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Incremental acidification reveals phosphorus release dynamics in alkaline vertic soils

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ABSTRACT

Phosphorus (P) available to plants in alkaline, vertic soils is thought to be buffered by the dissolution of various calcium phosphate minerals (CaP), driven by pH and the concentration of Ca and/or P in solution. To investigate this hypothesis we incrementally acidified 6 alkaline vertic soils of CaP 300–6000 mg kg^{-1} in the presence or absence of an anion exchange P sink. Following the early removal of solution and sorbed P sources, P recovery remained low until soil pH passed key thresholds. These thresholds varied little between soils and with the sink (pH 6.0–6.3), and soil pH buffer capacity affected the amount of acid required to approach the thresholds. Dissolution of CaP species occurred 0.7–1.0 pH units higher where the solution P concentration was kept below 1 μM using the anion exchange membrane sink compared to acidification without the sink. The data support the hypothesis that rhizosphere acidification may increase the availability of CaP minerals to plants; however, the dependence of P release dynamics on pH buffering capacity may put P release beyond the reach of some plant species. Consequently, research is necessary to quantify both plant acidification potential in these soils and the effect of concomitant removal of Ca on release of CaP species into plant available forms.

1. Introduction

Vertosols (Isbell, 2002), also known as Vertisols in the World Reference Base (IUSS Working Group WRB, 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 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 the Vertosols in the NGR with little to no phosphorus (P) fertiliser (Bell et al., 2013; Schwenke, 2002). However, removal of P from the soil at rates greater than replacement for periods of up to two decades has resulted in increasingly common responses to P fertiliser (Bell et al., 2012, 2013; Schwenke, 2002). The responses to P fertiliser can be variable, and uncertainty regarding the solubility of soil P and its contribution to plant nutrition limits the efficient use of fertiliser (Dorahy et al., 2004; McLaren et al., 2014a).

The concentration of P in the soil solution of alkaline soils is thought to be controlled by calcium phosphate (CaP) mineral species (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 CaP minerals may be native, or both native and fertiliser reaction products in fertilised soils (Lindsay, 1979; Moody and Bolland, 1999; Pierzynski et al., 2005). The various CaP minerals are increasingly soluble below pH 8, although solubility varies with species (Lindsay, 1979), 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, $CaHPO_4·2H_2O$), monetite (or dicalcium phosphate, DCP, $CaHPO_4$), octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6·5H_2O$), β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), hydroxyapatite (HAp, $Ca_5(PO_4)_3OH$) and fluorapatite (FP, $Ca_5(PO_4)_3F$). The concentration of the less soluble minerals tends to accumulate relative to the more soluble minerals over time (Lindsay, 1979). The molar Ca:P ratio in the minerals increases in the reverse order as the solubility, from 1 in DCPD and DCP, to 1.33 in OCP, 1.5 in TCP and 1.67 in HAp and FP (Lindsay, 1979).

The concentration of readily available P, or labile-P, that rapidly replenishes the soil solution has traditionally been measured in alkaline soils using the bicarbonate extraction methods of Olsen et al. (1954)

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or Colwell (1963), with the latter more commonly used in Australia. Combining the bicarbonate measures with an estimate of P buffer capacity, such as the phosphorus buffer index (PBI, Burkitt et al., 2002), is a useful predictor of crop response to P fertiliser (Burkitt et al., 2001; Holford, 1980; Moody et al., 2013). However, crop response trials both with and without P fertilisation in Vertosols (Chan et al., 1988; Dalal, 1997; Guo et al., 2000; Lester et al., 2003; Pundarikakshudu, 1989; Solis and Torrent, 1989; Wang et al., 2007) and other soils (Hinsinger and Gilkes, 1995; Johnston and Poulton, 1992; Ziadi et al., 2001) have shown that plants access acid soluble P not measured by the bicarbonate method.

A more recent approach to estimating the P fertility of these soils involves two soil P tests; a bicarbonate extraction that estimates readily available P (the method of Colwell (1963)) and an acidic extraction that includes mineral P (the method of Kerr and von Stieglitz (1938), known as the Bureau of Sugar Experiment Stations soil P test (BSES-P)). The difference between Colwell-P and BSES-P is thought of as slowly available or relatively unavailable reserve-P, composed mainly of CaP minerals (McLaren et al., accepted for publication; Moody et al., 2013), and may also include sorbed P (Weng et al., 2011). The contribution of reserve-P to plant nutrition will depend on the rate at which it replenishes labile-P against the competing processes of sorption, precipitation, and microbial immobilisation (Conyers and Moody, 2009; Pierzynski et al., 2005). 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 or 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.

