FINAL PROJECT REPORT

Identifying the processes for unlocking soil phosphorus to increase soil productivity

Project 3.1.002

Authors	Dr Dane Lamb, Dr Anitha Kunhikrishnan, Dr Hasintha Wijesekera
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PROJECT PARTICIPANTS

THE UNIVERSITY OF
NEWCASTLE
AUSTRALIA

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EXECUTIVE SUMMARY

Phosphate rock is the major source of phosphorus (P) in modern agricultural systems. However, it is well documented that the supply of P from known ore reserves globally will cease within 100 years. The available resources of P from geological sources is somewhat controversial. Nevertheless, it is widely agreed that P supply from phosphate rock is finite. To supply sufficient P to large-scale agricultural systems will therefore require the recycling of P from other sources. Organic sources of P from municipal waste streams and animal husbandry are important potential sources in the future. Supply of P from organic sources is complicated by a variety of factors, most importantly the processes controlling the release of organic P to soluble orthophosphate in soil matrices.

The overall aim of this project was to investigate the P dynamics from organic amendment application in farms with different soil types and land use patterns. In order to do this, soils were sampled at 0.1 m increments from organic amendment (either Chicken Litter (CL) or Pig Manure (PM)) treated soils and their respective control sites (12 sites in total). The control soils were typically not used for agricultural purposes. Phosphorus dynamics were investigated using a range of techniques, including Diffusive Gradients in Thin films (DGT), isotopic dilution techniques, nuclear magnetic resonance (NMR) and bioavailable P as measured by bicarbonate extractable P (i.e., Colwell P). The study also investigated the effect of CL and PM amendments over time on the available P dynamics and mineral Fe transformations.

The main findings of the study were:

- Sites with short term and low application rates appear to have little influence on the P availability in soil in the field.
- In long-term CL amended soils, there was an improvement in the concentration of labile P. However, this typically was only in the top 0.07 m of the profile, and reduced rapidly at lower depths. Of all the soil types, the CL field amended Vertosol appeared to show greater improvement in labile P concentration with depth.
- The CL amendments to control or previously field-amended soils reduced the available P over time in our short-term incubation study. In contrast, PM enhanced or maintained the available P over the 49-day incubation period.
- The DGT microniche analysis revealed zones of highly localised P availability ranging from around 1 mm to <100 µm in diameter. High-resolution techniques provided unique information relating P availability in soils.
- NMR results showed that amendment with CL and PM even on low application rates increased the total NaOH-EDTA extractable P. Monoesters increased in amended soils, however, only when applied frequently or at higher application rates. Phosphodiesters and pyrophosphates were not consistently increased from amendment.

Phosphorus dynamics in agricultural systems are highly complex and can be studied at different spatial and temporal scales. Further research is recommended to utilise emerging technologies. These include:

- Probing P speciation in agricultural soils at the sub-micron scale with spectroscopic techniques. The research should include bulk and high resolution spectra from extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) to provide information relation to overall speciation. In addition, high resolution Fourier transform infrared spectroscopy would enable detailed insight into the unique geochemistry of organic microinches.
- Further research on DGT microniches in manure-amended soils is needed. Phosphorus mobilisation from organic sources is a complex area which has received significant research attention for several decades. DGT is a useful tool that has been underutilised in this regard, largely due to some limitations. Further development of this technique for soil environments is needed. Approaches aside from laser ablation inductively coupled plasma mass spectrometry could be used for analysing a larger area, such as Laser Induced Breakdown Spectroscopy (LIBS).
- Further research on land use and changes in P stock. Although the change in total P from conversion of conventional (use of chemical fertilisers) cropping to organic amendment application was significantly high, the number of studies included was less. Other limitations of the study were

variation in soil sampling depth and inclusion of very few studies from Australia. Long-term studies on relative change in P stock under different land use systems are imperative to manage P in soils and to make better fertiliser decisions.

OBJECTIVES

To unlock occluded soil P, the following objectives need to be addressed:

1. Quantify and characterise soil P pools under different farming systems and soil types with depth;
2. Identify the influence of key organic waste resource inputs ("nutrient products") on plant-available P in farming systems; and
3. Understand the role of various soil chemical (e.g., pH and redox) and biological (i.e. microbial activity) processes in P mobilisation in soils

The project aims to identify soils with moderate to high loadings of P, and understand the soil chemical attributes that result in the lock-up of P, and mechanisms to assist in the release of this bound P to plants.

RESULTS

The project results have largely been achieved within the limited timeframe of this project. For each objective, the following have been recorded in the report:

Objective 1: samples within the profile of manure amended and non-amended soils from different farms were taken. It was found that when manures were amended consistently the size of the labile P pool, as measured by NMR, bicarbonate extractable P and isotopic dilution techniques, increased. Monoesters and orthophosphate were the two major forms to increase to the greatest extent. Low applications of amendments did not appear to increase P fertility.

Objective 2: the project investigated only chicken litter and pig manure. Short-term studies from the project indicate that in the case of chicken litter, the high C content appears to result in immobilisation of P, presumably in to the microbial biomass (non-labile fraction).

Objective 3: the Diffusive Gradients in Thin Films study indicated localised mobilisation of P under reducing conditions. In addition, localised P accumulation was shown for aerobic soils. Within a given profile, P mobility was related to oxalate extractable Fe but not in the dataset as a whole.

NEXT STEPS

The next steps for improving our understanding P in manure amended soils are:

1. Develop new DGT gels to enable improved understanding of P in around organic microniches in surface and especially subsurface soils; and
2. Use μ-XANES to probe P and Fe speciation around micro-niches.

TIMING

1. The development of new custom built DGT devices will require approximately 9 months developing and validating in the laboratory.
2. Application for beamtime for XANES and travel could be achieved in 12 months. Applications for beamtime are infrequent. Travel to the Stanford synchrotron would be required for this work.

INTRODUCTION

Most modern agricultural systems are heavily reliant on recurrent inputs of nutrients including nitrogen (N), phosphorus (P), potassium (K), sulphur (S), calcium (Ca), magnesium (Mg) and trace elements. These nutrients are derived primarily from synthetic fertilisers using nutrient rich mineral resources such as phosphate rock and elemental sulphur. With increasing costs of fertiliser production and decline in the supply of natural mineral resources, one of humanity's greatest challenges will be to ensure that the world's farmers have sufficient access to plant nutrients in the long term to safeguard food security.

Some of the agricultural and horticultural soils in Australia and New Zealand contain huge reserves of nutrients such as N, P and S resulting from both natural and anthropogenic processes. For example, in the intensive dairy farming soils of Australia and New Zealand, soils can contain a large reserve of P (up to 2400 kg P/ha) in the rhizosphere. The annual uptake of P in these regions is 40-60 kg P/ha, of which the majority is returned to the soil as unused herbage, urine and dung. This equates to an annual net loss of approximately 8 kg P/ha. Anthropogenic processes including the addition of organic waste streams such as animal manures, biosolids and composts are also a major contributor of elevated P concentrations in soils. Many of these organic amendments are applied based on the N requirement, and depending on the crop species grown, they have the potential to accumulate other macro- and micro-nutrients (especially P) in soil if these are above that of N for any given agricultural plant species.

Although P may be present in significant quantities in many agricultural soils, the majority exists in strongly adsorbed or insoluble inorganic forms (occluded) and therefore is not bioavailable to agricultural crops. The common question in the farming sector is 'Is it possible to unlock the occluded soil P, so that soil-P becomes bioavailable to plant species?' In order to answer this question, we need to understand the reactions of P fertilisers in soils and various chemical and biological processes involved in unlocking this nutrient to sustain food production.

To unlock occluded soil P, the following objectives need to be addressed:

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3. Understand the role of various soil chemical (e.g., pH and redox) and biological (i.e. microbial activity) processes in P mobilisation in soils

The project aims to identify soils with moderate to high loadings of P, and understand the soil chemical attributes that result in the lock-up of P, and mechanisms to assist in the release of this bound P to plants.

BACKGROUND

Global demand for food is rising and is estimated to increase anywhere between 59% and 98% by 2050. Fertiliser use, including P, has quadrupled over the past half century due to food demand and will continue rising as the population expands. Phosphorus is an essential nutrient for all forms of life and it cannot be replaced. Phosphorus is not a renewable resource and it has been estimated that the world is left with only 70 to 100 years supply of high-quality rock phosphate (Naidu et al., 2012). This scenario underscores the need for sustainable and responsible use of P in agriculture.

Improving P cycling in soils is key, although not a complete solution, in delaying and reducing the effect on P scarcity (Stutter et al., 2012). The major issue with this essential nutrient is its limited bioavailability in soil. Approximately, 6% (range 1.5 to 11%) of total soil P is readily available (Olsen P) and the remainder is fixed in a form that is unavailable to plants (Helfenstein et al., 2018). The fixed P is usually bound to positively charged compounds of aluminium (Al) and iron (Fe) in the soil in precipitated, adsorbed or in organically-complexed forms (Helfenstein et al., 2018; Syers et al., 2008; Syers et al., 2011). To overcome soil P fixation and meet optimal plant growth, phosphate fertilisers are applied to agricultural soils in excess of what is required (Syers et al., 2008). Furthermore, fertiliser application rates that are designed to meet crop N requirements result in P over-fertilisation (McDowell and Sharpley, 2004; Pierzynski and McDowell, 2005; Pizzeghello et al., 2011; Sharpley and Moyer, 2000). Studies have demonstrated considerable amounts of P accumulation in soils from long-term application of chemical fertilisers and manures (Pizzeghello et al., 2011, 2016; Sharpley et al., 1994). This excess P ends up in aquatic systems causing eutrophication or algal blooms (Qin et al., 2018). For instance, in Sweden, annual P losses from such high P farming soils are among the highest recorded within the Swedish nutrient loss monitoring program (Stjernman Forsberg et al., 2012).

Improved understanding of soil P pools and its dynamics is critical for efficient P management in soil-plant systems. In soil, P exists in inorganic and organic forms. The primary P mineral is typically apatite, while various calcium phosphates and mainly amorphous Al and Fe phosphates are the secondary P minerals (Frossard et al., 1995). Plants can only take up P from the soil solution as the orthophosphate anion (inorganic form), however, a considerable fraction (30% to 65%) of soil P is present as organic P forms (Burton and Turner, 2003; Condron et al., 2005). Soil organic P is present as orthophosphate monoesters, including inositol hexakisphosphate (phytate), and as orthophosphate diesters, organic polyphosphates and phosphonates (Condron et al., 2005; Moata et al., 2016). After mineralisation, the organic P forms play a major role to meet the P requirements of plants and soil organisms (Oberson et al., 2001). Soil P availability is controlled by various chemical processes such as sorption/desorption, precipitation/dissolution, immobilisation/mineralisation, weathering, and solid-phase P transformations (Condron et al., 2005; Stutter et al., 2012). The P dynamics in soils is also regulated by a number of physical and chemical factors, such as soil pH, redox potential (pe), soil organic carbon and surface active mineral content (Kjaergaard et al., 2012; Tiemeyer et al., 2009; Zak and Gelbrecht, 2007).

Organic sources of P such as manure, compost and biosolids affect P availability by: (i) providing a source of P to plants; (ii) reducing P adsorption through competition for fixation sites by organic acids; (ii) favouring the formation of metal–humate–phosphate complexes (von Wandruszka, 2006); (iii) decreasing the rate of precipitation of non-soluble calcium (Ca) phosphates (Vu et al., 2009) and (iv) influencing the behaviour of microbial communities (Bünemann et al., 2012). While understanding the way organic amendments behave in the environment and its interaction with P is crucial, the fate of P input through organic and inorganic fertiliser depends on its transport mechanisms and soil properties (e.g. soil pH, P sorption sites) (Eghball et al., 1996). Knowledge on movement and redistribution of P in the soil profile is important both for plant uptake and the risk of P loss. Earlier studies show P accumulation in the sub-soil up to a depth of 1.8 m following long-term application of organic and inorganic P fertilisers (Kingery et al., 1994; Sharpley et al., 1993). However, the source and rate of P, and soil properties will affect P sorption and P species that move through the soil profile. Contradictory results have been noted with both higher and lower P sorption capacity in the subsoil compared to the topsoil. Mozaffari and Sims (1994), for example, noticed that soil P capacity, measured by P sorption isotherms or through a single-point P sorption index, increased with depth, whereas Peltovuori et al. (2002) observed an opposite result as estimated by ammonium oxalate extractable Fe and Al. In a long-term (44 years) study, Pizzeghello et al. (2016) noticed that the soil P was affected by soil type (clay, sandy, peaty), treatment (farmyard manure and mineral fertilisers) and depth. Farmyard manure increased the P forms by >7-fold that of unamended down to 0.5 m in clay and peaty soils, and 28-folds down to 0.9 m in sandy soils. Phosphorus accumulation in the manure-treated deeper layers was attributed to increased movement of organic P species to subsoil horizons and the subsequent precipitation and co-precipitation of P with carbonates and iron oxides in those soils.

Phosphorus loss is generally less in calcareous soils due to their significant capacity to bind P. In neutral and calcareous soils, the fate of P is controlled by sorption to surfaces of calcium carbonate ($CaCO_3$) and clay minerals and/or precipitation as secondary calcium phosphate (Ca-P) minerals (Helfenstein et al., 2018; von Wandruszka, 2006). In acidic soils, adsorption to surfaces of Fe and Al oxides and clay minerals and precipitation as secondary Fe- and Al-P minerals, are major reactions for solution P. Leaching of P can still occur in high sorbing soils, particularly when intensive and/or long-term applications of fertilisers saturate the P sorption capacity. Colloidal P is also a significant source of P leaching from the upper soil horizon (Glæsner et al., 2012). Soil pH plays a major role in P retention in soils by altering the sorption capacity of soils. In a recent study, Yan et al. (2018) found lowered pH due to manure application resulted in P transformation and release in a calcareous soil. Six years of manure application decreased the proportion of stable Ca-phosphates and increased the proportion of Fe-P and inositol hexakisphosphate in surface soils (0–0.3 m), while labile P was increased at both depths (0–0.3 m and 0.3–0.6 m).

Understanding of P speciation in soils has relied mostly on wet chemical extraction schemes. However, those results can only describe the distribution of soil P over operationally defined fractions whose composition may vary according to soil types. Advanced techniques can overcome the drawbacks of conventional approaches. For example, in animal manure, P is composed of both inorganic and organic P fractions, the latter containing 5 to 25% of total P (Dou et al., 2000; Sharpley and Moyer, 2000). The suitable method for direct speciation of organic P form is liquid-state ^{31}P nuclear magnetic resonance spectroscopy (^{31}P-NMR; Cade-Menun, 2005; Newman and Tate, 1980). Compounds can be identified and quantified by comparison with spectra of known compounds added to soil NaOH-EDTA extracts (Burton and Turner, 2003; Doolette et al., 2009). The main advantage of NMR is that it has the potential to be able to detect and quantify all P species simultaneously. For example, Annaheim et al. (2015) used NMR technique to demonstrate that after 62 years of organic fertiliser application (dairy manure, compost and sewage sludge), soil organic P forms remained largely unaffected, and only changes in inorganic P were noticed (Annaheim et al., 2015).

The use of advanced techniques such as diffusive gradients in thin films (DGT), isotopic dilution and spectroscopic techniques are also being employed to understand the dynamics of P. Mössbauer spectroscopy, for example, is a powerful tool used to identify the different forms of Fe hydroxides which play an important role in controlling P dynamics in soil. The isotopic dilution technique is useful for quantifying P transformation and contributes to further understanding of P dynamics in native and farming systems. Plant-available P generally equates to isotopically exchangeable P (Morel and Plenchette, 1994); while the L value represents the plant-labile pool, E value corresponds to the isotopically exchangeable pool (potentially bioavailable pool) measured using the specific activity of P in soil solution labelled with radioactive P (Fardeau, 1993; Russell et al., 1957; Schneider and Morel, 2000).

