiwan soils. Plant Soil 133(2), 219-226. DOI: 10.1007/bf00009194

Lindsay, W., L., 1979. Chemical equilibria in soils. Wiley-Interscience, New York.

Liu, C., Muchhal, U.S., Uthappa, M., Kononowicz, A.K., Raghothama, K.G., 1998. Tomato phosphate transporter genes are differentially regulated in plant tissues by phosphorus. Plant Physiol. 116, 91-99. DOI:

Liu, G.-d., James, D., Thai, P., 2006. Induction of root hair growth in a phosphorus-buffered culture solution. Agricultural Sciences in China 5(5), 370-376. DOI: http://dx.doi.org/10.1016/S1671-2927(06)60063-1

Liu, J., Hu, Y., Yang, J., Abdi, D., Cade-Menun, B.J., 2015. Investigation of soil legacy phosphorus transformation in long-term agricultural fields using sequential fractionation, P K-edge XANES and solution P NMR spectroscopy. Environ. Sci. Technol. 49(1), 168. DOI:

Loeppert, R.H., Inskeep, W.P., 1996. Iron, Methods of Soil Analysis. Part 3. Chemical Methods. Soil Science Society of America and American Society of Agronomy, Madison, WI USA

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. Soil Sci. Soc. Am. J. 70(6), 2038-2048. DOI: 10.2136/sssaj2006.0051

Lookman, R., Freese, D., Merckx, R., Vlassak, K., van Riemsdijk, W.H., 1995. Long-term kinetics of phosphate release from soil. Environ. Sci. Technol. 29(6), 1569-1575. DOI: 10.1021/es00006a020

Lovley, D.R., 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiological Reviews 55(2), 259-287. DOI:

Lu, S., Braunberger, P.G., Miller, M.H., 1994. Response of vesicular-arbuscular mycorrhizas of maize to various rates of P addition to different rooting zones. Plant Soil 158(1), 119-128. DOI: 10.1007/bf00007924

Lumsdon, D.G., 2012. Comment on "Fertilization and pH effects on processes and mechanisms controlling dissolved inorganic phosphorus in soils" by Nicolas Devau et al. (2011). Geochim. Cosmochim. Acta 92, 260-264. DOI: http://dx.doi.org/10.1016/j.gca.2012.05.042

Lund, K., Fogler, H.S., McCune, C.C., Ault, J.W., 1975. Acidization—II. The dissolution of calcite in hydrochloric acid. Chem. Eng. Sci. 30(8), 825-835. DOI: http://dx.doi.org/10.1016/0009-2509(75)80047-9

Lynch, J.P., 1995. Root architecture and plant productivity. Plant Physiol. 109, 7-13. DOI: 10.1104/pp.109.1.7

Lynch, J.P., 2007. Roots of the second green revolution. Australian Journal of Botany 55(5), 493-512. DOI: http://dx.doi.org/10.1071/BT06118

Lynch, J.P., Ho, M.D., 2005. Rhizoeconomics: Carbon costs of phosphorus acquisition. Plant Soil 269(1-2), 45-56. DOI: 10.1007/s11104-004-1096-4

Maguire, R.O., Sims, J.T., 2002. Measuring agronomic and environmental soil phosphorus saturation and predicting phosphorus leaching with Mehlich 3. Soil Sci. Soc. Am. J. 66(6), 2033-2039. DOI: 10.2136/sssaj2002.2033

Mallarino, A.P., Atia, A.M., 2005. Correlation of a resin membrane soil phosphorus test with corn yield and routine soil tests. Soil Sci. Soc. Am. J. 69, 266-272. DOI:

Marschner, H., 1995. Mineral nutrition of higher plants. 2 ed. Academic Press, London.

Marschner, H., Römheld, V., Horst, W.J., Martin, P., 1986a. Root-induced changes in the rhizosphere: Importance for the mineral nutrition of plants. Zeitschrift für Pflanzenernährung und Bodenkunde 149(4), 441-456. DOI: 10.1002/jpln.19861490408

Marschner, H., Römheld, V., Kissel, M., 1986b. Different strategies in higher plants in mobilization and uptake of iron. Journal of Plant Nutrition 9(3-7), 695-713. DOI: 10.1080/01904168609363475

Mason, S., Hamon, R., Zhang, H., Anderson, J., 2008. Investigating chemical constraints to the measurement of phosphorus in soils using diffusive gradients in thin films (DGT) and resin methods. Talanta 74(4), 779-787. DOI: http://dx.doi.org/10.1016/j.talanta.2007.07.005

Mason, S., McNeill, A., McLaughlin, M., Zhang, H., 2010. Prediction of wheat response to an application of phosphorus under field conditions using diffusive gradients in thin-films (DGT) and extraction methods. Plant Soil 337(1-2), 243-258. DOI: 10.1007/s11104-010-0521-0

Matamwa, W., Yunusa, I., Blair, G., Guppy, C., 2015. In situ acidulation of rock phosphate, 17th Australian Agronomy Conference, Hobart, Tasmania, Australia.

McDowell, R.W., Condron, L.M., Mahieu, N., 2003a. Analysis of phosphorus in sequentially extracted grassland soils using solid state NMR. Commun. Soil Sci. Plant Anal. 34(11-12), 1623-1636. DOI: 10.1081/css-120021301

McDowell, R.W., Mahieu, N., Brookes, P.C., Poulton, P.R., 2003b. Mechanisms of phosphorus solubilisation in a limed soil as a function of pH. Chemosphere 51(8), 685-692. DOI: http://dx.doi.org/10.1016/S0045-6535(03)00107-3

McDowell, R.W., Sharpley, A.N., 2003. Phosphorus solubility and release kinetics as a function of soil test P concentration. Geoderma 112(1–2), 143-154. DOI: http://dx.doi.org/10.1016/S0016-7061(02)00301-4

McKenzie, R.H., Stewart, J.W.B., Dormaar, J.F., Schaalje, G.B., 1992. Long-term crop rotation and fertilizer effects on phosphorus transformations: II. In a Luvisolic soil. Can. J. Soil Sci. 72(4), 581-589. DOI: 10.4141/cjss92-048

McLachlan, K.D., 1965. The nature of available phosphorus in some acid pasture soils and a comparison of estimating procedures. Aust. J. Exp. Ag. 5(17), 125-132. DOI: http://dx.doi.org/10.1071/EA9650125