Plants commonly decrease the rhizosphere pH in alkaline and neutral soils (Hinsinger, 2001; Marschner et al., 1986; Qin et al., 2011), and deplete solution P to concentrations below the solubility product of the CaP minerals (Lindsay, 1979). A decrease in the pH of the rhizosphere is likely to induce dissolution of P minerals. The fate of this solubilised P is likely to include: 1) P in the soil solution that is available for plant uptake, or 2) P in the soil solution that undergoes subsequent reactions to form Al and Fe mineral phosphates (variscite and strengite) (Lindsay, 1979), sorption or precipitation onto the surfaces of calcite (Freeman and Rowell, 1981; Ming, 2006), and sorption onto the surface of Al and Fe (oxy/hydr)oxides (Rahnemaie et al., 2007; Weng et al., 2011). 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 including calcite (Lund et al., 1975) as well as the form and concentration of CaP (Hinsinger, 2001; Hinsinger and Gilkes, 1995). The availability of reserve-P to plants is likely to differ between species and genotypes due 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., 1986; Schachtman et al., 1998). An anion sink can be used to generally mimic the removal of P from solution by plants (Myers et al., 2005). The replenishment of solution-P or labile-P by desorption has been described by maintaining a low solution P concentration with repeated ion sink extractions, using anion exchange membranes (AEM) (Sato and Comerford, 2006; Uusitalo and Tuhkanen, 2000) or iron oxide (Lookman et al., 1995; McLaren et al., 2014a). A combination of repeated ion sink extraction and soil acidification may illustrate the release of reserve-P.

Our aim was to measure the effects of acidification and P removal on the supply of acid soluble P to solution. We 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 AEM in the suspensions.

2. Methods

2.1. Soil description

Six alkaline Vertosols were selected from a larger group of soils previously studied by McLaren et al. (2014a). All soils contained measures of BSES Ca:P and BSES-P in the range where McLaren et al. (2014a) suggested that reserve-P contributes to available P, i.e. molar Ca:P of <57 and concentrations of BSES-P >61 mg kg^{-1} (Table 1). These soils covered a range from low to high Colwell-P concentrations (9–96 mg P kg^{-1}) (Bruce and Rayment, 1982) and pH buffering capacity (see below) in order to observe any associations these characteristics may have with the mobilisation of reserve-P. Site details and details on soil collection and preparation are reported in (McLaren et al., 2014a). Soil profiles were inspected and described as Vertosols (Isbell, 2002), and the presence of carbonates was assessed by response to dilute HCl.

2.2. Soil chemical analysis

Soil characterisation analyses included pH, EC, pH buffer capacity, exchangeable cations, and organic and inorganic carbon (IC). A measure of the activity of the soil (oxy/hydr)oxides of aluminium (Al) and iron(Fe) was determined using the oxalate extraction (Parfitt and Childs, 1988; Schwertmann, 1973). pH and EC of 1:5 soil:water solutions tumbled at 23 °C for 1 h were measured with a calibrated pH and conductivity meter (Model 901-CP and labCHEM, TPS, Brisbane, Australia). Exchangeable cations were measured by ICP-OES (Model 725 Agilent, Mulgrave, Victoria, Australia) after extraction into 1 M ammonium chloride at pH 8.5 (Rayment and Lyons, 2011). The concentration of exchangeable Ca was expressed in mg kg^{-1} for comparison with other estimates of Ca in Table 1. The concentrations of oxalate extractable Al (Al_{ox}) and Fe (Fe_{ox}) were determined using ICP-OES after extraction into 0.2 M ammonium oxalate–oxalic acid for 4 h in the dark at pH 3 (Rayment and Lyons, 2011). Soils containing carbonates were pretreated with 1.0 M ammonium acetate at pH 5.5 to remove the carbonate prior to oxalate extraction (Loeppert and Inskeep, 1996). Total soil carbon was measured by combustion (LECO Corporation, MI, USA) and the inorganic C (IC) calculated as the difference between samples pre-treated and not treated with 2% phosphoric acid to remove carbonates. An estimate of Ca contained in $CaCO_3$ was made by assuming all IC was present as $CaCO_3$ (Table 1).

The soil pH buffer capacity (pHBC) was measured with a modification of the method of Aitken and Moody (1994) which involved varying the concentrations of acid or base. Briefly, soil was equilibrated in vials with 1:5 soil: solution ratio (m:v) containing between 18.8 cmol kg^{-1} soil of $Ca(OH)_2$ to 51.2 cmol kg^{-1} soil of HCl. The vials were tumbled overnight, then shaken for 2 min each subsequent day to resuspend the sediment. The final pH was measured after 7 d. Indices of pHBC (mmol H^+ kg^{-1} pH unit^{-1}) used previously were based on the slope of the linear region of the titration curve between pH 4.5–6.5 (Kissel et al., 2012), or the slope through the initial 0.5 to 1.5 pH unit decrease (Aitken and Moody, 1994; Federer and Hornbeck, 1985). However, the slope of the titration curve for these soils was not linear in these regions and neither method was able to differentiate between the differences in pH buffering observed during the following incremental acidification. Therefore, the pHBC was estimated from the slope of the titration curve between pH 6.5 and pH 7 where the slopes of the titration curves were closest to linear for these soils. The pHBC was performed on single samples, the C tests were performed in duplicate, and all other tests were performed in triplicate. All soils were weights were accurate to ± 0.005 g.

Labile-P and reserve-P of all soils were approximated via Colwell-P and BSES-P tests, respectively, and the ability of the soil to retain P was measured by the PBI according to the methods described in Rayment and Lyons (2011). Colwell-P was extracted by weighing 0.4 g of soil into a 50 mL centrifuge tube and then adding 40 mL of