To specifically map the distribution and changes of labile, plant-available P around soil-grown plant roots at submicron scale, combining DGT hydrogels with laser ablation inductively coupled plasma mass spectrometric analysis (LA-ICP-MS) is being employed in the recent decades (Santner et al., 2010; Santner et al., 2012). The DGT technique was introduced by Davison and Zhang (1994) and Stockdale et al. (2008) and originally was developed to measure labile species quantitatively in marine and freshwater systems. However, it has been successfully applied to sediments and soils. This in situ technique is capable of rapid measurements of labile P, arsenic, vanadium and other analytes at high spatial resolution. Measurement of DGT depends on the diffusion-controlled flux of a solute from the surface of a DGT probe to a binding phase (e.g. Fe hydroxide/zirconia-based binding gels) contained within the probe. The DGT technique is widely being implemented in Australia as a standard soil testing method and also has been successfully used to investigate P availability in agricultural soils under diverse conditions (Mason et al., 2010; Mason et al., 2013; Six et al., 2013).

For complete understanding of P availability in soils, it is crucial to understand the forms and processes such as sorption-desorption characteristics of P in fertilised soils, which will help in the prediction of long-term P accumulation and release dynamics. While there are studies on the effect of fertilisers on P accumulation and release, more in-depth research involving nano-scale techniques on long-term impact of fertilisers on P stocks and P forms in topsoils and more importantly, in the underlying soils are very important to identify the processes involved in unlocking P.

METHODOLOGY

1.1 SOILS AND SAMPLING LOCATIONS

Soils were sourced from 5 agricultural areas consisting of 12 sites that represent different farming systems, climatic conditions and soil types in New South Wales (NSW) and Victoria (VIC) (Table 1). Soils from Lismore and Teven, NSW were horticultural, whereas soils from Uralla, NSW, and Somers and Tarwin Lower, Victoria, were from pastoral (mainly sheep and cattle) farms. Soils were also collected from a broadacre farm in Condobolin, NSW. All the agricultural farms had a history of organic fertiliser application. In soils collected from NSW, chicken litter was being applied as a source of P. Soils from Tarwin Lower and Somers were amended with phosphorus (P)-rich pig manure. The years of application varied amongst the sites with one site in Uralla having an organic fertiliser history of 11–12 years, while one of the sites in Tarwin Lower had a manure application history of one year (see Table 1 for details). Similarly, the application rates also differed amongst the soil sampling sites. The soil types ranged from sodic soils to clay-rich Dermosol to sandy Podosols. Soil type designations are included in Table 1 (Isbell, 1996). Soil samples were collected from mainly eight depth intervals (0.0–0.1, 0.1–0.2, 0.2–0.3, 0.3–0.4, 0.4–0.5, 0.5–0.6, 0.6–0.8, 0.8–1.0 m), and in some sites, soils were augured up to 2 m depth. In total, 275 soil samples were collected. The soils were oven-dried and passed through a 2 mm stainless steel sieve. In addition, intact cores of soil were collected from every sampling site using a hand-operated soil sampler.

Table 1. Sampling locations and characteristics. Rainfall sourced from Bureau of Meteorology.

Nearest town	Soil type	Land use	Amendments	Amend. rates (Mg/ha)	Period of amend. (yr)	Average annual Rainfall (mm)
Lismore, NSW	Red Ferrosol	Macadamia orchard	Chicken litter	Unknown	Unknown	1516
Teven, NSW	Red Ferrosol	Macadamia orchard	Inorganic P fertiliser	Unknown	Unknown	1516
Uralla, NSW	Yellow Sodosol	Grazing	Chicken litter	8	11-12	794
Uralla, NSW	Black Vertosol	Grazing	Chicken litter	8	11-12	794
Uralla, NSW	Alluvial Tenosol	Grazing	Chicken litter	8	4-5	794
Tarwin Lower, Vic	Aquic Podosol	Grazing	Pig manure	1	12-13	1023
Tarwin Lower, Vic	Aeric Podosol	Grazing	Pig manure/ inorganic P	1	1	1023
Somers, Vic	Grey Dermosol	Grazing	Pig manure	3	5	722
****Condobolin, NSW**	Red Chromosol	Broadacre	Chicken litter	2	2	461

** Farmer was organised through central west farming systems (cwfs)

1.2 CHARACTERISATION OF SOILS

The soil samples were analysed for pH, electrical conductivity (EC), clay content, total carbon (C) and nitrogen (N) content, effective cation exchange capacity (ECEC), Olsen and Colwell P, and extractable Fe and Al. The soil pH and EC were determined using end-over-end equilibration of soil with water at a ratio of 1:5 for an hour and measuring the solution with calibrated pH and conductivity meters. The clay content was determined using the micro-pipette method (Miller and Miller, 1987), while the total C and N contents were measured using elemental analyser (LECO Trumac CNS analyser). The total amount of exchangeable cations were measured by extraction with 1 M ammonium chloride and analysed using inductively coupled plasma mass spectroscopy (ICP-OES, PerkinElmer, Avio 200) (Amacher et al., 1990). Together with ECEC determination, exchangeable sodium percentage (ESP) was also determined. Ammonium oxalate extraction in the dark was used to estimate non-crystalline and poorly crystalline Fe and Al compounds and measured using ICP-OES (Rayment and Higginson, 1992).

1.3 LABILE AND PHYTOAVAILABLE P

Plant available and mobile P was determined by Olsen P, Colwell P and Diffusive Gradients in Thin Films (DGT). For Olsen P and Colwell P measurements, soils were extracted with 0.5 M $NaHCO_3$ (99.7%, Sigma-Aldrich CAS 144-55-8) after reaction for 0.5 and 16 h, respectively, at 24°C (solid solution ratio of 1:20) (Olsen, 1954). Following centrifugation, solutions were filtered (0.2 µm, PES). Orthophosphate was determined colorimetrically using the malachite green method and determined on a plate reader at 614 nm (PerkinElmer Multiplate reader, Ensight). This method was preferred over the Murphy-Riley phosphomolybdenum blue method due to its enhanced sensitivity. The malachite green assay kit provides fast and reproducible results. This assay is based on the complex formed between malachite green molybdate and orthophosphate under acidic conditions. The method detection limit was 1 mg/kg P.

Diffusive Gradients in Thin Films is a technique that, in principle, simulates plant uptake processes of P and metal(loid)s (Glæsner et al., 2012; Pagès et al., 2011; Zhang et al., 1998; Zhang et al., 2001). The technique generates a concentration gradient by introducing a sink in the form of a binding gel, which is separated from soil solution by diffusive and filter membranes. The measurement of P by a DGT device is a function of time, solution P concentration, and P that may be desorbed from the solid phase. The DGT devices purchased from DGT Research Ltd. (UK) use the zirconium oxide (ZrO) binding gel (Guan et al., 2015). To determine DGT-available P, soil samples were wet to a saturation paste with deionised water and allowed to equilibrate for 24 h (see Image 1). Subsequently, DGT devices were deployed for between 2 and 30 h at 24°C. The different deployment time was based on previously determined bioavailable P content as measured by Olsen P data. In soils with high Olsen P values, the short deployment time was selected to avoid saturation of the binding gel. Following the deployment period, the DGT devices were disassembled, the binding gel was rinsed with deionised water (18.2 MΩ.cm) and placed in high purity (99.99%, Sigma Aldrich, CAS 1310-73-2) 0.5 M NaOH solution for 24 h on an orbital shaker (150 rpm). Extracted P was determined in extracts using ICP-OES (PerkinElmer, Avio 200) and the malachite green method. Other anionic solutes including arsenic (As), Molybdenum (Mo) and selenium (Se) were also determined by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7900). The DGT parameter, C_{DGT} (ng/mL), was calculated according to:

$$C_{DGT} = \frac{M\Delta g}{DtA}$$

Where, M is the mass of P, Mo or Se (ng), Δg is the thickness of the diffusive membrane plus filter membrane (cm), A is the effective area (cm^2), t is time (s) and D is the Diffusion Coefficient at 25°C (cm^2/s). As the temperature ranged was within 25±1°C, the diffusion coefficient was not temperature corrected. Thus, the diffusion coefficients used for As, Mo, P and Se were 6.83×10^{-6}, 6.81×10^{-6}, 6.05×10^{-6} and 9.46×10^{-6} cm^2/s, respectively (Bennett et al., 2010; Panther et al., 2013; Zhang et al., 1998).

Image 1. Examples of DGT devices being deployed. On the left are standard piston devices. On the right are 15 cm DGT devices being deployed to intact cores.

1.4 LABILITY OF P IN AMENDED SOILS

The labile fraction of P in soil, as opposed to the total concentration, is the most relevant indicator of plant available P content in soils. The labile content of P in soil is typically a small fraction and can be influenced by fresh additions of fertilisers. The labile proportion can be considered the chemically reversible fraction and is typically measured using isotopic dilution techniques. The E-value (mg/kg) was estimated by relating the added radioactivity to the soluble fraction in soil according to:

$$E = \frac{R_i}{R_f} . C_s . \frac{V}{m}$$

Where, R_i and R_f are the level of radioactivity added and at steady state (Bq/mL), respectively, C_s is the measured non-radioactive P in soil (µg/mL) and V and m are the volume of solution (mL) and the weight of soil (g), respectively.

Phosphorus E-values were determined in selected field collected samples. Preliminary experiments defining the experimental parameters were initially determined, including the required amount of radioactivity of ^{33}P (^{33}P as orthophosphoric acid; American Radiolabelled Chemicals Inc., U.S.A), reaction time and quench curves. The E-values were thus determined by adding 50 µL of 500 kBq/mL to soils at solution solid ratio of 1:10. Samples were reacted with ^{33}P for a period of 24 h at 150 rpm at 24°C. Under the same conditions, non-labelled samples were equilibrated and soluble P determined using the malachite green method and ICP-OES. All samples were filtered after equilibration with 0.22 µm syringe driven filters.

1.5 HIGH RESOLUTION ANALYSIS OF P, AS, SE AND MO IN AMENDED SOILS

Phosphorus biogeochemical cycling in soils at the millimetre to micrometre scale has scarcely been studied in agricultural soil systems. The sub-millimetre geochemistry of P plays a critical role on P in soil. Although the importance of spatial heterogeneity is acknowledged in the scientific literature, there are relatively few attempts at understanding the spatial and temporal variation and localised geochemical processes. In this series of experiments, the high resolution imaging of P (also As and Mo) was studied in organically amended agricultural soils using DGT gels (Stockdale et al., 2008). This approach has been attempted in aquatic sediments but not soils (to our knowledge).

In order to study the sub-millimeter dynamics of As, Mo and P, we sampled intact cores from the top 0.15 m for study in the laboratory at the University of Newcastle. Three field amended soils were included in this study (Red Chromosol, Grey Vertosol and Yellow Sodosol). Stainless steel samplers with tight fitting plastic cylinders were driven into the top 0.15 m. Cores were retrieved and intact samples sealed on each end, wrapped in several layers of bubble wrap, and placed in eskies for delivery to the lab. Samples were stored at 0-4°C until required.

Samples were removed by carefully forcing samples out and placed into purpose-built core holders. The samples were vertically spliced to expose a flat and even surface for exposure to DGT devices (ZrO binding gels) (Guan et al., 2015) (see Image 1). Samples were placed in 25°C room and wet with deionised water for 24 h. Subsequently, DGT gels with exposure window dimensions of 0.15 m and 0.018 m were pushed onto the exposed soils. Pressure was maintained using elastic bands. Depending on the level of labile P in each sample (based on Olsen P data), the exposure time ranged from 24 h to 40 h. Following the exposure time, devices were removed and washed with high purity water. Select areas were chosen for two dimensional analysis (areas of approximately 1 cm^2). These areas were carefully cut with stainless steel blades and placed on glass plates for drying at 37°C. These samples were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in lines separated by 50 µm intervals. LA-ICP-MS provides semi-quantitative data of P, As and Mo in two-dimensions. The time intervals for samples were related to between 10 and 20 µm measurement distances. Data analysis and presentation was achieved using Matlab.

The remaining gel area was cut into 0.5 cm intervals for determination of available As, Mo, P and Se. These samples were eluted in high purity 0.5 NaOH for 24 h on an orbital shaker. Subsequently, P was determined using the malachite green method. Arsenic, Mo and Se were determined using ICP-MS. In addition, soil cores were sectioned into 1 cm increments for measurement of Olsen-P for comparison.

1.6 PHOSPHORUS-31 NUCLEAR MAGNETIC RESONANCE (^{31}P NMR) SPECTROSCOPY

Phosphorus forms in control and manure-treated soils were extracted with NaOH-EDTA solution according to the method described by Jin et al. (2016). Briefly, 4 g of soil samples were placed in 50 mL falcon tubes and extracted with 40 mL solution containing 0.25 M NaOH and 0.05 M EDTA. The tubes were shaken at 150 rpm for 16 hours before being centrifuged at 1600 g for 10 minutes. To remove paramagnetic ions (i.e., iron and manganese), thereby improving the NMR spectral resolution, 4 g of chelating resin (Chelex100) was added to 40 mL of the supernatant solution and was shaken for 2 hours (Crouse et al., 2000). The paramagnetic ion-adsorbed Chelex 100 was separated from the solution by filtering through Whatman No. 40 filter paper. The samples were freeze dried and stored at 4°C until analysis.

For the ^{31}P NMR analysis, a modified protocol by Jarosch et al. (2015) was followed. In brief, 500 mg of freeze-dried soil extract was ground finely, redissolved in 5 ml of MQ water, centrifuged at 1400 g for 20 minutes, and the supernatant solution was adjusted to pH of >12 using 10 M NaOH. Then, to 3.5 ml of pH adjusted solution, 0.3 mL of D_2O was added and mixed well. Finally, 550 µL of solution was transferred to a 5 mm NMR capillary tube and a co-axial insert that was filled with 65 µL of 10 mM methylene diphosphonic acid (MDP, Sigma Aldrich) was inserted into the NMR tube. Solution ^{31}P NMR spectra were recorded at 242.9 MHz on a Bruker AVANCE III 600MHz system. The solution ^{31}P NMR spectra were obtained using the following instrumentation parameters: 90 pulse angle, 0.68-s acquisition time, 4.0-s pulse delay, 17.9-ls pulse width, 10 Hz spinning and 20°C. Depending on the P concentration, between 2400 and 2800 scans were acquired for all soil samples. The chemical shifts of signals on spectra are reported in parts per million (ppm) relative to an external standard of 85% orthophosphoric acid (H_3PO_4), whereas MDP in co-axial inserts was the internal standard. The NMR spectra were processed using Topspin 4.0.6 software. Concentration (mg/kg) of various P compounds was calculated by comparing integration of peak areas with external standards.

1.7 INCUBATION STUDY

The objective of the incubation study was to investigate the role that soil and manure types play in P mobilisation or immobilisation. The soils (0–0.2 m) chosen for the incubation study were: Red Ferrosol, Yellow Sodosol, Black Vertosol, Aquic Podosol, Grey Dermosol and the Red Chromosol. Both pig manure (PM) and chicken litter (CL) were used in this study (Appendix A, Table A5). The concentration of P in PM was 5.1%, whereas the CL had a P concentration of 1.9% (see Appendix A). The moisture content in the soils were measured using a moisture probe from a LI-8100A automated soil gas flux system (LI-COR, USA). Both control and manured soils were treated with pig and chicken manures at 1% application rate (approximately of 16-29 Mg/ha, depending on bulk density in the top 0.2 m). To achieve homogeneity, the soils were mixed thoroughly in an end-over-end shaker for 2 hours. Then, MQ-water was added to all the manure-amended soils, adjusted to 60% water holding capacity and placed in 2 L pots. Control pots with no manure treatment were also maintained during the study. The moisture content and a constant temperature of 25°C were retained during the incubation period. A sub-sample of the treated soils was collected at various intervals (day 1, 7 d, 21 d and 49 d). Changes in inorganic P concentrations (Olsen P), pH and EC were determined in the sub-samples. For E-value determination, only 1 and 49 days were determined.