McLaren, T.I., Bell, M.J., Rochester, I.J., Guppy, C.N., Tighe, M.K., Flavel, R.J., 2013. Growth and phosphorus uptake of faba bean and cotton are related to Colwell-P concentrations in the subsoil of Vertosols. Crop Pasture Sci. 64(8), 825-833. DOI: http://dx.doi.org/10.1071/CP13025

McLaren, T.I., Guppy, C.N., Tighe, M.K., Forster, N., Grave, P., Lisle, L.M., Bennett, J.W., 2012. Rapid, nondestructive total elemental analysis of vertisol soils using portable X-ray fluorescence. Soil Sci. Soc. Am. J. 76(4), 1436-1445. DOI: 10.2136/sssaj2011.0354

McLaren, T.I., Guppy, C.N., Tighe, M.K., Moody, P., Bell, M., 2014a. Dilute acid extraction is a useful indicator of the supply of slowly available phosphorus in Vertisols. Soil Sci. Soc. Am. J. 78(1), 139-146. DOI: 10.2136/sssaj2013.05.0188

McLaren, T.I., Guppy, C.N., Tighe, M.K., Schefe, C.R., Flavel, R.J., Cowie, B.A., Tadich, A., 2015a. Validation of soil phosphate removal by alkaline and acidic reagents in a Vertosol soil using XANES spectroscopy. Commun. Soil Sci. Plant Anal. 46(16), 1998-2017. DOI: 10.1080/00103624.2015.1048252

McLaren, T.I., McLaughlin, M.J., McBeath, T.M., Simpson, R.J., Smernik, R.J., Guppy, C.N., Richardson, A.E., 2015b. The fate of fertiliser P in soil under pasture and uptake by subterraneum clover – a field study using 33P-labelled single superphosphate. Plant Soil, 1-16. DOI: 10.1007/s11104-015-2610-6

McLaren, T.I., Smernik, R.J., Guppy, C.N., Bell, M.J., Tighe, M.K., 2014b. The organic P composition of vertisols as determined by ^{31}P NMR spectroscopy. Soil Sci. Soc. Am. J. 78(6), 1893-1902. DOI: 10.2136/sssaj2014.04.0139

McLaren, T.I., Smernik, R.J., McLaughlin, M.J., McBeath, T., Kirby, J.K., Simpson, R.J., Guppy, C.N., Doolette, A., Richardson, A., 2015c. Complex forms of soil organic phosphorus – a major component of soil phosphorus. Environ. Sci. Technol. DOI: 10.1021/acs.est.5b02948

Mclaughlin, M., Lancaster, P., Sale, P., Uren, N., Peverill, K., 1994. Comparison of cation/anion exchange resin methods for multi-element testing of acidic soils. Soil Res. 32(2), 229-240. DOI: http://dx.doi.org/10.1071/SR9940229

Mclaughlin, M.J., Alston, A.M., Martin, J.K., 1988a. Phosphorus cycling in wheat-pasture rotations III. Organic phosphorus turnover and phosphorus cycling. Soil Res. 26(2), 343-353. DOI: http://dx.doi.org/10.1071/SR9880343

Mclaughlin, M.J., Alston, A.M., Martin, J.K., 1988b. Phosphorus cycling in wheat pasture rotations I. The source of phosphorus taken up by wheat. Soil Res. 26(2), 323-331. DOI: http://dx.doi.org/10.1071/SR9880323

Mclaughlin, M.J., Alston, A.M., Martin, J.K., 1988c. Phosphorus cycling in wheat pasture rotations II. The role of the microbial biomass in phosphorus cycling. Soil Res. 26(2), 333-342. DOI: http://dx.doi.org/10.1071/SR9880333

McLaughlin, M.J., McBeath, T.M., Smernik, R., Stacey, S.P., Ajiboye, B., Guppy, C., 2011. The chemical nature of P accumulation in agricultural soils—implications for fertiliser management and design: an Australian perspective. Plant Soil 349(1-2), 69-87. DOI: 10.1007/s11104-011-0907-7

McLaughlin, M.J., Reuter, D.J., Rayment, G.E., 1999. Soil testing - principles and concepts. In: K.I. Peverill, L.A. Sparrow, D.J. Reuter (Eds.), Soil analysis: an interpretation manual. CSIRO, Collingwood, Victoria, pp. 1-21

Mehlich, A., 1953. Determination of P, Ca, Mg, K, Na, and NH_4., North Carolina Soil Test Division, Mimeo.

Mehlich, A., 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15(12), 1409-1416. DOI: 10.1080/00103628409367568

Menon, R.G., Chien, S.H., Gadalla, A.N., 1991. Comparison of Olsen and Pi soil tests for evaluating phosphorus bioavailability in a calcareous soil treated with single superphosphate and partially acidulated phosphate rock. Fertilizer Res. 29(2), 153-158. DOI: 10.1007/bf01048954

Menon, R.G., Chien, S.H., Hammond, L.L., Arora, B.R., 1990. Sorption of phosphorus by the iron oxide-impregnated filter paper (Pi soil test) embedded in soils. Plant Soil 126(2), 287-294. DOI: 10.1007/bf00012831

Menon, R.G., Chien, S.H., Hammond, L.L., Henao, J., 1989. Modified techniques for preparing paper strips for the new Pi soil test for phosphorus. Fertilizer Res. 19(2), 85-91. DOI: 10.1007/bf01054679

Miller, R.O., Jacobsen, J.S., Skogley, E.O., 1994. Aerial accumulation and partitioning of nutrients by hard red spring wheat. Commun. Soil Sci. Plant Anal. 25(11-12), 1891-1911. DOI: 10.1080/00103629409369162

Ming, D.W., 2006. Carbonates. In: R. Lal (Ed.), Encyclopedia of Soil Science. Taylor & Francis, Boca Raton, Florida, pp. 202-205. DOI:10.1081/E-ESS-120001813

Modaihsh, A.S., Al-Mustafa, W.A., Metwally, A.I., 1989. Effect of elemental sulphur on chemical changes and nutrient availability in calcareous soils. Plant Soil 116(1), 95-101. DOI: 10.1007/bf02327261

Mohamed, G.E.S., Marshall, C., 1979. The pattern of distribution of phosphorus and dry matter with time in spring wheat. Ann. Bot. 44(6), 721-730. DOI:

Mollier, A., Pellerin, S., 1999. Maize root system growth and development as influenced by phosphorus deficiency. J. Exp. Bot. 50(333), 487-497. DOI: 10.1093/jxb/50.333.487

Moody, P.W., 1991. Intensity quantity aspects of soil phosphorus - Reply. Soil Res. 29(1), 13-14. DOI: http://dx.doi.org/10.1071/SR9910013