For the Red Chromosol and Red Ferrosol, possible mineralogical transformations where investigated using X-ray diffraction (Schoepfer et al., 2019). Mineralogical changes during incubation of soils with various amendments were measured by X-ray diffraction (XRD) using a Bruker D4 endeavour using CoKα radiation. Dried soil samples were homogenised, finely ground and loaded on standard sample holders and scanned from 10-80° 2θ step size of 0.02 with 2 s counting time per step. The diffraction patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Germany).

RESULTS

Soils were selected based on their texture, farming systems, type and duration of organic fertiliser application. The pH, EC, ECEC, clay content, total carbon content, Olsen P and Colwell P were determined for these soils in this study. Selected physico-chemical characteristics are presented in Tables 2-6 for the Yellow Sodosol, Red Ferrosol, Grey Dermosol, Black Vertosol and Red Chromosol. Data from other profiles are shown in Appendix A (Tables A1–A4).

1.8 BICARBONATE EXTRACTABLE P

In the Ferrosol, a significant increase in bicarbonate extractable P was observed in manure amended sites compared to unamended sites. Compared to the control (43.66 mg/kg), the Olsen P measurements was 7-folds higher in the treated surface soil (315.5 mg/kg) and 10- and 20-folds higher in 0.1–0.2 m and 0.2–0.3 m depths, respectively. A decrease in Olsen P with soil depth was also observed. In the Sodosol, no significant difference between the control and the treated soil was observed. The Olsen P values ranged from 16.77 mg/kg to 11.51 mg/kg with depth in control soil and from 17.89 mg/kg to 15.73 mg/kg in the treated soil. The treated Vertosol exhibited a significant increase in the top soil (37.26 mg/kg) when compared to the control soil (19.08 mg/kg). Both treated and control soils displayed a decrease in Olsen P concentrations with depth. In the Dermosol, Olsen P values were only slightly higher in the treated surface soil. In the subsoil, the Olsen P concentrations in the control soils of the Dermosol were slightly higher than the amended soils. Olsen P measurements in the Red Chromosol, lowered with depth, however, no significant difference between the control and the treated soil was observed.

Colwell P was estimated in select profiles. These included the Chromosol, Dermosol, Ferrosol, Sodosol and Vertosol soils. Colwell P concentrations were 2- to 5-folds higher than the Olsen P concentrations in all soils. It followed a similar trend to Olsen P both with soil depth and manure application. A strong positive linear relationship ($R^2 = 0.95$) was obtained between Olsen P and Colwell P (Figure A1).

1.9 SOIL TEXTURE, PH AND EC

The soil pH, in general, varied from acidic (4.23) to alkaline (8.70) amongst the soils and differences leading to an increase or decrease with depth was observed. While the site 1 Ferrosol (Lismore) showed a noticeable difference between the control and treated soils, with a pH decrease in the treated soils, site 2 Ferrosol (Teven) showed no or very little difference with depth. Electrical conductivity showed similar trends. While the EC values ranged from 80.07 to 38.48 µS/cm with depth in the control soils, in manured soils, it varied from 274.9 to 137.4 µS/cm. Similarly, the manured Sodosol and Vertosol displayed a decrease in pH compared to the control. While Sodosol was slightly acidic ranging from 5.85 to 5.92, the Vertosol ranged from 6.57 to highly alkaline 8.31 with depth. In the Dermosol, manure treatment increased the pH in all depths with more than one unit increase in the lower-most depths (0.4 – 0.8 m). Control soils ranged from 5.23 to 4.23, whereas the pH in the treated soil ranged from 5.92 to 5.45. The EC in the control top soil was 269.6 µS/cm and it was > 2.5-folds higher in the 0.6–0.8 m depth where the pH was highly acidic (4.23). pH increased with depth from slightly acidic to alkaline in control and manured Chromosol and there was not much variation amongst the control and treated (both surface-applied and deep-ripped) soils.

In general, the clay content increased with depth. In the Ferrosol, the clay content ranged from 47% to 63% with depth. While the Dermosol had the highest clay content with subsoils displaying more than 80%. Podosols showed the lowest percentage of clay. However, in depths greater than a metre, the Podosols exhibited a rise (greater than 25% in site 1 and 2) in the clay content. In the Sodosol, a significant increase in clay content was noticed in the manured soil when compared to the control.

1.10 ORGANIC CARBON AND EXTRACTABLE FE AND AL

In all the soils, the organic C (OC) content decreased with depth. Manured soils had higher OC% than the control soils. Sodosols had the least amount of OC, whereas the Hydrosol and the manured Podosol (elevated site) demonstrated high levels of OC (Tables 2, A2 and A3). A strong positive linear relationship between total C content and Olsen P concentrations was observed in Dermosol, Chromosol and Ferrosol.

Oxalate-extractable Fe and Al was measured in the Chromosol, Dermosol, Ferrosol and Sodosol soils. Oxalate-extractable Fe and Al represents non-crystalline and reactive forms of Fe and Al minerals in soils. In the amended Ferrosol, the Fe concentrations increased with depth, whereas it was the opposite trend in the control soils, although it increased in the 0.1–0.2 m depth. A similar trend was followed in the case of Sodosol in both treated and control soils. In the Dermosol, while the Fe content decreased with depth overall, increases were noticed in 0.1–0.2 and 0.2–0.3 m depths. In the Chromosol, increasing and decreasing patterns with soil depth in both control and treated soils were observed.

While there was a strong relationship ($R^2 = 0.64$) between oxalate extractable Fe and Olsen P concentrations in the Ferrosol control, the amended soils exhibited a negative relationship ($R^2 = 0.80$). Olsen P was positively correlated to extractable Fe in the Dermosol ($R^2 = 0.55$), whereas Sodosol and Chromosol showed very weak relationships.

1.11 DIFFUSIVE GRADIENTS IN THIN FILMS

Measurements of available P from DGT devices in homogenised soil samples were obtained at all depths for Chromosol, Ferrosol, Dermosol, Sodosol and Vertosol for comparison of manured and unmanured soils (Figure 1). From the C_{DGT} data, the only two profiles which demonstrated no increase in P C_{DGT} over unamended soil were the Chromosol and Dermosol soil profiles. The remaining three soils showed an enhancement in P C_{DGT} in A horizon(s) of the profile. The Ferrosol, similarly to the Olsen-P and Colwell P data, had the highest measured P C_{DGT} content in the amended soils. The unamended Ferrosol also showed high C_{DGT} results for P. The C_{DGT} P data decreased dramatically with depth in the manured profiles of the Sodosol and Vertosol, and the trend is C_{DGT} P data with depth was similar between the soils. Both of these soils were manured with chicken litter at approximately the same application rate. However, the Sodosol only showed an overall improvement in available P as indicated by C_{DGT} P in the top 0.1 m of the profile. Improvement was observed in the Vertosol down to 0.2 m. These latter soil profiles had received long-term amendments, whilst the Chromosol and Dermosol had received manure amendments for a shorter period (<2 Chromosol; <5 years Dermosol).

1.12 ISOTOPIC DILUTION OF P

Figure 2 shows the estimated labile concentration of P in 5 soils as a function of depth. The ‘soluble’ P fraction was measured using both ICP-OES and orthophosphate P (malachite green), resulting in different estimates of labile P. The difference between the orthophosphate and total P is attributable to colloidal P from both organic and inorganic P forms. The trend is for % orthophosphate to increase with depth, presumably due to a decrease in colloidal organic P. However, the amended Ferrosol showed a slight decrease in % orthophosphate with increasing depth, which is assumed to be associated with colloidal mineral particles.

Orthophosphate estimated E- values are the traditional values used to estimate labile P. The E-values (orthophosphate) tend to decrease down profile for both amended and unamended soil profiles. However, an increase was observed to occur in both texture contrast soils in the P profiles. Similarly, the Ferrosol increased in the lower depths, especially in the unamended soil profile.

Manured soils in general always showed an increase in estimated labile P (E-value) in the A-horizons of the profile. With the exception of the Chromosol, all manure was surface applied without incorporation below the surface. The Sodosol amended soil showed a large spike at the top of the B-horizon. This accumulation agrees with Olsen-P and Colwell-P measurements, clay content and CEC.

1.13 HIGH-RESOLUTION IMAGING OF AVAILABLE P IN SOIL

Figure 3 depicts C_{DGT} data in 5 mm increments of the 0.15 m cores. These included the top 0.15 m of the Sodosol receiving long-term applications of chicken litter, the top 0.15 m of the B-horizon of the Sodosol, the top 0.15 m for the Red Chromosol and the top 0.15 m of the Grey Dermosol (pig manure amended).The As C_{DGT} data indicate a low amount of labile As relative to P, Se and to a lesser degree, Mo. Importantly, this was also shown in the long-term chicken litter applied Sodosol. There were no trends observed in these cores for As, Mo and Se with depth. Only in the long-term amended Sodosol was there a clear increase in the C_{DGT} data for P. The available P in this profile decreases rapidly from the surface. Within 7 cm of the profile surface, the C_{DGT} P data was reduced. This data illustrates the high level of P localisation in some soil profiles.

Figures 4 to 6 depict the high-resolution C_{DGT} distribution of P, Mo and As from three surface intact cores. The results demonstrate the high degree of localisation of available As, P, and Mo in each of the 3 cores. In each of the three areas analysed, there are large areas of the gels with relatively low available As, P and Mo. By contrast, there are also incidences with each gel indicating extremely concentrated points of high available As, P and Mo. These incidences of high availability are likely <100 μm.

The most prominent features of the DGT gels are typically a few millimetres (mm^2) in area. Due to the high concentrations of P, these P areas are far clearer than the trace elements As and Mo. The surface amended Sodosol shows an area at the top of the soil profile of appropriately 1 mm^2. Indeed, each gel provides unique P distributions. The Red Chromosol, despite receiving low application rates of chicken litter, indicates substantial movement of P, and appears to accumulate at approximately 0.07 m for the top of profile surface.

The Grey Dermosol provides an interesting illustration of the importance of localised P geochemistry in soils, particularly when changing redox conditions may occur. The area chosen for laser ablation work was associated with Fe accumulation, as indicated in Figure 6. The depth was approximately 0.12 m from the soil surface, but the high clay content, compaction from grazing and significant rainfall appears to result in sub-oxic conditions. The discrete areas of mobile P is the most prominent feature of these gels. The remaining area appears to have relatively low available P. This agrees with the macroscopic data reported by bulk DGT, Olsen P and Colwell P.

The trace elements As and Mo to some degree are associated with available (C_{DGT}) P. However, As and Mo do not show such a clear demarcation between areas of low and high mobility as noted for P.

1.14 SPECIATION OF PHOSPHORUS: NMR RESULTS

The NMR spectra are shown for selected control and manured soils in Figure 7. The quantified inorganic P species (orthophosphate, pyrophosphate) and organic species (monoesters, phosphodiester) are shown in Table 7. The results showed that total NaOH-EDTA extractable P increased in the field-manured samples relative to non-manured. The greatest relative increase in in total extractable P was found in the Sodosol. This farmer had added CL annually for over a decade. However, the Vertosol on the same farm increased total P by only 1.7 times the control. The profile distribution of the Vertosol had shown that, in contrast to the Sodosol, the Vertosol had increased the available P to a greater depth. This redistribution down profile may explain these differences. The lowest increase was found in the Red Chromosol, which also was due to the low frequency and rates of application in this farm. The Ferrosol showed an increase in the total P as measured by NMR from 1026 mg/kg in the inter-row to 3800 mg/kg in the manured soils. However, the inorganic orthophosphate content in the manured soil (3680 mg/kg) increased by almost 6 times the inter-row soil (722 mg/kg). These results indicate that a high rate of inorganic P forms have been added in within or in addition to CL. Similarly, the total extractable P was extremely high compared to the other Australian soils sampled in this study.

The results showed an expected increase in inorganic P for each soils except the Chromosol. These results agree with results from the Olsen-P, Colwell P and, to a lesser degree, DGT results. Furthermore, the data and spectra clearly show the increase in organic P in the long-term manure amended soils. In all soils except the Ferrosol, the monoester P increased in manure-amended soils. Phosphodiester and pyrophosphate contributed small amounts to the total extractable pools of P.

1.15 MOBILISATION OF P: INCUBATION STUDY

The Olsen P concentrations varied amongst the soils and between the manures (Table A6). In the incubation study, two soil samples were used per site: a control and a field amended soil (with either CL or PM depending on land use history). The control and field amendment soil were amended with both CL and PM at the same rate. It was observed that less differences were observed between the PM and CL manured (field amended) Ferrosol, Sodosol, Vertosol and Podosol. However, in control (not field amended) amended and manured amended Chromosol and Dermosol, significant changes in Olsen P were noted between the PM and CL treatments. Only slight variability in Olsen P concentrations with time was noticed particularly from day 1 to day 21, however a significant decrease in Olsen P was noticed at day 49 in majority of the treatments. Changes in EC values varied amongst the soil types. While in Ferrosols, the EC values increased with time and then decreased after 21 days, the other soil types displayed an increasing trend in EC with time. In the case of pH, overall, a decreasing pattern with time was observed. In PM amended Ferrosol, although a sharp increase in pH was found after 7 days, a gradual decline was noticed after that.

The E-values from the mobilisation of CL and PM are shown in Figure 8. Shown are estimated values for control (not field amended) and manured (field amended).

Pig manure showed larger and more consistent increases in the E-values than CL. Since the PM samples has significantly higher P content than CL, the greater total increase may not be surprising. However, the results reflect the labile P concentration at 0 and 49 days. Interestingly, the PM amendment either increased the E-value from 0 to 49 days or remained relatively constant. The CL amendment, by contrast, increased the labile P content at 0 days. Between 0 and 49 days, the E-valules in CL amended samples consistently declined at 49 days incubation. The CL amended Podosol was the only soil to maintain the labile P for 49 days.

Figure 9 shows the change in measured E-values for amended soils expressed as a percentage of added P from CL or PM. Figure 9 clearly demonstrates that labile P declined substantially between 0 and 49 incubations for all soils excluding the Ferrosol. Indeed, in the field manured Chromosol, there was a net decrease in P E-values relative to that of added. Again, this clearly contrasts with PM, where there was consistent maintenance or a increase in label P as a result of the amendment.

Both PM and CL decreased the labile P in the Ferrosol rather than increasing the labile P size. The Ferrosol was an extreme soil with regard to P. Rather than displaying high P sequestration to the solid phase, the opposite was generally true. Amendment of organic sources of P in this high P soil resulted in large reductions in the kinetically labile P pool.

XRD spectral components (Figures 10) of the Ferrosol (manured and control) and Chromosol were identified as goethite and microcrystalline Fe(III) oxyhydroxides based (Schoepfer et al., 2019). Incubation of these soils with amendments (PM and CL) did not influence the proportion of goethite and microcrystalline Fe(III) oxyhydroxides within the time frame of this study.

Table 2. Selected physico-chemical properties of Ferrosol amended with chicken litter (Lismore, NSW)

	Depth (m)	**pH**	**EC (µS/cm)**	**Clay (%)**	**ECEC (cmol/kg)**	**Olsen P (mg/kg)**	**Colwell P (mg/kg)**	**Extr. Fe (mg/kg)**	**Extr. Al (mg/kg)**	**ESP (%)**	**OC (%)**
Control	0-0.1	6.40	80.07	n.d.	21.1	43.66	150.2	1370	1050	0.48	5.94
	0.1-0.2	6.11	79.07	n.d.	11.1	12.63	52.65	1350	1090	0.58	3.96
	0.2-0.3	5.80	70.93	n.d.	7.28	8.275	31.28	989	839	0.54	3.19
	0.3-0.4	5.73	50.17	n.d.	5.67	4.376	68.62	987	645	0.60	2.16
	0.4-0.5	5.85	37.71	n.d.	5.37	3.757	70.41	899	578	0.46	1.80
	0.5-0.6	5.95	31.98	n.d.	5.18	3.599	70.55	932	560	0.76	1.35
	0.6-0.8	5.89	38.48	n.d.	5.46	3.187	72.79	934	509	0.46	1.46
Treated	0-0.1	5.97	274.8	n.d.	28.8	315.5	808.7	962	837	0.68	12.1
	0.1-0.2	6.03	164.3	n.d.	20.9	282.1	448.4	1090	922	0.81	5.22
	0.2-0.3	5.36	174.9	n.d.	10.3	92.55	268.8	1160	970	0.99	5.28
	0.3-0.4	5.35	166.4	n.d.	12.7	50.36	197.7	1160	925	1.04	6.09
	0.4-0.5	5.41	133.5	n.d.	10.6	31.60	91.52	1190	916	1.05	6.62
	0.5-0.6	-	-	-	-	-	-	-	-	-	-
	0.6-0.8	5.25	137.4	n.d.	5.84	8.953	30.23	1300	629	1.51	1.69

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table 3. Selected physico-chemical properties of Sodosol amended with chicken litter (Uralla, NSW)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	5.86	38.29	15.44	4.71	16.78	29.91	943	216	0.64	1.80
	0.1-0.2	5.90	27.62	15.21	3.79	12.38	29.50	788	180	1.07	0.90
	0.2-0.3	5.93	15.38	15.41	3.22	11.58	25.07	617	144	2.66	0.46
	0.3-0.4	5.99	20.11	21.26	3.99	11.20	27.35	328	113	5.66	0.40
	0.4-0.5	5.90	22.19	23.94	4.96	12.64	24.64	460	322	12.8	0.37
	0.5-0.6	5.93	45.88	37.61	11.6	11.51	33.52	525	510	15.2	0.49
Treated	0-0.1	5.27	119.1	29.61	8.54	17.90	82.24	1050	365	0.70	3.21
	0.1-0.2	5.55	77.63	20.38	8.15	10.95	54.70	1014	390	0.70	2.12
	0.2-0.3	5.68	66.26	26.18	8.75	14.42	39.34	722	432	0.87	1.43
	0.3-0.4	5.80	64.71	40.70	10.2	20.44	27.49	792	606	1.29	1.08
	0.4-0.5	5.59	68.48	42.74	14.9	8.984	29.71	1054	893	1.74	1.09
	0.5-0.6	5.63	61.26	42.61	15.0	24.97	22.09	711	751	2.79	0.66
	0.6-0.8	5.67	47.43	20.55	17.2	15.73	35.62	532	490	3.47	0.51

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table 4. Selected physico-chemical properties of Vertosol amended with chicken litter (Uralla, NSW)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	7.24	89.25	36.41	23.97	19.09	48.19	n.d.	n.d.	1.13	3.48
	0.1-0.2	7.79	81.00	35.16	24.40	16.23	38.79	n.d.	n.d.	1.42	0.95
	0.2-0.3	8.27	86.10	33.76	23.13	9.639	28.22	n.d.	n.d.	1.65	0.81
	0.3-0.4	8.26	121.3	34.20	25.42	9.309	23.53	n.d.	n.d.	1.81	0.70
	0.4-0.5	8.70	129.5	26.20	24.87	11.96	23.23	n.d.	n.d.	2.04	0.55
	0.5-0.6	8.35	96.60	40.04	27.60	14.74	27.71	n.d.	n.d.	2.76	1.07
	0.6-0.8	8.34	123.0	51.40	36.01	9.930	31.48	n.d.	n.d.	3.58	1.99
Treated	0-0.1	6.58	108.2	39.46	27.97	37.26	100.9	n.d.	n.d.	1.36	4.80
	0.1-0.2	7.16	74.95	40.05	26.65	18.26	49.50	n.d.	n.d.	1.70	2.07
	0.2-0.3	7.57	80.65	39.35	24.39	20.44	36.45	n.d.	n.d.	2.24	1.21
	0.3-0.4	7.98	75.25	37.71	23.49	24.01	34.14	n.d.	n.d.	2.89	0.93
	0.4-0.5	8.24	96.95	38.77	24.68	22.56	34.00	n.d.	n.d.	3.38	0.86
	0.5-0.6	8.45	141.0	37.45	27.48	15.60	32.65	n.d.	n.d.	3.37	1.12
	0.6-0.8	8.31	103.1	41.19	27.08	16.49	30.24	n.d.	n.d.	4.01	1.70

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table 5. Selected physico-chemical properties of Dermosol amended with pig manure (Somers, Victoria)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	5.24	269.6	26.40	24.12	24.53	89.84	5910	724	7.72	10.1
	0.1-0.2	5.28	186.0	33.07	20.27	20.67	79.58	7100	801	6.78	5.52
	0.2-0.3	5.19	137.8	48.95	20.37	13.87	54.02	4930	1020	6.04	3.97
	0.3-0.4	5.22	116.6	61.53	22.21	9.370	35.41	3730	1250	5.76	2.67
	0.4-0.5	4.97	147.7	57.86	20.52	8.794	30.24	3300	1060	7.16	2.04
	0.5-0.6	4.84	202.0	75.31	23.96	5.978	29.02	3010	1250	5.92	1.48
	0.6-0.8	4.23	716.0	81.35	28.66	6.589	25.96	1710	1010	6.48	0.99
Treated	0-0.1	5.92	248.0	33.83	29.19	31.55	73.37	5610	699	3.47	7.81
	0.1-0.2	5.66	159.5	27.01	23.62	16.59	41.95	6350	768	4.09	5.27
	0.2-0.3	5.79	94.55	50.89	24.20	10.64	34.82	6360	894	5.44	3.52
	0.3-0.4	6.00	90.60	71.38	29.73	8.260	34.42	3720	900	6.35	2.10
	0.4-0.5	6.24	100.0	83.59	30.38	6.426	21.03	1710	959	7.18	1.36
	0.5-0.6	5.94	150.6	81.62	29.08	5.547	30.29	1070	939	8.00	1.06
	0.6-0.8	5.45	220.0	79.92	30.98	5.929	27.65	883	800	9.43	0.88

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table 6. Selected physico-chemical properties of Red Chromosol amended with chicken litter (Condobolin, NSW)

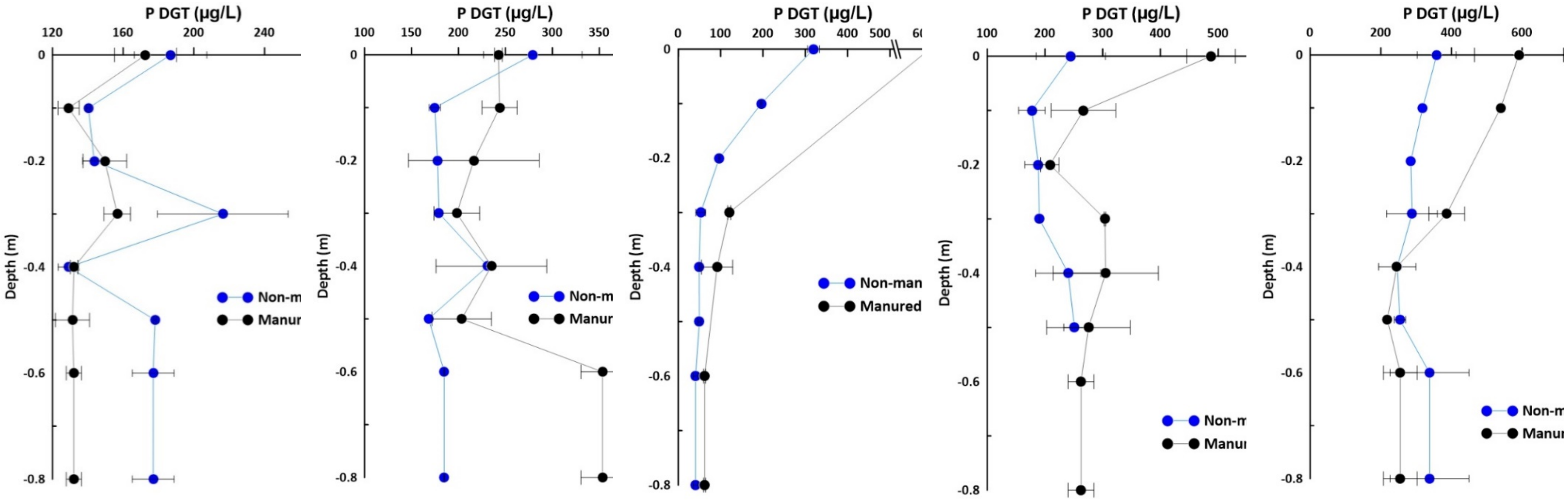
	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	6.47	77.60	22.29	14.48	17.36	46.97	686.32	375.06	0.92	1.46
	0.1-0.2	6.90	125.5	33.54	20.64	9.237	30.34	592.98	432.20	0.72	1.09
	0.2-0.3	7.15	100.0	40.80	18.49	8.887	27.71	752.42	442.95	0.82	0.85
	0.3-0.4	7.41	83.60	49.47	20.28	7.224	28.17	1002.5	489.65	0.82	0.67
	0.4-0.5	7.67	84.80	52.19	24.03	6.606	31.63	991.08	600.18	1.40	0.53
	0.5-0.6	7.81	79.20	33.72	22.15	8.192	29.92	854.49	598.37	1.80	0.47
	0.6-0.8	7.99	74.45	51.83	21.06	7.497	29.62	680.71	475.92	2.32	0.37
	0.8-1.0	7.96	74.95	47.62	18.86	6.668	32.99	512.46	343.52	2.82	0.34
Treated	0-0.1	6.26	73.80	26.27	12.12	15.82	52.21	543.70	410.23	0.90	1.45
	0.1-0.2	6.63	49.20	31.72	13.46	9.661	33.17	621.72	392.66	0.87	1.08
	0.2-0.3	6.94	46.93	38.76	14.87	7.627	37.72	591.47	426.23	0.90	0.83
	0.3-0.4	7.23	39.85	48.54	14.77	7.071	30.83	700.09	424.88	1.19	0.55
	0.4-0.5	7.63	92.90	50.82	18.06	6.673	22.86	515.36	445.49	1.41	0.51
	0.5-0.6	7.86	94.40	53.52	23.27	5.974	25.23	491.73	410.18	1.94	0.41
	0.6-0.8	8.09	89.30	52.15	22.01	5.880	23.26	387.73	371.29	2.68	0.30
	0.8-1.0	8.15	96.25	50.89	20.17	5.819	29.78	346.87	387.35	3.78	0.22
Treated-Deep ripped	0-0.1	6.52	55.10	22.18	11.78	13.27	n.d.	n.d.	n.d.	0.93	1.22
	0.1-0.2	6.23	53.00	29.78	12.66	8.689	n.d.	n.d.	n.d.	0.94	0.83
	0.2-0.3	6.75	56.10	36.96	13.60	6.776	n.d.	n.d.	n.d.	1.02	0.57
	0.3-0.4	7.16	43.20	39.29	16.68	6.849	n.d.	n.d.	n.d.	1.13	0.53
	0.4-0.5	7.31	39.80	42.85	17.67	7.325	n.d.	n.d.	n.d.	1.46	0.52
	0.5-0.6	7.80	55.40	43.10	15.48	5.899	n.d.	n.d.	n.d.	1.85	0.41
	0.6-0.8	8.05	69.20	44.58	19.51	5.027	n.d.	n.d.	n.d.	2.42	0.30
	0.8-1.0	8.48	36.20	40.22	17.64	5.144	n.d.	n.d.	n.d.	2.94	0.26

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table 7. Total P and NaOH-EDTA extractable P classes determined by ^{31}P NMR spectroscopy in various control and manured soils.

Soil	**Orthophosphate (mg/kg)**	**Monoester (mg/kg)**	**Phosphodiester (mg/kg)**	**Pyrophosphate (mg/kg)**	**Total P (mg/kg)**
Vertosol Manured	38.7	45.7	2.90	5.05	38.7
Vertosol Manured	107	46.4	n.a.	n.a.	153
Ferrosol Control	722	267	27.5	9.72	1026
Ferrosol Manured	3680	112.8	5.60	5.12	3800
Sodosol Control	22.9	33.9	1.33	n.a.	58.1
Sodosol Manured	158.9	81.5	14.0	26.5	281
Chromosol Control	85.1	9.49	n.a.	2.64	97.3
Chromosol Manured	71.2	31.7	8.66	0.00	112

n.a. no identifiable peaks.



Chromosol **Dermosol** **Ferrosol** **Sodosol** **Vertosol**

Figure 1. Estimated C_{DGT} values (µg/L) as influenced by organic amendments in 5 different soil types as function of depth.

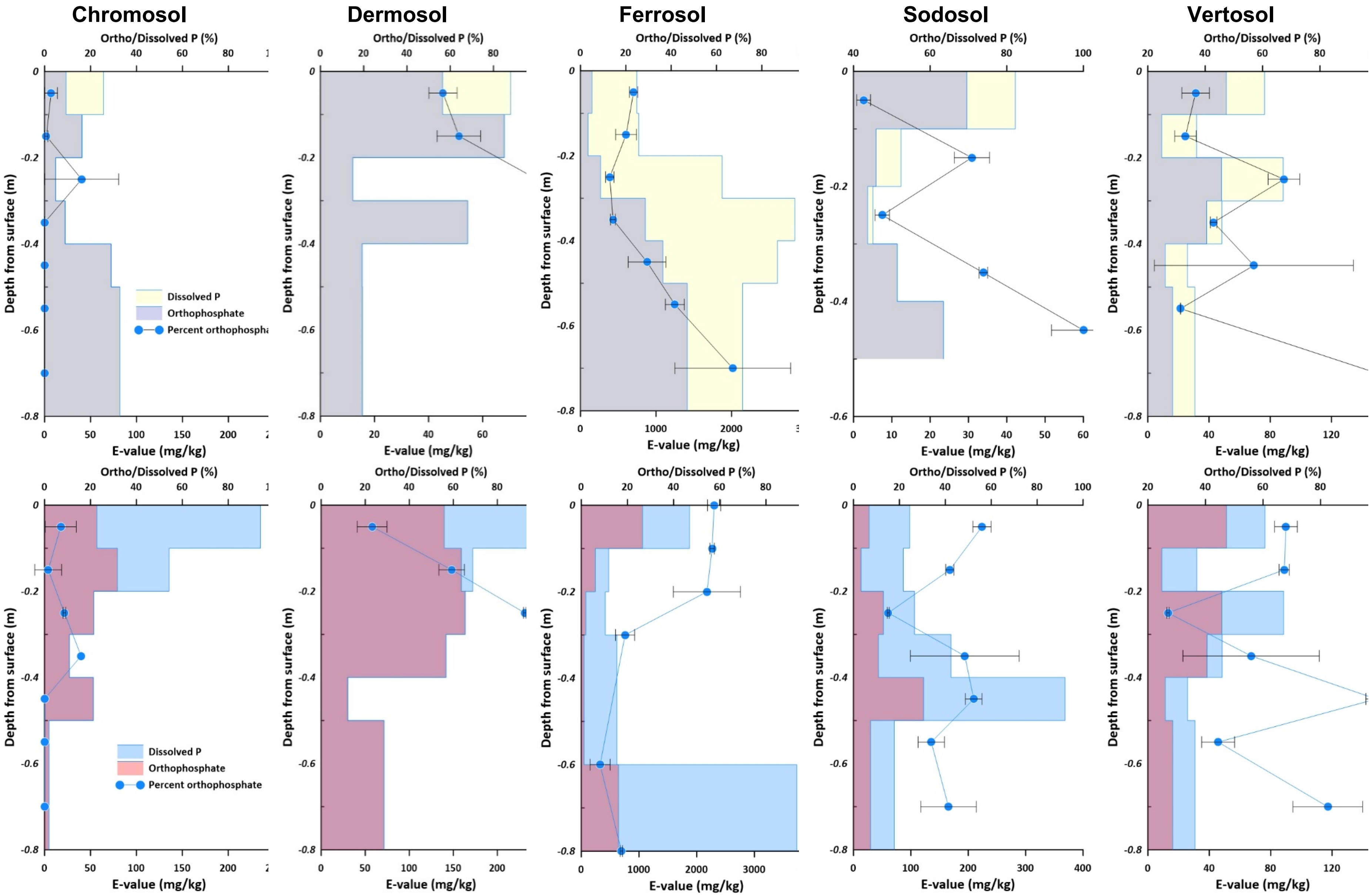


Figure 2. Measured E values down profile for selected soil types for both unamended and manured field sites. Top figures indicate non-amended profiles; bottom graphs indicate manured profiles. Yellow in non-manured profiles indicates values for colloidal P above orthophosphate E values; blue in amended indicates values for colloidal P above orthophosphate E values.