Moody, P.W., 2007. Interpretation of a single-point P buffering index for adjusting critical levels of the Colwell soil P test. Soil Res. 45(1), 55-62. DOI: http://dx.doi.org/10.1071/SR06056

Moody, P.W., 2011. Environmental risk indicators for soil phosphorus status. Soil Res. 49(3), 247-252. DOI: http://dx.doi.org/10.1071/SR10140

Moody, P.W., Aitken, R.L., Compton, B.L., Hunt, S., 1988. Soil phosphorus parameters affecting phosphorus availability to, and fertilizer requirements of, maize (*Zea mays*). Soil Res. 26(4), 611-622. DOI: http://dx.doi.org/10.1071/SR9880611

Moody, P.W., Bolland, M.D.A., 1999. Phosphorus. In: K.I. Peverill, L.A. Sparrow, D.J. Reuter (Eds.), Soil analysis: an interpretation manual. CSIRO, Collingwood, Vic, pp. 187-220

Moody, P.W., Dickson, T., Aitken, R.L., 1997. Soil phosphorus tests and grain yield responsiveness of maize (*Zea mays*) on Ferrosols. Soil Res. 35(3), 609-614. DOI: http://dx.doi.org/10.1071/S96103

Moody, P.W., Dickson, T., Dwyer, J.C., Compton, B.L., 1990. Predicting yield responsiveness and phosphorus fertilizer requirements of soybeans from soil tests. Soil Res. 28(3), 399-406. DOI: http://dx.doi.org/10.1071/SR9900399

Moody, P.W., Haydon, G.F., Dickson, T., 1983. Mineral nutrition of soybeans grown in the South Burnett region of south eastern Queensland. 2. Prediction of grain yield response to phosphorus with soil tests. Aust. J. Exp. Ag. 23(120), 38-42. DOI: http://dx.doi.org/10.1071/EA9830038

Moody, P.W., Speirs, S.D., Scott, B.J., Mason, S.D., 2013. Soil phosphorus tests I: What soil phosphorus pools and processes do they measure? Crop Pasture Sci. 64(5), 461-468. DOI: http://dx.doi.org/10.1071/CP13112

Moshi, A.O., Wild, A., Greenland, D.J., 1974. Effect of organic matter on the charge and phosphate adsorption characteristics of kikuyu red clay from kenya. Geoderma 11(4), 275-285. DOI: http://dx.doi.org/10.1016/0016-7061(74)90054-8

Motomizu, S., Wakimoto, T., Tôei, K., 1983. Spectrophotometric determination of phosphate in river waters with molybdate and malachite green. Analyst 108(1284), 361-367. DOI: 10.1039/AN9830800361

Mowbray, T., Schlesinger, W.H., 1988. The buffer capacity of organic soils of the Bluff Mountain fen, North Carolina. Soil Sci. 146(2), 73-79. DOI:

Murray, G.C., Hesterberg, D., 2006. Iron and phosphate dissolution during abiotic reduction of ferrihydrite-boehmite mixtures. Soil Sci. Soc. Am. J. 70(4), 1318-1327. DOI: 10.2136/sssaj2005.0292

Murrmann, R.P., Peech, M., 1969a. Effect of pH on labile and soluble phosphate in soils. Soil Sci. Soc. Am. J. 33(2), 205-210. DOI: 10.2136/sssaj1969.03615995003300020015x

Murrmann, R.P., Peech, M., 1969b. Relative significance of labile and crystalline phosphates in soil. Soil Sci. 107(4), 249-255. DOI:

Myers, R.G., Sharpley, A.N., Thien, S.J., Pierzynski, G.M., 2005. Ion-sink phosphorus extraction methods applied on 24 soils from the continental USA. Soil Sci. Soc. Am. J. 69, 511-521. DOI: 10.2136/sssaj2005.0511

Myers, R.G., Thien, S.J., Pierzynski, G.M., 1999. Using an ion sink to extract microbial phosphorus from soil. Soil Sci. Soc. Am. J. 63(5), 1229-1237. DOI: 10.2136/sssaj1999.6351229x

Nafiu, A., 2009. Effects of soil properties on the kinetics of desorption of phosphate from Alfisols by anion-exchange resins. Journal of Plant Nutrition and Soil Science 172(1), 101-107. DOI: 10.1002/jpln.200625226

Nezat, C.A., Blum, J.D., Yanai, R.D., Park, B.B., 2008. Mineral sources of calcium and phosphorus in soils of the Northeastern United States. Soil Sci. Soc. Am. J. 72(6), 1786-1794. DOI: 10.2136/sssaj2007.0344

Niu, Y.F., Chai, R.S., Jin, G.L., Wang, H., Tang, C.X., Zhang, Y.S., 2013. Responses of root architecture development to low phosphorus availability: a review. Ann. Bot. 112(2), 391-408. DOI: 10.1093/aob/mcs285

Northcote, K.H., 1964. Atlas of Australian Soils. Sheet 3, Sydney - Canberra - Bourke - Armidale area. CSIRO Division of Soils, Melbourne.

Northcote, K.H., Isbell, R.F., McArthur, W.M., 1961-1964. Atlas of Australian Soils, Sheets 3 and 4. CSIRO Australia and Melbourne University Press, Melbourne.

Nuruzzaman, M., Lambers, H., Bolland, M.D.A., Veneklaas, E.J., 2006. Distribution of carboxylates and acid phosphatase and depletion of different phosphorus fractions in the rhizosphere of a cereal and three grain legumes. Plant Soil 281(1-2), 109-120. DOI: 10.1007/s11104-005-3936-2

O'Halloran, I.P., Cade-Menun, B.J., 2008. Total and organic phosphorus. In: P. Cartes, E.G. Gregorich (Eds.), Soil sampling and methods of analysis. Canadian Society of Soil Science and CRC Press, pp. 265-291

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dep. of Agric. Circ. 939.

Oxmann, J.F., 2013. An X-ray absorption method for the identification of calcium phosphate species using peak height ratios. Biogeosci. Disc. 10(11), 18723. DOI: 10.5194/bg-11-2169-2014

Oxmann, J.F., Pham, Q.H., Lara, R.J., 2008. Quantification of individual phosphorus species in sediment: a sequential conversion and extraction method. Eur. J. Soil Sci. 59(6), 1177-1190. DOI: 10.1111/j.1365-2389.2008.01062.x

Ozanne, P., Shaw, T., 1967. Phosphate sorption by soils as a measure of the phosphate requirement for pasture growth. Australian Journal of Agricultural Research 18(4), 601-612. DOI: http://dx.doi.org/10.1071/AR9670601

Ozanne, P., Shaw, T.C., 1968. Advantages of the recently developed phosphate sorption test over older extractant methods for soil phosphate. In: J.W. Holmes (Ed.), Transactions of the 9th International Congress of Soil Science. International Society of Soil Science, Adelaide, S. Aust., pp. 273-280.

Page, K.L., Dalal, R.C., Strong, W.M., Menzies, N.W., 2002. Nitrification in a Vertisol subsoil and its relationship to the accumulation of ammonium-nitrogen at depth. Soil Res. 40(5), 727-735. DOI: http://dx.doi.org/10.1071/SR01087

Paige, C.R., Snodgrass, W.J., Nicholson, R.V., Scharer, J.M., He, Q.H., 1997. The effect of phosphate on the transformation of ferrihydrite into crystalline products in alkaline media. Water, Air, Soil Pollut. 97, 397-412. DOI:

Parfitt, R., Childs, C., 1988. Estimation of forms of Fe and Al - a review, and analysis of contrasting soils by dissolution and Mossbauer methods. Soil Res. 26(1), 121-144. DOI: http://dx.doi.org/10.1071/SR9880121

Parfitt, R.L., 1989. Phosphate reactions with natural allophane, ferrihydrite and goethite. J. Soil Sci. 40(2), 359-369. DOI: 10.1111/j.1365-2389.1989.tb01280.x

Pautler, M.C., Sims, J.T., 2000. Relationships between soil test phosphorus, soluble phosphorus, and phosphorus saturation in delaware soils. Soil Sci. Soc. Am. J. 64(2), 765-773. DOI: 10.2136/sssaj2000.642765x

Pierzynski, G.M., Logan, T.J., Traina, S.J., 1990a. Phosphorus chemistry and mineralogy in excessively fertilized soils: solubility equilibria. Soil Sci. Soc. Am. J. 54(6), 1589-1595. DOI: 10.2136/sssaj1990.03615995005400060013x

Pierzynski, G.M., Logan, T.J., Traina, S.J., Bigham, J.M., 1990b. Phosphorus chemistry and mineralogy in excessively fertilized soils: quantitative analysis of phosphorus-rich particles. Soil Sci. Soc. Am. J. 54(6), 1576-1583. DOI: 10.2136/sssaj1990.03615995005400060011x

Pierzynski, G.M., McDowell, R.W., Sims, J.T., 2005. Chemistry, cycling, and potential movement of inorganic P in soils. In: J.T. Sims, A.N. Sharpley (Eds.), Phosphorus: agriculture and the environment. Agronomy Monograph. American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc, Madison, Wisconsin, USA, pp. 53-86

Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils. In: N.C. Brady (Ed.), Advances in agronomy. Academic Press, pp. 29-96. DOI:http://dx.doi.org/10.1016/S0065-2113(08)60633-1

Prietzel, J., Dümig, A., Wu, Y., Zhou, J., Klysubun, W., 2013. Synchrotron-based P K-edge XANES spectroscopy reveals rapid changes of phosphorus speciation in the topsoil of two glacier foreland chronosequences. Geochim. Cosmochim. Acta 108(0), 154-171. DOI: http://dx.doi.org/10.1016/j.gca.2013.01.029

Pundarikakshudu, R., 1989. Studies of the phosphate dynamics in a Vertisol in relation to the yield and nutrient uptake of rainfed cotton. Exp. Agric. 25(01), 39-45. DOI: 10.1017/S0014479700016422

Qian, P., Schoenau, J.J., 2002. Practical applications of ion exchange resins in agricultural and environmental soil research. Can. J. Soil Sci. 82(1), 9-21. DOI: 10.4141/s00-091

Qin, L., Jiang, H., Tian, J., Zhao, J., Liao, H., 2011. Rhizobia enhance acquisition of phosphorus from different sources by soybean plants. Plant Soil 349(1-2), 25-36. DOI: 10.1007/s11104-011-0947-z

Qin, L., Zhang, W., Lu, J., Stack, A.G., Wang, L., 2013. Direct imaging of nanoscale dissolution of dicalcium phosphate dihydrate by an organic ligand: concentration matters. Environ. Sci. Technol. 47(23), 13365-13374. DOI: 10.1021/es402748t

R Development Core Team, 2014a. R: A language and environment for statistical computing, reference index version 3.1.0 Version Reference index version 3.1.0. Available at: http://www.R-project.org. Date accessed:

R Development Core Team, 2014b. R: A language and environment for statistical computing, reference index version 3.1.2 Version Reference index version 3.1.2. Available at: http://www.R-project.org. Date accessed:

Rahnemaie, R., Hiemstra, T., van Riemsdijk, W.H., 2007. Geometry, charge distribution, and surface speciation of phosphate on goethite. Langmuir 23, 3680-3689. DOI: 10.1021/la062965n

Rajan, S.S.S., 1976. Changes in net surface charge of hydrous alumina with phosphate adsorption. Nature 262(5563), 45-46. DOI:

Rájan, S.S.S., Fox, R.L., 1972. Phosphate adsorption by soils 1. Influence of time and ionic environment on phosphate adsorption. Commun. Soil Sci. Plant Anal. 3(6), 493-504. DOI: 10.1080/00103627209366406

Rausch, C., Bucher, M., 2002. Molecular mechanisms of phosphate transport in plants. Planta 216(1), 23-37. DOI: 10.1007/s00425-002-0921-3

Ravel, B., 2011. More for dealing the LCF - Science Physics Ifeffit. URL: http://t5619.science-physics-ifeffit.sciencetalk.info/more-for-dealing-the-lcf-t5619.html. Date accessed: 21 May 2015

Ravel, B., 2014. Meaning of linear combination fit reports. URL: http://comments.gmane.org/gmane.science.physics.ifeffit/2724. Date accessed: 1 June 2015

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrot. Radiat. 12, 537–541. DOI: doi:10.1107/S0909049505012719

Raven, M.D., Self, P.G., 2015. XRD Report – Quantitative XRD Analysis of Vertisol Soil Samples, CSIRO, Australia.

Rayment, G.E., Lyons, D.J., 2011. Soil chemical methods - Australasia. Australian soil and land survey handbooks. CSIRO, Collingwood, Victoria.