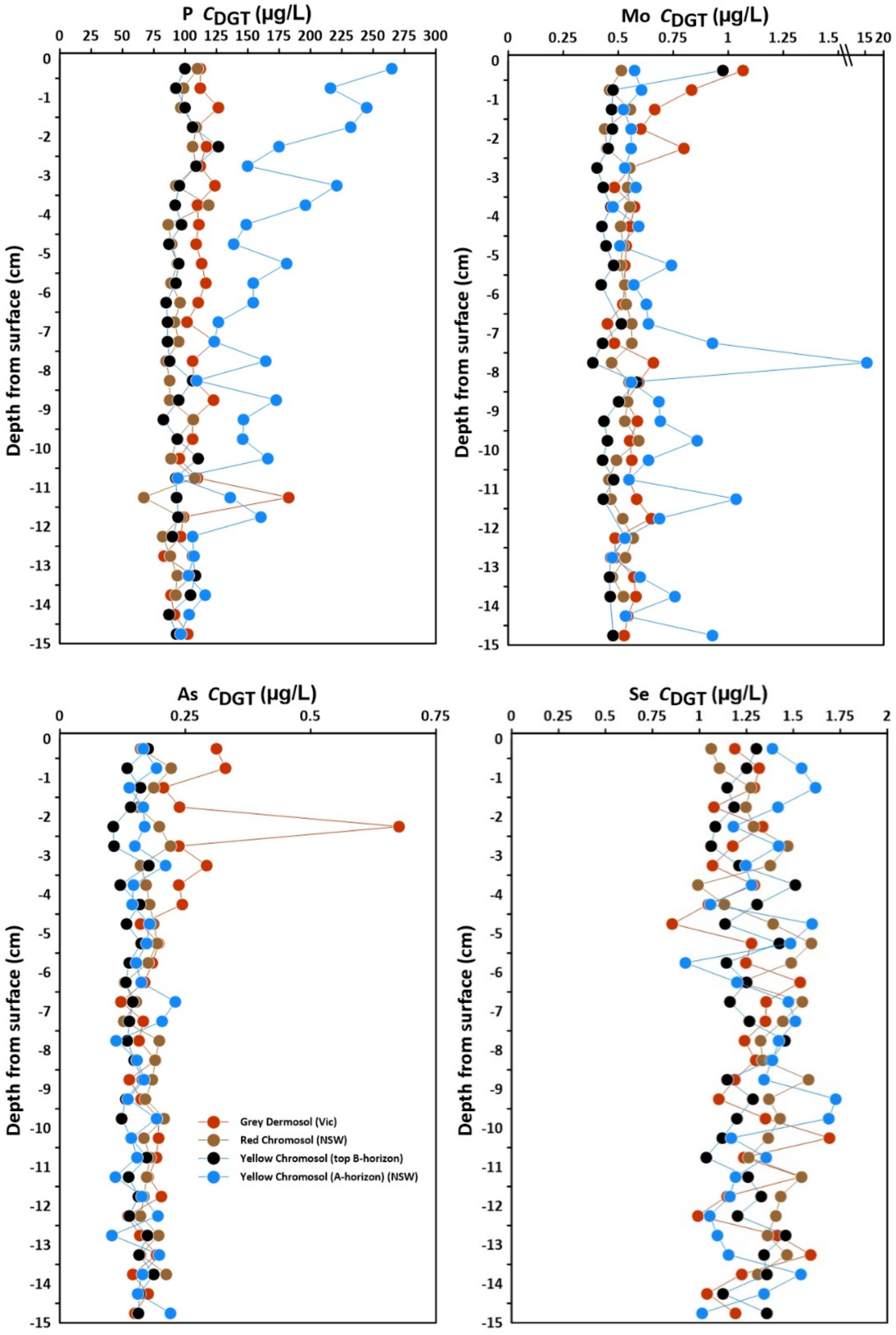


Figure 3. Diffusive Gradients in Thin films from intact cores of four soils for P, Mo, As and Se in the top 0.13 to 0.15 metres

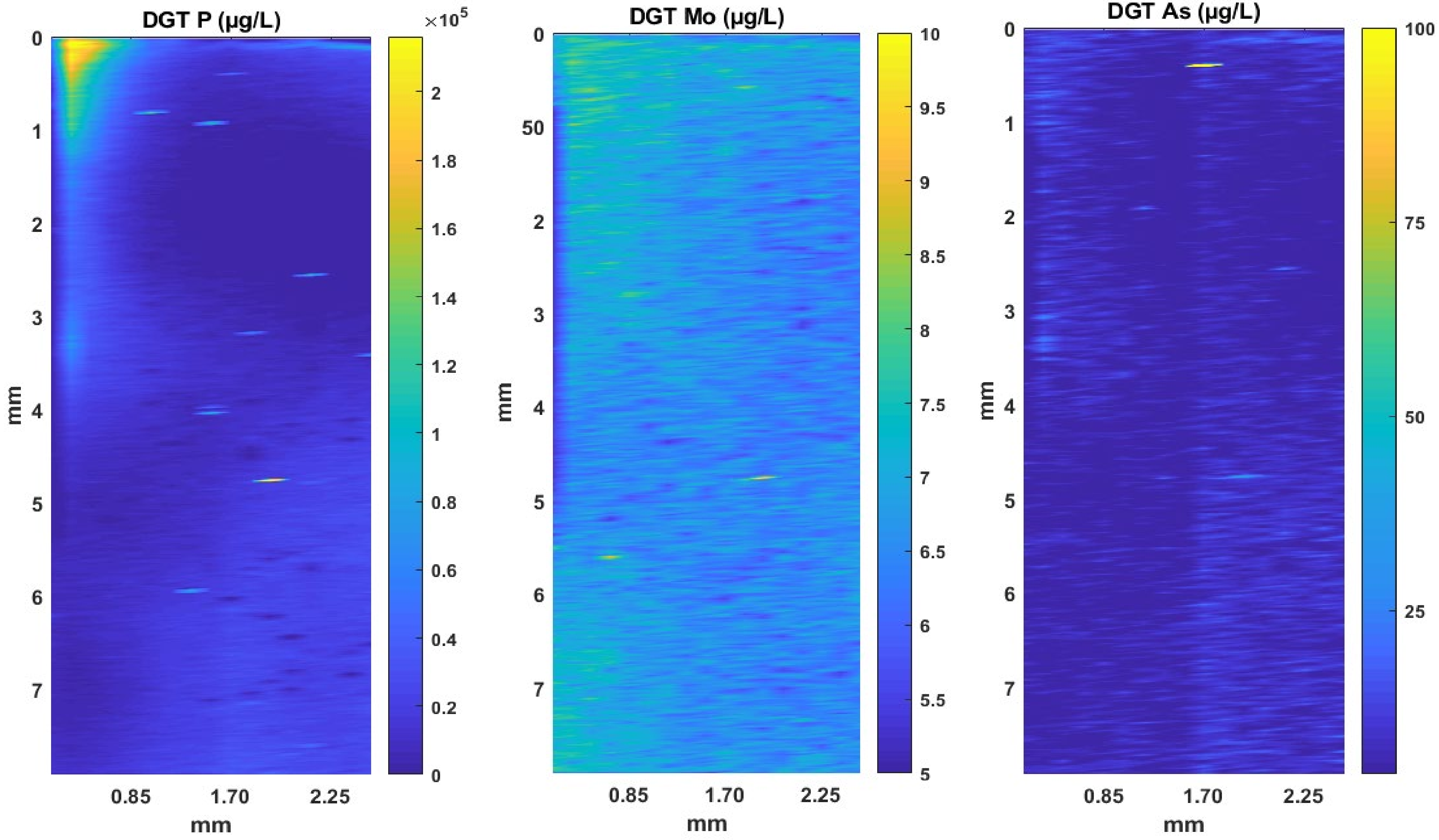


Figure 4. High resolution two-dimensional depiction for P, Mo and As plant availability using DGT (μg/L) in Yellow Sodosol top soil (Top 7 mm)

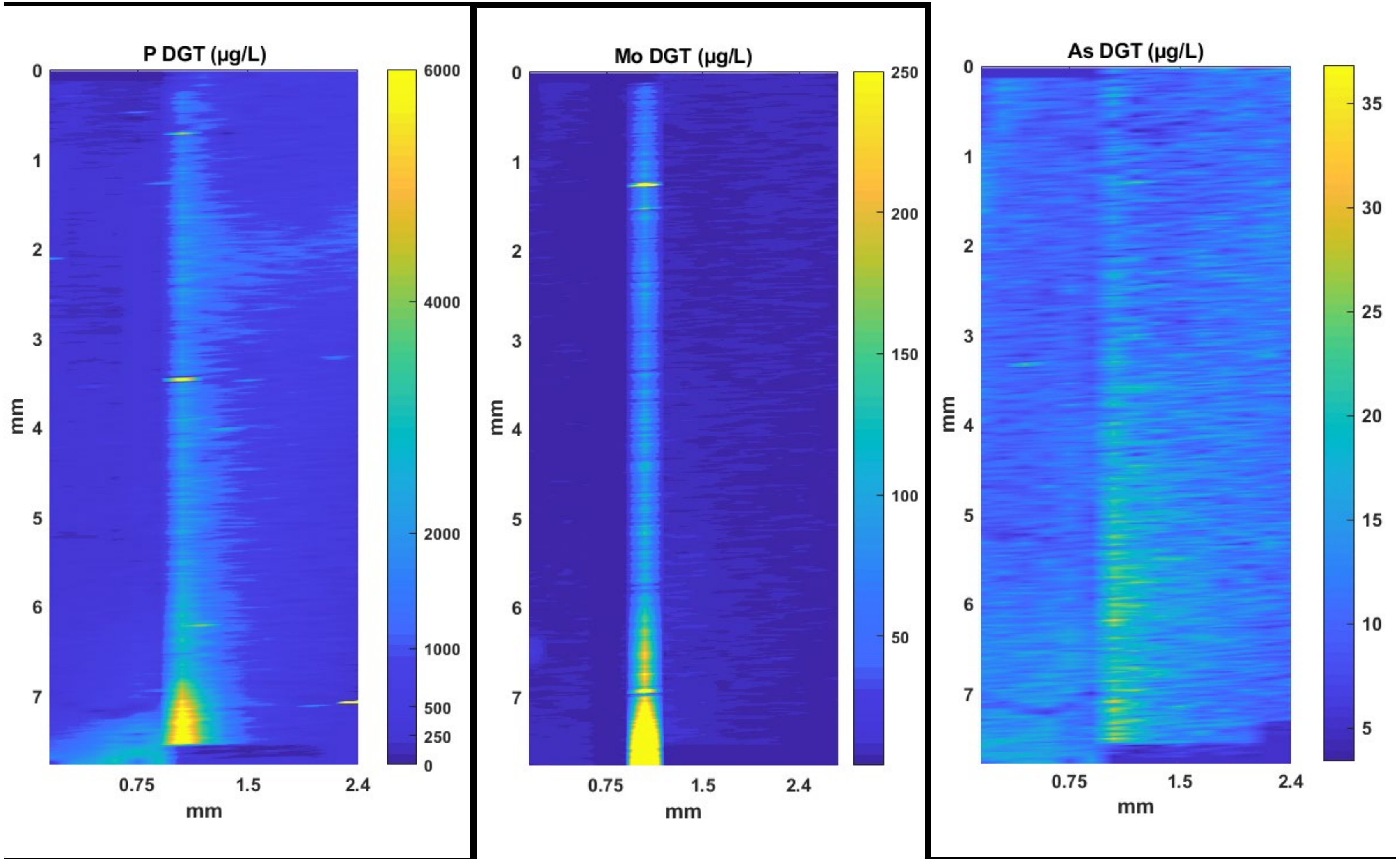


Figure 5. High resolution two-dimensional depiction for P, Mo and As plant availability using DGT (µg/L) in Red Chromosol top soil (Top 7 mm).

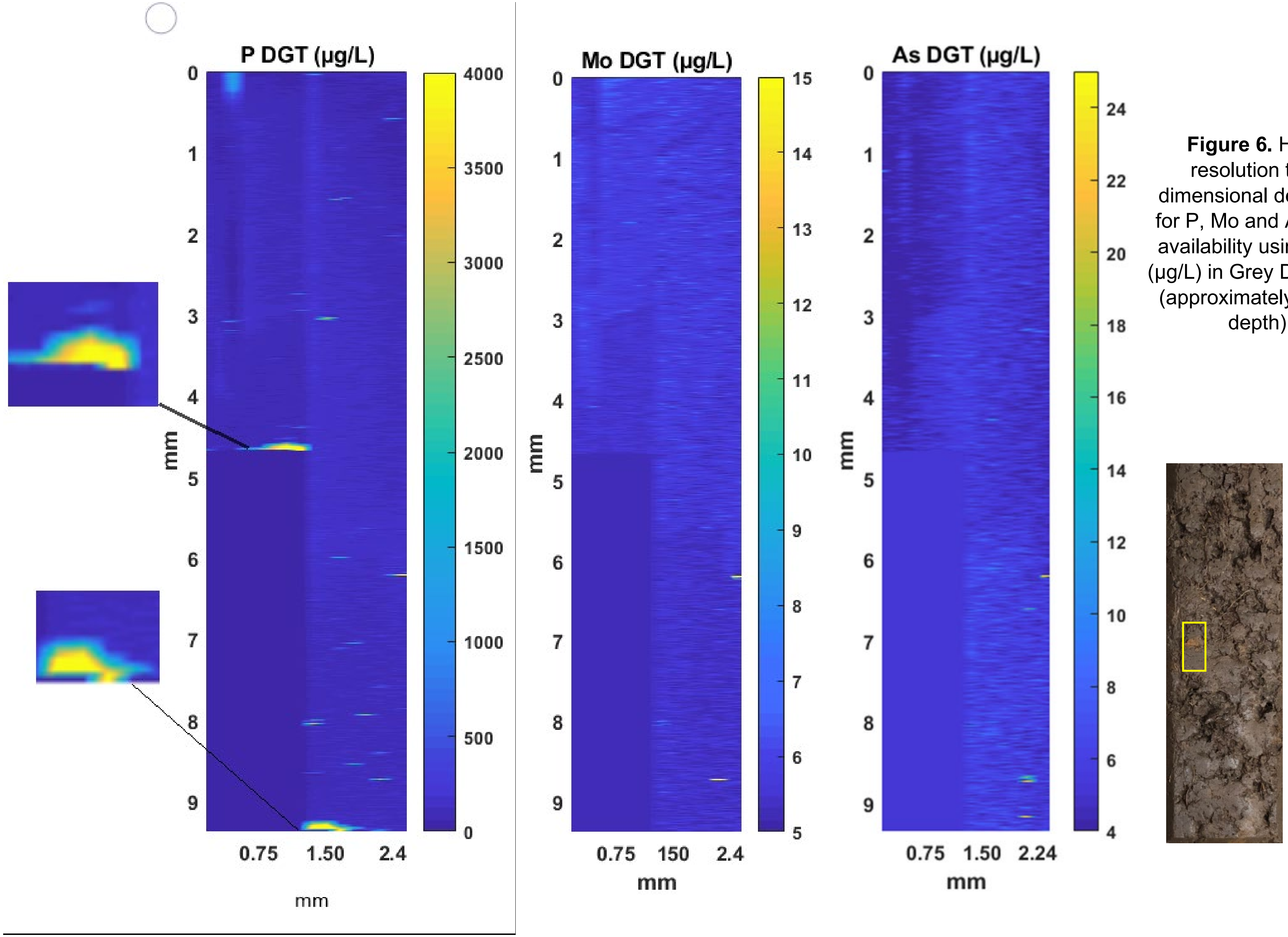


Figure 6. High-resolution two-dimensional depiction for P, Mo and As plant availability using DGT (µg/L) in Grey Dermosol (approximately 10 cm depth)