Reddy, K.R., Patrick, W.H., 1983. Effects of aeration on reactivity and mobility of soil constituents. In: D.W. Nelson (Ed.), Chemical Mobility and Reactivity in Soil Systems. SSSA Special Publication. Soil Science Society of America and American Society of Agronomy, pp. 11-33. DOI:10.2136/sssaspecpub11.c2

Renneson, M., Vandenberghe, C., Dufey, J., Marcoen, J.M., Bock, L., Colinet, G., 2015. Degree of phosphorus saturation in agricultural loamy soils with a near-neutral pH. Eur. J. Soil Sci. 66(1), 33-41. DOI: 10.1111/ejss.12207

Richardson, A.E., Barea, J.-M., McNeill, A.M., Prigent-Combaret, C., 2009. Acquisition of phosphorus and nitrogen in the rhizosphere and plant growth promotion by microorganisms. Plant Soil 321, 305-339. DOI: 10.1007/s11104-009-9895-2

Richardson, S.J., Peltzer, D.A., Allen, R.B., McGlone, M.S., Parfitt, R.L., 2004. Rapid development of phosphorus limitation in temperate rainforest along the Franz Josef soil chronosequence. Oecologia 139(2), 267-276. DOI: 10.1007/s00442-004-1501-y

Rietra, R.P.J.J., Hiemstra, T., van Riemsdijk, W.H., 2001. Interaction between calcium and phosphate adsorption on goethite. Environ. Sci. Technol. 35(16), 3369-3374. DOI: 10.1021/es000210b

Ritchie, G.S.P., Dolling, P.J., 1985. The role of organic matter in soil acidification. Soil Res. 23(4), 569-576. DOI: http://dx.doi.org/10.1071/SR9850569

Robinson, J.S., Syers, J.K., Bolan, N.S., 1992. Importance of proton supply and calcium-sink size in the dissolution of phosphate rock materials of different reactivity in soil. J. Soil Sci. 43(3), 447-459. DOI: 10.1111/j.1365-2389.1992.tb00151.x

Roboredo, M., Coutinho, J., 2006. Chemical characterization of inorganic phosphorus desorbed by ion exchange membranes in short- and long-term extraction periods. Commun. Soil Sci. Plant Anal. 37(11-12), 1611-1626. DOI: 10.1080/00103620600710215

Römer, W., Schilling, G., 1986. Phosphorus requirements of the wheat plant in various stages of its life cycle. Plant Soil 91(2), 221-229. DOI: 10.1007/bf02181789

Rose, T.J., Rengel, Z., Ma, Q., Bowden, J.W., 2007. Differential accumulation patterns of phosphorus and potassium by canola cultivars compared to wheat. Journal of Plant Nutrition and Soil Science 170(3), 404-411. DOI: 10.1002/jpln.200625163

Rosling, A., Suttle, K.B., Johansson, E., Van Hees, P.A.W., Banfield, J.F., 2007. Phosphorous availability influences the dissolution of apatite by soil fungi. Geobiology 5(3), 265-280. DOI: 10.1111/j.1472-4669.2007.00107.x

Ryan, J., Curtin, D., Cheema, M.A., 1985. Significance of iron oxides and calcium carbonate particle size in phosphate sorption by calcareous soils. Soil Sci. Soc. Am. J. 49(1), 74-76. DOI: 10.2136/sssaj1985.03615995004900010014x

Samadi, A., Gilkes, R.J., 1998. Forms of phosphorus in virgin and fertilised calcareous soils of Western Australia. Soil Res. 36(4), 585-602. DOI: http://dx.doi.org/10.1071/S97060

Santner, J., Mannel, M., Burrell, L., Hoefer, C., Kreuzeder, A., Wenzel, W., 2015. Phosphorus uptake by Zea mays L. is quantitatively predicted by infinite sink extraction of soil P. Plant Soil 386(1-2), 371-383. DOI: 10.1007/s11104-014-2271-x

Sato, S., Comerford, N.B., 2005. Influence of soil pH on inorganic phosphorus sorption and desorption in a humid brazilian Ultisol. R. Bras. Ci. Solo 29, 685-694. DOI:

Sato, S., Comerford, N.B., 2006. Assessing methods for developing phosphorus desorption isotherms from soils using anion exchange membranes. Plant Soil 279(1-2), 107-117. DOI: 10.1007/s11104-005-0437-2

Sato, S., Neves, E.G., Solomon, D., Liang, B., Lehmann, J., 2009. Biogenic calcium phosphate transformation in soils over millennial time scales. J. Soils Sed. 9(3), 194-205. DOI: 10.1007/s11368-009-0082-0

Sato, S., Solomon, D., Hyland, C., Ketterings, Q.M., Lehmann, J., 2005. Phosphorus speciation in manure and manure-amended soils using XANES spectroscopy. Environ. Sci. Technol. 39(19), 7485-7491. DOI: 10.1021/es0503130

Saunders, W.M.H., 1964. Extraction of soil phosphate by anion-exchange membrane. New Zealand Journal of Agricultural Research 7(3), 427-431. DOI: 10.1080/00288233.1964.10416423

Scalenghe, R., Edwards, A.C., Ajmone Marsan, F., Barberis, E., 2002. The effect of reducing conditions on the solubility of phosphorus in a diverse range of European agricultural soils. Eur. J. Soil Sci. 53(3), 439-447. DOI: 10.1046/j.1365-2389.2002.00462.x

Schachtman, D.P., Reid, R.J., Ayling, S.M., 1998. Phosphorus uptake by plants: from soil to cell. Plant Physiol. 116, 447-453. DOI: 10.1104/pp.116.2.447

Schefe, C.R., Kappen, P., Pigram, P.J., 2011. Carboxylic acids affect sorption and micro-scale distribution of phosphorus in an acidic soil. Soil Sci. Soc. Am. J. 75, 35-44. DOI:

Schmidt, A., Smernik, R.J., McBeath, T.M., 2012. Measuring organic carbon in Calcarosols: understanding the pitfalls and complications. Soil Res., 397-405. DOI: http://dx.doi.org/10.1071/SR12134

Schubert, S., Schubert, E., Mengel, K., 1990. Effect of low pH of the root medium on proton release, growth, and nutrient uptake of field beans (Vicia faba). Plant Soil 124(2), 239-244. DOI: 10.1007/bf00009266

Schwab, P., 2011. Soil solution. In: P.M. Huan, Y. Li, M.E. Sumner (Eds.), Handbook of Soil Sciences, Properties and Processes. CRC Press.

Schwenke, G.D., 2002. Soil nutrient survey - the current status of black soils on the Liverpool Plains, Grains Research and Development Corporation research update. Grains Research and Development Corporation.