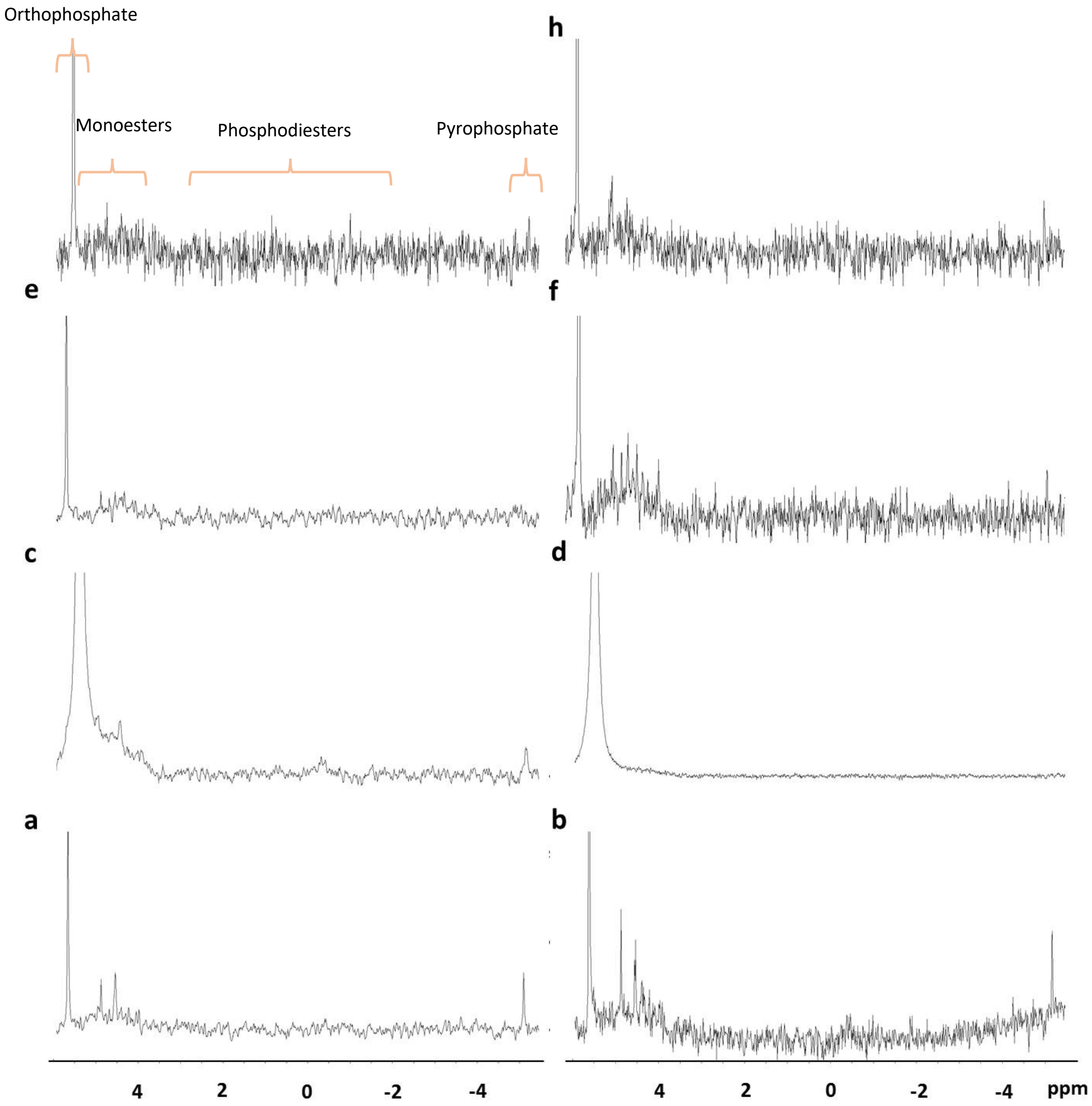


Figure 7. ^{31}P NMR solution spectra of control and manured soils extracted with NaOH-EDTA solution. Spectra on left (a, c, e, g) and right (b, d, f, h) represent control and manured soils, respectively. a and b: Vertosol control and manured; c and d: Ferrosol control and manured; e and f: Sodosol control and manured; g and h: Chromosol control and manured. Species range (ppm) is used as a visual guide only.

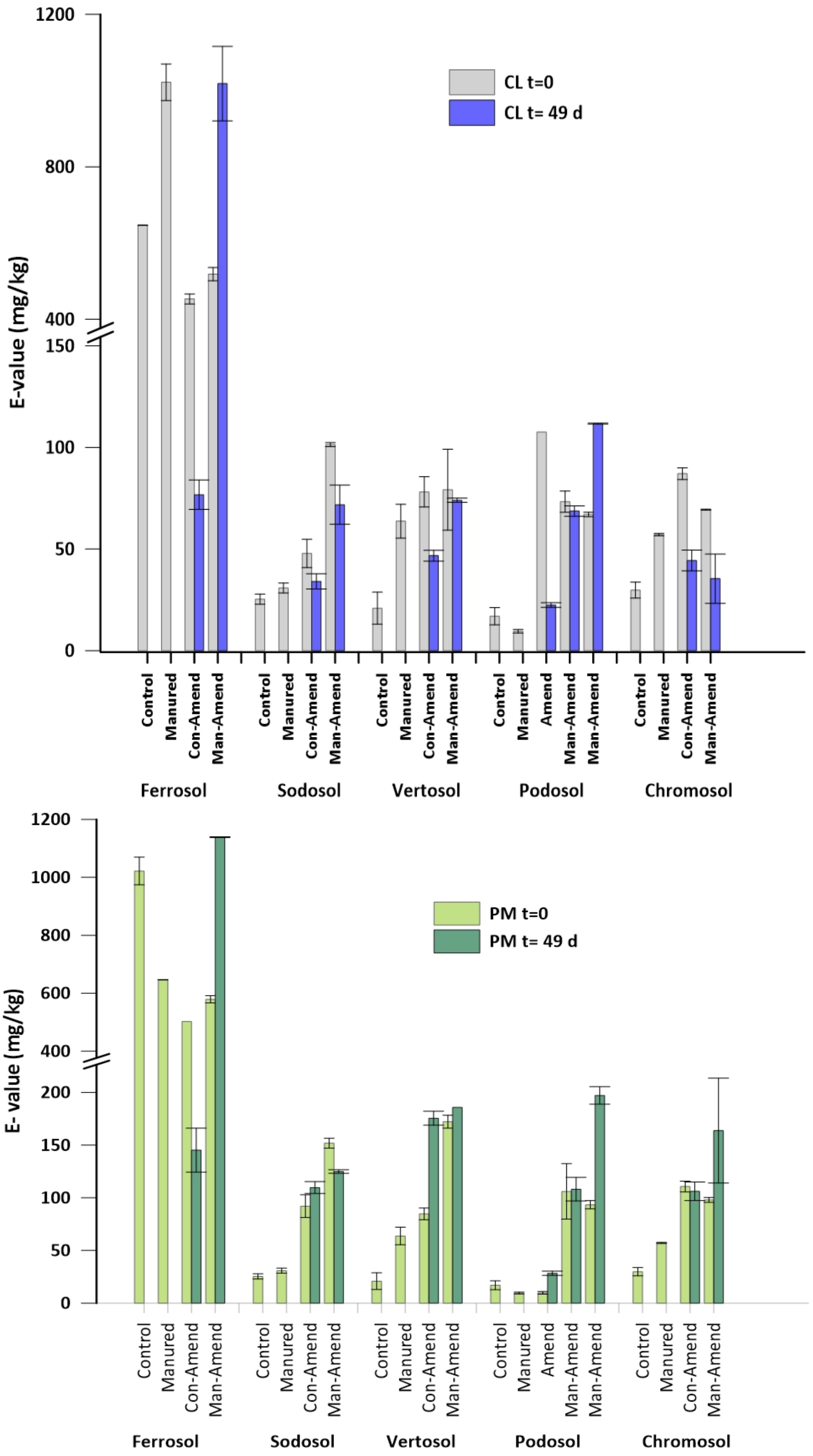
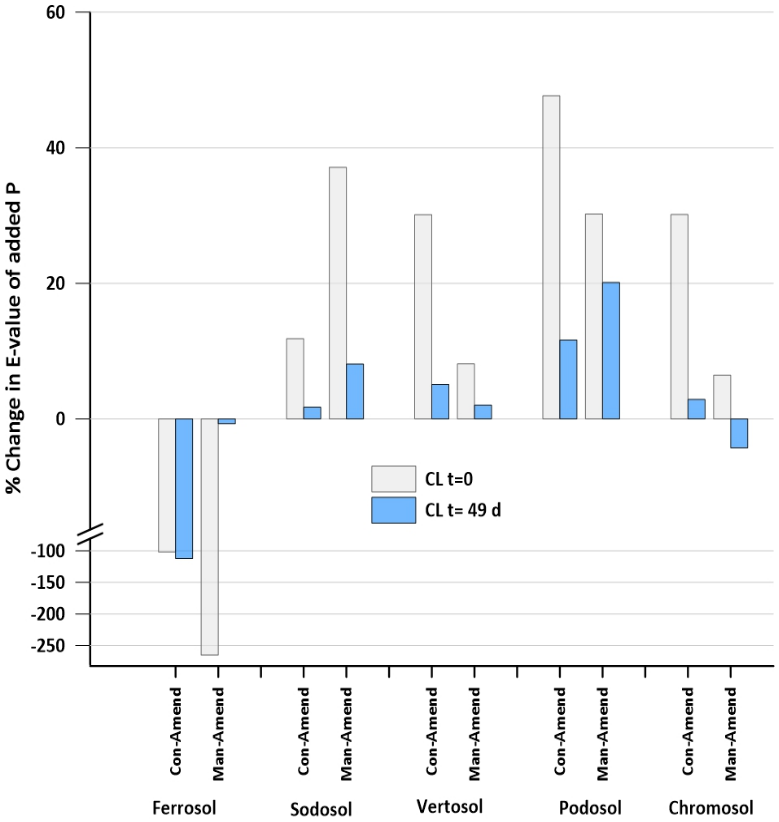


Figure 8. Estimated E-values for P in incubated soil samples with chicken litter (CL) and pig manure (PM) (mg/kg).



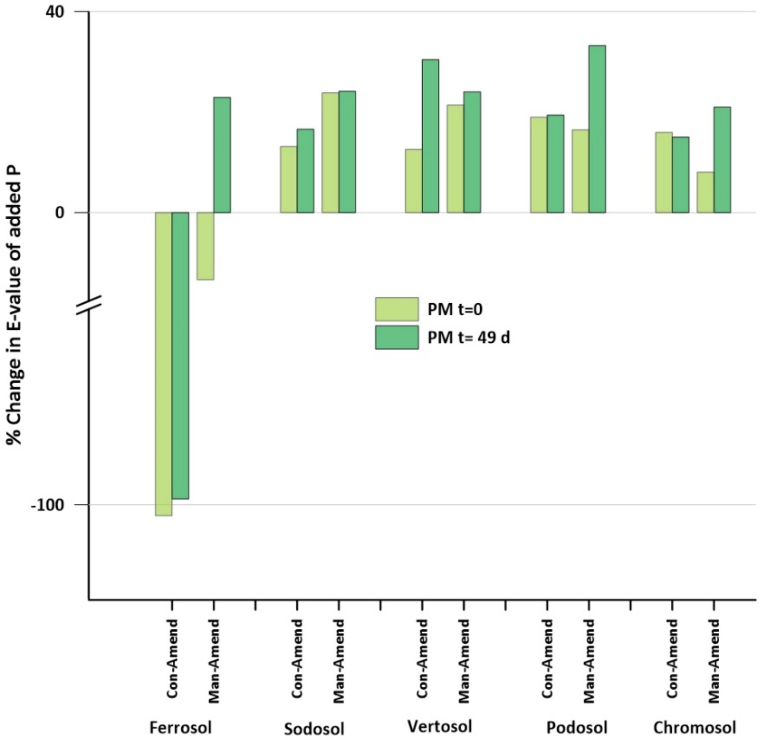
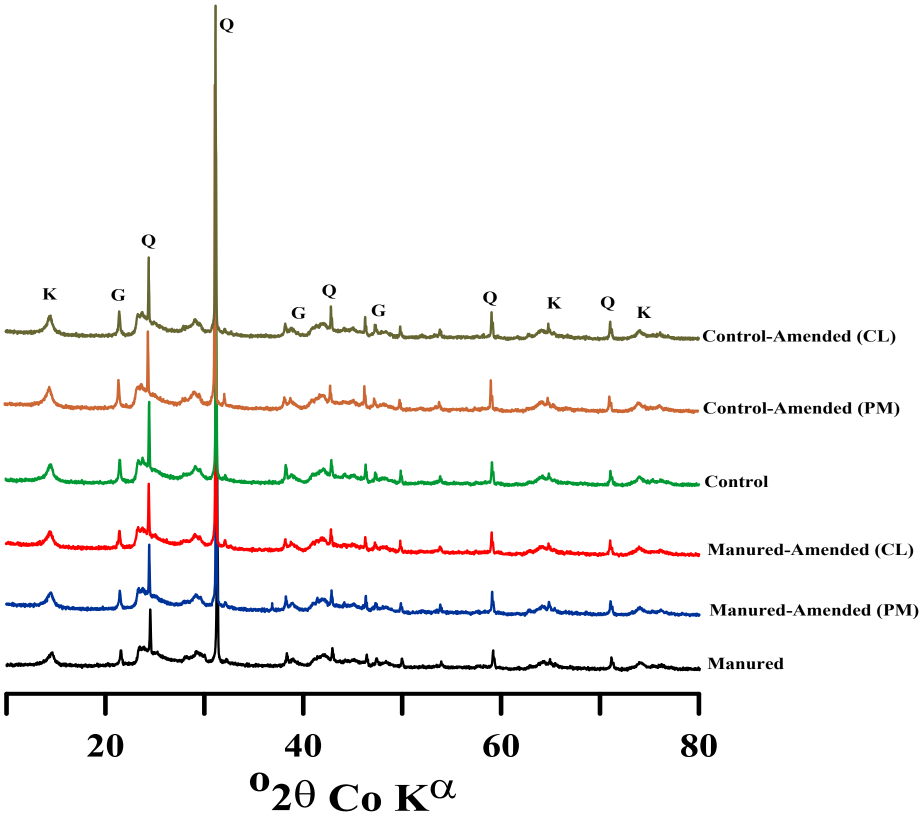


Figure 9. The percentage change in labile P from addition of P from CL and PM manures for 5 soils. Data are shown for control and field amended soils at 0 and 49 days incubation (25°C).



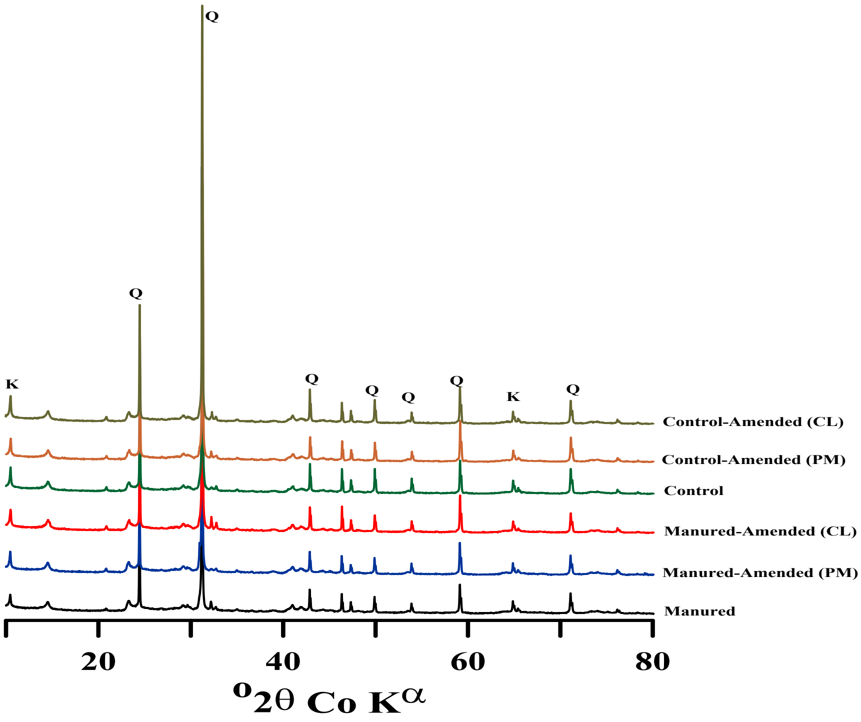


Figure 10. Top X-ray diffraction (XRD) patterns of Ferrosol from addition of P from CL and PM manures at 24 h incubation. Identified minerals: K - Kaolinite; G - Goethite; Q - Quartz (Silica)

Bottom: X-ray diffraction (XRD) patterns of Red Chromosol from addition of P from CL and PM manures at 24 h incubation. Identified minerals: K - Kaolinite; G - Goethite; Q - Quartz (Silica)

DISCUSSION

Organic amendments to agricultural soils confer many potential benefits to the health and productivity of agricultural systems. Among these, the application of organic waste products from municipalities or animal husbandry farms contributes to the addition of essential nutrients such as N and P, in soil. However, much of the P, N and S is locked up in organic and inorganic forms, and are unavailable for plant uptake in the short term. In this study, soil samples were collected from farms which had received chicken litter (CL) or pig manure (PM) amendments and compared with control plots which had not received organic amendments.

The major focus of this study was to examine the value of organic amendments on mobilising/increasing plant available (or bioavailable) P in soil. The bioavailable P, as measured by the bicarbonate extractable (i.e. Olsen and Colwell P), DGT, NMR and isotopically labile P determinations for the field samples indicated a general improvement of the P status of amended soils. Two sites did not show a consistent improvement in the P status from organic amendment inputs. These sites were the Red Chromosol (Condobolin, NSW) and Grey Dermosol (Somers, Victoria). In both of these sites, the amendment was recently applied and at relatively low rates in total. The data indicated that even in the top 10 cm soil layer the application of manure had not increased the available P at the time of sampling. The remaining soils (Ferrosol, Sodosol and Vertosol) showed large increases in the available P as result of the CL amendments. This was clearly demonstrated by bicarbonate extractable, DGT and NMR results. Although the effect of manure application on available P indices was more pronounced in the surface layer, the effect was also noticed at lower depths in soils, indicating a movement of P in these soils.

The Ferrosol showed the highest bicarbonate extractable P, C_{DGT} results and E-values of all the soils in the top 0.3 m of the profile. This reduced dramatically below 0.5 m. Due to the higher Fe oxyhydroxide content of these soils, it had been anticipated that the available P would be low despite the addition of CL annually. Although it was communicated on sampling that no inorganic P sources had been utilised to improve production, the P data strongly indicates otherwise. Interestingly, this farm produced only macadamia nuts, and therefore, the main crop is from the Proteaceae family. Proteaceae, particularly in Australia, are known to be sensitive to P (i.e. high P negatively impacts growth) or requires low P amendments for sufficient production (Lambers et al., 2015). Indeed, a reason for producing macadamia on Ferrosols is linked to the low available P typically observed in these soils. Compared to other macadamia orchards visited, the trees on this site were visibly less productive than other farms with higher planting rates. Indeed, our results have shown that further organic P amendment dramatically reduced the kinetically labile P from CL and PM.

The data derived from the short term incubation experiment showed two distinct responses between the two amendments (CL and PM) over time. The PM manure clearly increased the labile P or maintained it. The CL amendments, whilst increasing the total P content, actually decreased the labile pool size over the 49 day period. Soil microbial populations can either result in the mineralisation of organic P or mineral P from soils, or they may immobilise the available P through sequestration within their biomass (Damon et al., 2014). It is commonly observed that there is a decrease with time in the soluble or reactive

P (Jin et al., 2016). This may be related to microbial degradation of P associated with colloidal organic matter. This *initial* flux of P, whether inorganic or organic, is also subjected to a range of sorption reactions to mineral surfaces of soils. The XRD data indicate that there were large differences in the mineralogy between soils. It is reasonable to expect vast differences in P im(mobilisation) dynamics as impacted by manure input between soils if the main mechanism of immobilisation was sorption. The Podosol with CL did show the smallest reduction in E-values with time. However, this does not account for the consistent differences between the two manure sources of P. Furthermore, P sorbed to mineral surfaces would be included to a large degree in the isotopically labelled fraction.

Microbial communities are known to immobilise P when amended from organic substrates to a greater degree than inorganic fertilisers (Bünemann et al., 2012; Damon et al., 2014; Mclaughlin and Alston, 1986). Bünemann et al. (2012) used isotopic dilution techniques (^{33}P) to determine the P turnover in grassland soils. The study showed that at low available P soils, the addition of P resulted an extremely fast sequestration into the microbial biomass, indicating that microorganisms tend to assimilate the freshly added P input. This study also strongly suggested that the available amount of P in the soils was a key factor controlling mineralisation and immobilisation rates. The addition of inorganic P resulted in lower mineralisation rates, and higher rates of immobilisation. The results of Bünemann et al. (2012) to some degree agree with results found in this work. The Ferrosol with very high bicarbonate extractable P showed a large net immobilisation of added P. However, CL amended soils always showed a significant immobilisation overtime regardless of soils. The carbon:P ratio in relation to the available P is likely to be a factor contributing to the P sequestration differences between PM and CL. The CL C: P ratio was 15:1 (%OC: 29), whilst the C:P ratio of the PM was 3:1 (%OC: 13). Although the high C:N ratio in the CL is beneficial, it may potentially have the effect of sequestering P into the microbial biomass.

Microbial communities are highly diverse in soil environments and establish themselves within physical and ecological niches (Helfenstein et al., 2018; Lennon et al., 2012). Factors which influence the composition of microbial communities within a soil profile, include water availability, available nutrients and composition and, oxygen content of the soil atmosphere. Therefore, the spatially heterogeneous mineral composition and soil atmospheric composition can be associated with unique microbial populations (Hernandez-Soriano et al., 2018; Stockdale et al., 2008). In sediments, it has often been shown that organic-rich zones result in the development of unique geochemical environments controlling metal and nutrient behaviour (Stockdale et al., 2008).

Similar work in soil environments does not appear to have investigated in sufficient detail to understand the unique geochemical environments controlling nutrients. Recent work has been published in relation to carbon stabilisation within aggregates, illustrating the important of microscale geochemical environments (Hernandez-Soriano et al., 2018). The importance of local geochemical environments on P dynamics is perhaps recognized but has not been investigated. The high-resolution spatial-temporal analysis of P in intact cores is likely the first attempt to study the availability of P, As and Mo simultaneously. The limited work outlined in this report points to likely importance of P enriched micro and nano-volumes of soil. The two-dimensional diffusive gels demonstrate highly localised solubilisation of P, most likely associated with Fe and Mn oxyhydroxide reductive dissolution. However, this could not be confirmed in the current study. Locally modified zones of biogeochemical processes (i.e. microniches) in sediments have been able to indicate correlation between reducing conditions and reductive release of P by using a gel able to identify sulphides. In the soil environment, sulphide generation is not likely to be of high importance. To better understand the unique geochemical environments, DGT gels will need to be able to collect data for cations and anions simultaneously. This will better enable an analysis of Fe, Mn, and Al geochemistry concurrently. Currently, there are no DGT gels available to enable this analysis with an appropriate level of resolution.

CONCLUSION

This project investigated the impact of organic amendments on the P dynamics in soils. The project investigated a range of soil types under different agricultural systems. In order to do this, soils were sampled at 0.1 m increments in organic amendment (either CL or PM) and in control sites. These samples were investigated using a range of techniques, including Diffusive Gradients in Thin films, isotopic dilution techniques, NMR for estimating the labile P concentration, and bicarbonate extractable P.

The study also investigated the effect of CL and PM amendments over time on the available P dynamics and lability.

The study found that:

- Sites with short term and low application rates of manure addition appear to have little influence on the P availability in soil.
- In long-term CL amended soils, there is an improvement in the concentration of available and labile P. However, this typically was only in the top 0.07 m of the profile, and reduced rapidly at lower depths. The CL field amended Vertosol appeared to show greater improvement with depth.
- The CL amendments to unamended control or previously field-amended soils reduced the available P over time in our short-term incubation study. In contrast, PM enhanced or maintained the available P over the 49-day incubation period.
- NMR results showed that amendment with CL and PM even on low application rates increased the total NaOH-EDTA extractable P. Organic P as measured by monoesters increased in all amended soils, however, only at higher frequency of application and volumes increased the orthophosphate.
- The DGT microniche analysis revealed zones of localised P availability ranging from around 1 mm to <100 µm in diameter. High-resolution techniques provided unique information relating P availability in soils.

RECOMMENDATIONS

- **Reaching out to growers on adopting beneficial and advanced techniques.** The DGT technique closely reflects the plant available P compared to chemical extraction methods like Olsen and Colwell P. In addition, the soil P chemistry using the DGT-P test is advantageous by (i) avoiding dilution of the soil-solution system and (ii) preventing soil pH changes, as only water is added. The DGT-P test is becoming more available in commercial laboratories, particularly in Australia. Their benefits in predicting P availability need to be widely communicated to farmers and consultants. Knowledge on total and orthophosphate (available) P measured using DGT should also be taken into consideration. Similar to Olsen P, optimal/adequate DGT range which vary with type of cropping, should be conveyed to the growers. For example, in wheat, the DGT range is 57–100 µg/L, whereas in canola, it is 25–44 µg/L. There is a need to establish a relationship between DGT P and fertiliser requirements, since there is a large volume of data on bicarbonate extractable P and fertiliser requirements.

- **Need for improved understanding of P species in the soil microbial biomass.** Soil microorganisms play an important role in P cycling in soil-plant systems. Microbially-mediated P availability can be enhanced by improving the capacity of P mobilisation by native microorganisms or through the use of P-solubilising microorganisms. Furthermore, higher biological biomass and activity, especially in carbon depleted soils, is observed in organically managed agricultural soils when compared to chemical fertiliser-applied soils. When it comes to understanding of P dynamics, P forms locked in the soil microbial biomass is mostly ignored. This knowledge is crucial, because, even when P is mobilised by P-solubilising microbes, P immobilisation in the native microbial biomass can negate P uptake by plants. In addition, the effect of rate and type of fertiliser, period of fertiliser use, soil type and land use should be considered.
- **Further investigation on P management in subsoils and strategies to unlock P.** Phosphorus stock in the subsoil can act as a P nutrient reservoir, if it is accessible by plant roots. Earlier and current studies have ignored or investigated very little on P pools in the subsoils for fertiliser recommendations. Ongoing and future studies should focus on (i) role of P pools in subsoils for plant nutrition and P translocation processes in the soil profile and (ii) management strategies to increase the plant accessibility of these unused P stocks in subsoils.
- **Considering a range of soil types to better understand P dynamics.** The soil type has a major impact on soil P concentrations and forms. For instance, available P is lower in Dermosols compared to Ferrosols and Sodosols. In contrast, the organic P in Sodosols is usually higher than those of Dermosols and Ferrosols. It is therefore recommended that soil type should be considered when investigating management practices to assess the optimum plant available P.
- **Soil phosphorus calculator and fertiliser use efficiency.** Appropriate P fertiliser application rates still do not exist after decades of research on P sorption capacity in soils. Current fertiliser recommendation tools are designed to manage P-deficient soils and cannot be used to calculate the optimum amount of P in soils that have adequate P. However, growers continue to use their usual rate leading to problems like P leaching. While optimising P rates based on plant requirement is vital to prevent P loss to aquatic systems, particular attention should also be paid to the type of P fertiliser.
- **Further research on land use and changes in P stock.** A recent meta-analysis study showed loss of total P during conversion of native vegetation to cropping, however, conversion to pasture resulted in an increase in P stock by 25%. Although the change in total P from conversion of conventional (use of chemical fertilisers) cropping to organic amendment application was significantly high, the number of studies included was less. Other limitations of the study were variation in soil sampling depth and inclusion of very few long-term field studies from Australia. Long-term studies on relative change in P stock under different land use systems are imperative to manage P in soils and to make better fertiliser decisions.
- **Further research on DGT microniches in manure-amended soils**. P mobilisation from organic sources is a complex area which has received significant research attention for several decades. Yet, there are still many unanswered questions.

Previous research has largely focused on bulk processes due to limitations in the spatial and temporal resolution of available techniques. There are increasingly available techniques from probing submicron scale biogeochemical approaches. DGT is a useful tool that has been underutilised in this regard, largely due to some limitations. Further development of this technique for soil environments is needed. Water content is an important issue, as is the pore-space. This clearly influences the effective flux of P in soil. Analysis of the 15 cm diffusive gels with LA-ICP-MS is not practical due to cost and instrument availability. In this study, as well as others, only select areas can be analysed rather than the full gel area. Other approaches have been used in aquatic sediments, which is unlikely to be suitable in agricultural soils. Other approaches, which could potentially be used for analysing a larger area, is the Laser Induced Breakdown Spectroscopy (LIBS) particularly in relation to gels supporting both cations and anions.

- **Sub-micron investigation on the P speciation of microniches in agricultural soils**. Concurrently with DGT imaging, use of detailed high-resolution spectroscopic imaging and speciation techniques is essential to probe geochemistry at the micron scale. The research should include bulk EXAFS, XANES to provide information relation to overall speciation. However, within the Australian Synchrotron facility, the ability for high resolution Fourier transform infrared spectroscopy would enable detailed insight into the unique geochemistry or organic microniches. High-resolution XANES will necessarily involve international collaboration for access to the Stanford synchrotron facility in the United States of America.