Schwertmann, U., 1966. Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. Nature 212(5062), 645-646. DOI:

Schwertmann, U., 1973. The use of oxalate for Fe extraction from soils. Can. J. Soil Sci. 53, 244-246. DOI:

Schwertmann, U., 2008. Iron oxides. In: W. Chesworth (Ed.), Encyclopedia of soil science. Encyclopedia of eath sciences series. Springer, Netherlands, pp. 363-369.

Schwertmann, U., Cornell, R.M., 2007. Ferrihydrite, Iron Oxides in the Laboratory. Wiley-VCH Verlag GmbH, pp. 103-112. DOI:10.1002/9783527613229.ch08

Shahandeh, H., Hossner, L.R., Turner, F.T., 2003. Phosphorus relationships to manganese and iron in rice soils. Soil Sci. 168(7), 489-500. DOI:

Shailaja, S., Sahrawat, K.L., 1990. Adsorption and desorption of phosphate in some semi-arid tropical Indian Vertisols. Fertilizer Res. 23(2), 87-96. DOI: 10.1007/bf01063335

Shane, M.W., Cawthray, G.R., Cramer, M.D., Kuo, J., Lambers, H., 2006. Specialized ‘dauciform’ roots of Cyperaceae are structurally distinct, but functionally analogous with ‘cluster’ roots. Plant, Cell Environ. 29(10), 1989-1999. DOI: 10.1111/j.1365-3040.2006.01574.x

Shao, X.H., Xing, C.H., Du, S.T., Yu, C.Y., Lin, X.Y., Zhang, Y.S., 2006. Phosphorus adsorption saturation of ferrihydrate as an index of phosphorus availability to paddy rice. Journal of Plant Nutrition 29(7), 1187-1197. DOI: 10.1080/01904160600767245

Shaw, R.J., Thorburn, P.J., 1985. Prediction of leaching fraction from soil properties, irrigation water and rainfall. Irrig Sci 6(2), 73-83. DOI: 10.1007/bf00251556

Sibanda, H.M., Young, S.D., 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J. Soil Sci. 37(2), 197-204. DOI: 10.1111/j.1365-2389.1986.tb00020.x

Sibbesen, E., 1983. Phosphate soil tests and their suitability to assess the phosphate status of soil. J. Sci. Food Agric. 34(12), 1368-1374. DOI: 10.1002/jsfa.2740341209

Simard, R.R., Cluis, D., Gangbazo, G., Pesant, A.R., 1994. Phosphorus sorption and desorption indices in soil. Commun. Soil Sci. Plant Anal. 25(9-10), 1483-1494. DOI: 10.1080/00103629409369129

Singh, B., Gilkes, R.J., 1992. Properties of soil kaolinites from south-western Australia. J. Soil Sci. 43(4), 645-667. DOI: 10.1111/j.1365-2389.1992.tb00165.x

Singh, U., Uehara, G., 1998. Electrochemistry of the double layer: principles and applications to soils. In: D.L. Sparks (Ed.), Soil physical chemistry. CRC Press, Boca Raton, FL, USA, pp. 1-46

Six, L., Pypers, P., Degryse, F., Smolders, E., Merckx, R., 2012. The performance of DGT versus conventional soil phosphorus tests in tropical soils - An isotope dilution study. Plant Soil 359(1-2), 267-279. DOI: 10.1007/s11104-012-1192-9

Skinner, P.W., Matthews, M.A., 1989. Reproductive development in grape (*Vitis vinifera* L.) under phosphorus-limited conditions. Scientia Horticulturae 38, 49-60. DOI:

Skogley, E.O., Dobermann, A., 1996. Synthetic ion-exchange resins: soil and environmental studies. J. Environ. Qual. 25(1), 13-24. DOI: 10.2134/jeq1996.00472425002500010004x

Smith, S.E., Read, D.J., 1997. Mycorrhizal Symbiosis. 2 ed. Academic Press, London.

Smith, S.E., Smith, F.A., Jakobsen, I., 2003. Mycorrhizal fungi can dominate phosphate supply to plants irrespective of growth responses Plant Physiol. 133, 16-20. DOI: 10.1104/pp.103.024380

Smyth, T.J., Cravo, M.S., 1990. Critical phosphorus levels for corn and cowpea in a Brazilian Amazon Oxisol. Agron. J. 82(2), 309-312. DOI: 10.2134/agronj1990.00021962008200020027x

Soil Survey Staff, 2014. Keys to Soil Taxonomy. 12 ed. USDA-Natural Resources Conservation Service, Washington, DC.

Solis, P., Torrent, J., 1989a. Phosphate fractions in calcareous vertisols and inceptisols of Spain. Soil Sci. Soc. Am. J. 53(2), 462-466. DOI: 10.2136/sssaj1989.03615995005300020026x

Solis, P., Torrent, J., 1989b. Phosphate sorption by calcareous Vertisols and Inceptisols of Spain. Soil Sci. Soc. Am. J. 53(2), 456-459. DOI: 10.2136/sssaj1989.03615995005300020024x

Song, Y.-h., Hahn, H.H., Hoffmann, E., Weidler, P.G., 2006. Effect of humic substances on the precipitation of calcium phosphate. Journal of Environmental Sciences 18(5), 852-857. DOI: http://dx.doi.org/10.1016/S1001-0742(06)60004-1

Soon, Y.K., 1990. Comparison of parameters of soil phosphate availability for the northwestern Canadian prairie. Can. J. Soil Sci. 70(2), 227-237. DOI: 10.4141/cjss90-024

Sparks, D.L., 1986. Kinetics of Ionic Reactions in Clay Minerals and Soils. In: N.C. Brady (Ed.), Advances in Agronomy. Academic Press, pp. 231-266. DOI:http://dx.doi.org/10.1016/S0065-2113(08)60677-X

Speirs, S.D., Scott, B.J., Moody, P.W., Mason, S.D., 2013. Soil phosphorus tests II: A comparison of soil test–crop response relationships for different soil tests and wheat. Crop Pasture Sci. 64(5), 469-479. DOI: http://dx.doi.org/10.1071/CP13111

Spellman, F.R., Stoudt, M.L., 2013. Environmental science: Principles and practices. Scarecrow Press, Plymouth, United Kingdom.

Sposito, G., 2008. The chemistry of soils. 2nd ed. Oxford University Press, New York, USA.

Stewart, J.W.B., Tiessen, H., 1987. Dynamics of soil organic phosphorus. Biogeochemistry 4(1), 41-60. DOI: 10.1007/bf02187361

Strong, J., Racz, G.J., 1970. Reaction products of applied orthophosphates in some manitoba soils as affected by soil calcium and magnesium content and time of incubation. Soil Sci. 110(4), 258-262. DOI:

Stumm, W., Sulzberger, B., 1992. The cycling of iron in natural environments: Considerations based on laboratory studies of heterogeneous redox processes. Geochim. Cosmochim. Acta 56(8), 3233-3257. DOI: http://dx.doi.org/10.1016/0016-7037(92)90301-X

Sutton, P.J., Peterseon, G.A., Sander, D.H., 1983. Dry matter production in tops and roots of winter wheat as affected by phosphorus availability during various growth stages. Agron. J. 75(4), 657-663. DOI: 10.2134/agronj1983.00021962007500040019x

Tandon, H.L.S., Motto, H.L., Kurtz, L.T., 1967. Composition of dilute-acid-fluoride (Bray P1) extracts of Illinois soils. Soil Sci. Soc. Am. J. 31(2), 168-171. DOI: 10.2136/sssaj1967.03615995003100020009x

Tang, C., Barton, L., McLay, C.D.A., 1997. A comparison of proton excretion of twelve pasture legumes grown in nutrient solution. Aust. J. Exp. Ag. 37(5), 563-570. DOI: http://dx.doi.org/10.1071/EA96151

Thomas, G.W., Peaslee, D.E., 1973. Testing soils for phosphorus. In: L.M. Walsh, J.D. Beaton (Eds.), Soil testing and plant analysis. Soil Science Society of America, Madison, WI., pp. 115-132

Tiessen, H., Moir, J.O., 2008. Characterization of available P by sequential extraction. In: P. Cartes, E.G. Gregorich (Eds.), Soil sampling and methods of analysis. Canadian Society of Soil Science and CRC Press, pp. 293-306

Tighe, M., Lockwood, P., Wilson, S., 2005. Adsorption of antimony(V) by floodplain soils, amorphous iron(III) hydroxide and humic acid. J. Environ. Monit. 7(12), 1177-1185. DOI: 10.1039/b508302h

Topalović, A., Pfendt, L., Perović, N., Đorđević, D., Trifunović, S., Pfendt, P., 2006. The chemical characteristics of soil which determine phosphorus partitioning in highly calcareous soils. J. Serb. Chem. Soc. 71(11), 1219-1236. DOI:

Truog, E., 1930. The determination of the readily available phosphorus of soils. Agron. J. 22(10), 874-882. DOI: 10.2134/agronj1930.00021962002200100008x

Tunesi, S., Poggi, V., Gessa, C., 1999. Phosphate adsorption and precipitation in calcareous soils: the role of calcium ions in solution and carbonate minerals. Nutrient Cycling in Agroecosystems 53(3), 219-227. DOI: 10.1023/a:1009709005147

Uusitalo, R., Tuhkanen, H.-R., 2000. Phosphorus saturation of Finnish soils: evaluating an easy oxalate extraction method. Agricultural and Food Science in Finland 9, 61-70. DOI:

van der Zee, S.E.A.T.M., Fokkink, L.G.J., van Riemsdijk, W.H., 1987. A new technique for assessment of reversibly adsorbed phosphate. Soil Sci. Soc. Am. J. 51(3), 599-604. DOI: 10.2136/sssaj1987.03615995005100030009x

van der Zee, S.E.A.T.M., van Riemsdijk, W.H., 1988. Model for long-term phosphate reaction kinetics in soil. J Environ Qual 17(1), 35-41. DOI: 10.2134/jeq1988.00472425001700010005x

van Lierop, W., 1988. Determination of available phosphorus in acid and calcareous soils with the Kelowna multiple-element extractant. Soil Sci. 146(4), 284-291. DOI:

van Raij, B., Quaggio, J.A., da Silva, N.M., 1986. Extraction of phosphorus, potassium, calcium, and magnesium from soils by an ion-exchange resin procedure. Commun. Soil Sci. Plant Anal. 17(5), 547-566. DOI: 10.1080/00103628609367733

Vance, C.P., Uhde-Stone, C., Allan, D.L., 2003. Phosphorus acquisition and use: critical adaptations by plants for securing a nonrenewable resource. New Phytol. 157(3), 423-447. DOI: 10.1046/j.1469-8137.2003.00695.x

Velázquez, M., Campillo, M.C., Torrent, J., 2005. Temporary flooding increases iron phytoavailability in calcareous Vertisols and Inceptisols. Plant Soil 266(1-2), 195-203. DOI: 10.1007/s11104-005-1095-0

Veneklaas, E.J., Lambers, H., Bragg, J., Finnegan, P.M., Lovelock, C.E., Plaxton, W.C., Price, C.A., Scheible, W.-R., Shane, M.W., White, P.J., Raven, J.A., 2012. Opportunities for improving phosphorus-use efficiency in crop plants. New Phytol. 195, 306-320. DOI: 10.1111/j.1469-8137.2012.04190.x

Vepraskas, M.J., Sprecher, S.W., 1994. Overview of aquic problems and hydric soils. In: M.J. Veprasksa, S.W. Sprecher (Eds.), Aquic conditions and hydric soils: the problem soils. SSSA Special Publication. Soil Science Society of America, Washington, USA, pp. 1-21.

Violante, A., Pigna, M., 2002. Competitive Sorption of Arsenate and Phosphate on Different Clay Minerals and Soils. Soil Sci. Soc. Am. J. 66(6). DOI: 10.2136/sssaj2002.1788

Volk, V.V., Jackson, M.L., 1963. Inorganic pH dependent cation exchange charge in soils. Clays Clay Miner. 12(1), 281-295. DOI:

Vu, D.T., Tang, C., Armstrong, R.D., 2010. Transformations and availability of phosphorus in three contrasting soil types from native and farming systems: A study using fractionation and isotopic labeling techniques. J. Soils Sed. 10(1), 18-29. DOI: 10.1007/s11368-009-0068-y

Walker, T.W., Adams, A.F.R., 1958. Studies on soil organic matter: I. Influence of phosphorus content of parent materials on accumulations of carbon, nitrogen, sulfur, and organic phosphorus in grassland soils. Soil Sci. 85(6), 307-318. DOI:

Walker, T.W., Syers, J.K., 1976. The fate of phosphorus during pedogenesis. Geoderma 15(1), 1-19. DOI: http://dx.doi.org/10.1016/0016-7061(76)90066-5

Wang, L., Putnis, C.V., Ruiz-Agudo, E., Hövelmann, J., Putnis, A., 2015a. In situ imaging of interfacial precipitation of phosphate on goethite. Environ. Sci. Technol. 49(7), 4184-4192. DOI: 10.1021/acs.est.5b00312

Wang, L., Ruiz-Agudo, E., Putnis, C.V., Menneken, M., Putnis, A., 2012. Kinetics of calcium phosphate nucleation and growth on calcite: implications for predicting the fate of dissolved phosphate species in alkaline soils. Environ. Sci. Technol. 46(2), 834-842. DOI: 10.1021/es202924f

Wang, X., Guppy, C.N., Watson, L., Sale, P.W.G., Tang, C., 2011. Availability of sparingly soluble phosphorus sources to cotton (Gossypium hirsutum L.), wheat (Triticum aestivum L.) and white lupin (Lupinus albus L.) with different forms of nitrogen as evaluated by a 32P isotopic dilution technique. Plant Soil 348(1-2), 85-98. DOI:

Wang, X., Lester, D.W., Guppy, C.N., Lockwood, P.V., Tang, C., 2007. Changes in phosphorus fractions at various soil depths following long-term P fertiliser application on a Black Vertosol from south-eastern Queensland. Soil Res. 45(7), 524-532. DOI: http://dx.doi.org/10.1071/SR07069

Wang, X., Liu, F., Tan, W., Li, W., Feng, X., Sparks, D.L., 2013. Characteristics of phosphate adsorption-desorption onto ferrihydrite: comparison with well-crystalline Fe (hydr)oxides. Soil Sci. 178(1), 1-11. DOI: 10.1097/SS.0b013e31828683f8

Wang, X., Tang, C., Mahony, S., Baldock, J.A., Butterly, C.R., 2015b. Factors affecting the measurement of soil pH buffer capacity: approaches to optimize the methods. Eur. J. Soil Sci. 66(1), 53-64. DOI: 10.1111/ejss.12195

Warren, G.P., Sahrawat, K.L., 1993. Assessment of fertilizer P residues in a calcareous vertisol. Fertilizer Res. 34(1), 45-53. DOI: 10.1007/bf00749959

Warren, R.G., Cooke, G.W., 1965. Comparisons between methods of measuring soluble phosphorus and potassium in soils used for fertilizer experiments on sugar beet, Soil Phosphorus. Bull Min. Agric. Fish. and Food, London, G.B., pp. 269-274

Webb, A.A., Grundy, M.J., Powell, B., Littleboy, M., 1997. The Australian subtropical cereal belt: soils, climate and agriculture. In: A.L. Clarke, P.B. Wylie (Eds.), Sustainable crop production in the sub-tropics. Queensland Department of Primary Industries, Brisbane, pp. 8–26

Wells, T., Fityus, S., Smith, D.W., 2007. Use of in situ air flow measurements to study permeability in cracked clay soils. Journal of Geotechnical and Geoenvironmental Engineering 133(12), 1577-1586. DOI:

Welp, G., Herms, U., Brumner, G., 1983. Eiflub von Bodenreaktion, Redoxbedingungen undorganischer substanz auf die Phosphatgehalte der Bodenlosung. Zeitschrift fur Pflanzenernahrung und Bodenkunde 146, 38-52. DOI:

Weng, L., Van Riemsdijk, W.H., Hiemstra, T., 2012. Factors controlling phosphate interaction with iron oxides. J. Environ. Qual. 41(3), 628-635. DOI: 10.2134/jeq2011.0250

Weng, L., Vega, F.A., Van Riemsdijk, W.H., 2011. Competitive and synergistic effects in pH dependent phosphate adsorption in soils: LCD modeling. Environ. Sci. Technol. 45(19), 8420-8428. DOI: 10.1021/es201844d

White, D.J., Noll, M.R., Makarewicz, J.C., 2008. Does manganese influence phosphorus cycling under suboxic lake water conditions? Journal of Great Lakes Research 34(4), 571-580. DOI: http://dx.doi.org/10.1016/S0380-1330(08)71602-2

Willett, I.R., 1989. Causes and prediction of changes in extractable phosphorus during flooding. Soil Res. 27(1), 45-54. DOI: http://dx.doi.org/10.1071/SR9890045

Willett, I.R., Higgins, M.L., 1978. Phosphate sorption by reduced and reoxidized rice soils. Soil Res. 16(3), 319-326. DOI: http://dx.doi.org/10.1071/SR9780319

Willett, I.R., Muirhead, W.A., Higgins, M.L., 1978. The effects of rice growing on soil phosphorus immobilization. Australian Journal of Experimental Agriculture and Animal Husbandry 18, 270-275. DOI:

Williams, J.D.H., Syers, J.K., Walker, T.W., 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Soc. Am. J. 31(6), 736-739. DOI: 10.2136/sssaj1967.03615995003100060012x

Wood, S.N., 2006. Generalized additive models: an introduction with R. Chapman and Hall/CRC.

Wright, B.C., Peech, M., 1960. Characterization of phosphate reaction products in acid soils by the application of solubility criteria. Soil Sci. 90(1), 32-43. DOI:

Xu, N., Chen, M., Zhou, K., Wang, Y., Yin, H., Chen, Z., 2014. Retention of phosphorus on calcite and dolomite: speciation and modeling. RSC Advances 4(66), 35205-35214. DOI: 10.1039/c4ra05461j

Youssef, R.A., Chino, M., 1989. Root-induced changes in the rhizosphere of plants. I. pH changes in relation to the bulk soil. Soil Sci. Plant Nutr. 35(3), 461-468. DOI: 10.1080/00380768.1989.10434779

Ziadi, N., Simard, R.R., Tran, T.S., Allard, G., 2001. Soil-available phosphorus as evaluated by desorption techniques and chemical extractions. Can. J. Soil Sci. 81(2), 167-174. DOI: 10.4141/s00-040

Zoysa, A.K.N., Loganathan, P., Hedley, M.J., 1998. Effect of forms of nitrogen supply on mobilisation of phosphorus from a phosphate rock and acidification in the rhizosphere of tea. Soil Res. 36(3), 373-388. DOI: http://dx.doi.org/10.1071/S97079

Zuo, M., Renman, G., Gustafsson, J.P., Renman, A., 2015. Phosphorus removal performance and speciation in virgin and modified argon oxygen decarburisation slag designed for wastewater treatment. Water Res. 87, 271-281. DOI: http://dx.doi.org/10.1016/j.watres.2015.09.035