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APPENDIX A

Table A1. Selected physico-chemical properties of Tenosol amended with chicken litter (Uralla, NSW)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	5.00	309.0	15.96	4.67	25.31	n.d.	n.d.	n.d.	0.27	1.75
	0.1-0.2	5.21	69.30	17.12	4.50	13.24	n.d.	n.d.	n.d.	0.30	1.36
	0.2-0.3	5.73	71.90	18.40	4.40	21.47	n.d.	n.d.	n.d.	0.37	7.81
	0.3-0.4	6.32	28.40	20.59	4.98	21.94	n.d.	n.d.	n.d.	0.27	0.62
	0.4-0.5	6.39	17.70	19.06	5.50	29.56	n.d.	n.d.	n.d.	0.43	3.99
	0.5-0.6	6.71	15.69	18.80	5.44	27.53	n.d.	n.d.	n.d.	0.70	3.75
	0.6-0.8	6.88	10.00	17.92	3.94	22.38	n.d.	n.d.	n.d.	0.58	3.85
	0.8-1.0	7.38	12.00	13.17	3.87	15.53	n.d.	n.d.	n.d.	0.72	2.55
Treated	0-0.1	5.95	35.86	14.18	4.92	16.84	n.d.	n.d.	n.d.	0.72	0.93
	0.1-0.2	5.92	18.58	13.84	3.78	13.60	n.d.	n.d.	n.d.	0.53	4.05
	0.2-0.3	6.27	19.18	12.98	2.84	14.55	n.d.	n.d.	n.d.	0.36	1.67
	0.3-0.4	6.58	12.26	15.31	3.49	19.91	n.d.	n.d.	n.d.	0.82	0.92
	0.4-0.5	6.83	11.40	12.92	3.68	20.68	n.d.	n.d.	n.d.	1.07	0.49
	0.5-0.6	6.79	9.250	19.85	5.20	36.19	n.d.	n.d.	n.d.	0.71	0.15
	0.6-0.8	6.96	10.17	25.28	6.91	27.11	n.d.	n.d.	n.d.	0.76	0.16
	0.8-1.0	7.00	13.42	24.91	7.43	19.75	n.d.	n.d.	n.d.	0.77	0.14
	1-1.2	7.13	34.20	25.25	9.94	14.62	n.d.	n.d.	n.d.	0.94	1.64
	1.2-1.4	7.20	20.10	25.05	9.26	19.50	n.d.	n.d.	n.d.	0.78	1.04
	1.4-1.6	7.29	14.78	21.84	10.4	15.42	n.d.	n.d.	n.d.	0.86	0.58

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table A2. Selected physico-chemical properties of Aquic Podosol and Hydrosol amended with pig manure (Tarwin Lower, Victoria)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	5.48	67.65	7.61	5.05	17.72	n.d.	n.d.	n.d.	4.17	4.87
	0.1-0.2	6.00	21.95	7.69	5.57	14.11	n.d.	n.d.	n.d.	2.02	3.89
	0.2-0.3	6.00	22.95	10.5	5.89	6.909	n.d.	n.d.	n.d.	2.48	1.68
	0.3-0.4	5.92	25.65	4.70	6.42	6.642	n.d.	n.d.	n.d.	2.54	3.16
	0.4-0.5	5.83	40.75	3.81	6.18	6.680	n.d.	n.d.	n.d.	4.05	2.31
	0.5-0.6	5.75	50.55	12.2	5.73	6.471	n.d.	n.d.	n.d.	5.69	1.49
	0.6-0.8	5.62	79.10	17.5	6.01	10.64	n.d.	n.d.	n.d.	9.32	n.d.
	0.8-1.0	5.56	85.10	15.5	4.64	5.499	n.d.	n.d.	n.d.	11.8	n.d.
	1-1.2	5.26	121.8	2.61	4.74	5.829	n.d.	n.d.	n.d.	14.2	0.48
	1.2-1.4	5.30	125.6	26.3	10.0	12.78	n.d.	n.d.	n.d.	10.7	0.67
Treated - Podosol	0-0.1	6.61	63.80	10.4	18.2	31.76	n.d.	n.d.	n.d.	1.70	7.64
	0.1-0.2	6.11	50.90	15.9	9.89	19.64	n.d.	n.d.	n.d.	2.03	4.51
	0.2-0.3	5.74	31.90	10.7	4.00	10.09	n.d.	n.d.	n.d.	3.65	1.62
	0.3-0.4	5.65	37.05	11.1	3.63	7.800	n.d.	n.d.	n.d.	4.00	1.03
	0.4-0.5	5.61	39.60	13.6	3.71	7.106	n.d.	n.d.	n.d.	3.62	0.94
	0.5-0.6	5.53	37.40	13.3	3.45	6.923	n.d.	n.d.	n.d.	3.88	0.86
	0.6-0.8	5.44	30.10	12.1	3.30	5.846	n.d.	n.d.	n.d.	4.37	n.d.
	0.8-1.0	5.71	23.00	8.78	2.23	4.981	n.d.	n.d.	n.d.	5.39	2.02
	1-1.2	5.94	40.00	8.48	2.01	4.667	n.d.	n.d.	n.d.	5.39	1.74
	1.2-1.4	5.26	24.00	9.31	1.67	24.58	n.d.	n.d.	n.d.	3.74	1.06
	1.4-1.6	5.79	32.90	7.86	1.71	5.363	n.d.	n.d.	n.d.	5.66	0.91
	1.6-1.8	5.55	30.30	6.89	1.73	4.346	n.d.	n.d.	n.d.	6.85	0.45

	1.8-2.0	5.60	135.3	7.16	1.45	4.503	n.d.	n.d.	n.d.	6.43	0.54

	Depth (m)	pH	EC (µS/cm)	Clay (%)	CEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Treated-Hydrosol	0-0.1	5.89	164.0	6.26	14.9	26.87	n.d.	n.d.	n.d.	3.75	9.79
	0.1-0.2	5.48	83.50	7.92	9.29	14.98	n.d.	n.d.	n.d.	5.32	6.29
	0.2-0.3	5.35	72.90	8.36	6.96	12.81	n.d.	n.d.	n.d.	6.09	4.52
	0.3-0.5	5.32	62.85	13.1	5.17	9.166	n.d.	n.d.	n.d.	6.01	2.68
	0.5-0.7	5.37	54.30	13.7	3.87	8.105	n.d.	n.d.	n.d.	5.81	1.56
	0.7-0.9	5.29	53.40	14.5	2.97	5.527	n.d.	n.d.	n.d.	6.08	1.45
Treated-Elevated site (Podosol)	0-0.1	5.27	148.3	2.58	13.7	48.35	n.d.	n.d.	n.d.	2.64	21.4
	0.1-0.2	4.78	74.60	3.65	4.73	28.23	n.d.	n.d.	n.d.	4.77	16.5
	0.2-0.3	4.74	53.05	4.10	2.64	24.45	n.d.	n.d.	n.d.	6.48	5.06
	0.3-0.4	4.80	42.45	4.73	1.42	17.43	n.d.	n.d.	n.d.	6.28	1.92
	0.4-0.5	5.07	31.05	3.56	2.95	39.40	n.d.	n.d.	n.d.	3.40	1.64
	0.5-0.6	4.55	65.25	5.55	4.65	33.37	n.d.	n.d.	n.d.	3.15	2.89
	0.6-0.8	4.88	21.90	3.63	1.91	10.75	n.d.	n.d.	n.d.	3.24	1.39
	0.8-1.0	4.94	19.60	7.51	1.21	5.197	n.d.	n.d.	n.d.	3.33	0.19
	1-1.2	4.86	39.90	8.28	1.67	57.15	n.d.	n.d.	n.d.	2.70	0.78
	1.2-1.4	5.30	76.60	10.5	1.68	5.210	n.d.	n.d.	n.d.	6.53	0.12
	1.4-1.6	5.47	51.40	8.98	1.48	5.102	n.d.	n.d.	n.d.	6.27	0.29

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table A3. Selected physico-chemical properties of Aeric Podosol amended with pig manure and inorganic P (Tarwin Lower, Victoria)

	Depth (m)	pH	EC (µS/cm)	Clay (%)	ECEC (cmol/kg)	Olsen P (mg/kg)	Colwell P (mg/kg)	Extr. Fe (mg/kg)	Extr. Al (mg/kg)	ESP (%)	OC (%)
Control	0-0.1	4.99	89.05	2.38	7.95	20.93	n.d.	n.d.	n.d.	2.97	7.72
	0.1-0.2	5.05	42.65	3.32	3.39	19.59	n.d.	n.d.	n.d.	5.72	3.45
	0.2-0.3	5.19	21.68	3.20	1.28	11.38	n.d.	n.d.	n.d.	7.45	1.01
	0.3-0.4	5.26	14.62	2.54	0.62	7.670	n.d.	n.d.	n.d.	7.40	0.55
	0.4-0.5	5.33	12.08	2.53	0.33	6.519	n.d.	n.d.	n.d.	8.62	0.23
	0.5-0.6	5.34	11.45	2.29	0.25	6.398	n.d.	n.d.	n.d.	8.88	0.17
	0.6-0.8	5.23	12.01	2.51	0.20	6.912	n.d.	n.d.	n.d.	10.6	0.10
	0.8-1.0	5.09	23.07	6.28	1.11	32.13	n.d.	n.d.	n.d.	6.31	0.36
Treated	0-0.1	5.02	98.05	2.02	10.9	29.52	n.d.	n.d.	n.d.	3.15	9.03
	0.1-0.2	4.89	34.55	5.15	3.88	18.61	n.d.	n.d.	n.d.	2.34	2.76
	0.2-0.3	5.02	25.40	5.23	2.16	14.46	n.d.	n.d.	n.d.	2.75	1.12
	0.3-0.4	4.94	27.55	5.08	1.91	16.37	n.d.	n.d.	n.d.	3.44	1.01
	0.4-0.5	4.83	30.30	4.76	1.77	22.19	n.d.	n.d.	n.d.	4.59	0.88
	0.5-0.6	4.63	44.40	4.87	2.64	28.55	n.d.	n.d.	n.d.	4.51	1.60
	0.6-0.8	4.51	50.35	5.72	4.03	34.40	n.d.	n.d.	n.d.	3.55	2.13
	0.8-1.0	4.38	59.00	6.06	2.48	23.50	n.d.	n.d.	n.d.	4.55	1.24
	1-1.2	4.61	104.4	25.8	8.70	5.918	n.d.	n.d.	n.d.	4.21	0.78
Fertiliser-treated	0-0.1	5.04	61.50	2.69	6.02	28.14	n.d.	n.d.	n.d.	2.50	5.37
	0.1-0.2	4.79	36.50	5.00	5.05	14.42	n.d.	n.d.	n.d.	3.03	2.37
	0.2-0.3	4.94	20.45	4.74	1.42	9.885	n.d.	n.d.	n.d.	2.92	0.92
	0.3-0.4	4.90	17.81	6.92	0.81	7.748	n.d.	n.d.	n.d.	4.12	0.43
	0.4-0.5	4.94	15.60	7.09	0.65	9.090	n.d.	n.d.	n.d.	4.47	0.52
	0.5-0.6	4.64	20.76	9.06	1.33	30.22	n.d.	n.d.	n.d.	3.18	2.52

	0.6-0.8	4.59	50.54	9.38	5.33	48.87	n.d.	n.d.	n.d.	1.90	4.79

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table A4. Selected physico-chemical properties of Ferrosol (Teven, NSW); unknown amendment history; likely inorganic P applications only.

	Depth (m)	**pH**	**EC (µS/cm)**	**Clay (%)**	**ECEC (cmol/kg)**	**Olsen P (mg/kg)**	**Colwell P (mg/kg)**	**Extr. Fe (mg/kg)**	**Extr. Al (mg/kg)**	**ESP (%)**	**OC (%)**
Control	0-0.1	5.35	181.2	47.01	16.7	55.91	n.d.	n.d.	n.d.	0.37	8.44
	0.1-0.2	5.03	214.9	58.80	8.77	16.46	n.d.	n.d.	n.d.	0.22	4.69
	0.2-0.3	5.13	152.3	64.32	7.52	11.51	n.d.	n.d.	n.d.	0.37	3.84
	0.3-0.4	5.26	114.1	65.60	6.00	9.612	n.d.	n.d.	n.d.	0.56	3.23
	0.4-0.5	5.21	105.9	69.83	4.80	12.30	n.d.	n.d.	n.d.	0.70	2.41
	0.5-0.6	4.76	137.4	71.60	3.64	14.58	n.d.	n.d.	n.d.	0.96	1.72
	0.6-0.8	4.62	129.4	72.40	3.83	13.56	n.d.	n.d.	n.d.	1.94	1.26
	0.8-1.0	4.63	111.7	62.96	3.37	14.35	n.d.	n.d.	n.d.	2.35	0.86
Treated	0-0.1	5.36	152.4	n.d.	11.9	46.47	n.d.	n.d.	n.d.	0.52	5.79
	0.1-0.2	5.08	200.2	n.d.	8.62	20.26	n.d.	n.d.	n.d.	0.56	4.12
	0.2-0.3	5.19	146.6	n.d.	7.12	13.06	n.d.	n.d.	n.d.	1.43	3.36
	0.3-0.4	5.18	148.4	n.d.	6.69	11.51	n.d.	n.d.	n.d.	2.16	2.97
	0.4-0.5	5.09	119.0	n.d.	5.38	11.29	n.d.	n.d.	n.d.	2.04	2.02
	0.5-0.6	4.81	107.6	n.d.	4.91	11.94	n.d.	n.d.	n.d.	2.34	7.10
	0.6-0.8	4.65	98.76	n.d.	6.48	7.417	n.d.	n.d.	n.d.	1.90	1.49
	0.8-1.0	4.65	95.48	n.d.	6.73	7.994	n.d.	n.d.	n.d.	2.42	0.95

#EC – Electrical conductivity; ECEC – Effective cation exchange capacity; ESP – Exchangeable sodium percentage; OC – Organic carbon

Table A5. Selected properties of pig manure and chicken litter

Amendments	pH	EC (µS/cm)	OC (%)	Total P (%)	Olsen P (mg/kg)
Pig manure	6.39	5840.0	13	5.1	2560
Chicken litter	6.94	11820	29	1.9	2060

Table A6. Changes in Olsen P (mg/kg) from addition of P from CL and PM manures for 5 soils. Data are shown for control and field amended soils at 1, 7, 21 and 49 days incubation (25°C).

Soils	day 1		day 7		day 21		day 49	
	PM	CL	PM	CL	PM	CL	PM	C
Ferrosol Control	123.4	50.97	91.04	23.21	71.57	44.33	22.29	15.
Ferrosol Manured	308.5	287.7	451.6	406.9	331.5	318.8	158.1	148
Sodosol Control	86.60	37.94	86.75	31.42	26.36	66.46	14.51	37.
Sodosol Manured	92.16	74.51	84.74	55.51	77.49	73.26	26.18	22.
Vertosol Control	46.54	18.26	43.80	18.93	49.65	32.44	11.01	11.
Vertosol Manured	71.27	41.71	62.28	41.47	53.01	47.75	26.95	25.
Podosol Control	37.75	10.94	39.54	16.23	46.50	27.18	16.06	9.7
Podosol Manured	66.46	39.75	68.59	68.59	64.69	46.88	26.18	21.
Podosol Manured-Elev. site	176.6	88.29	149.6	78.31	139.9	64.68	91.13	52.
Chromosol Manured	105.5	23.99	88.52	35.71	104.9	43.87	44.07	23.
Chromosol Control	90.86	36.31	92.55	40.96	84.53	37.34	39.01	20.

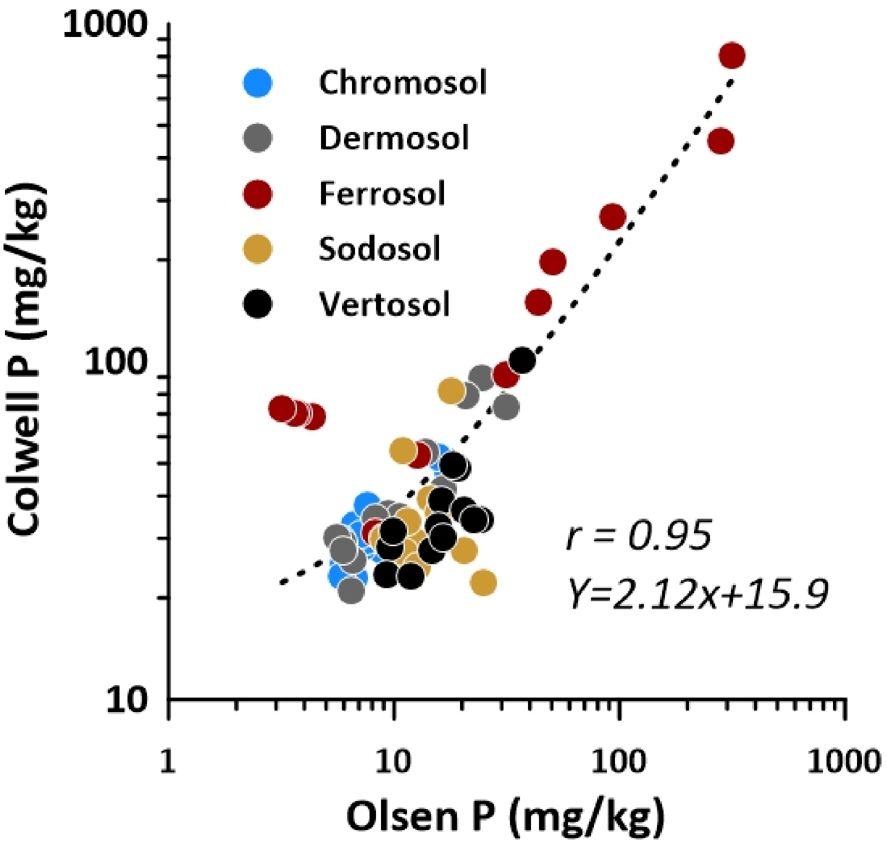

Figure A1. Correlation between Colwell P and Olsen P in selected soil types

CRC FOR HIGH PERFORMANCE SOILS

University of Newcastle
University Drive
Callaghan NSW 2308

T +61 2 4921 5473
E enquiries@soilcrc.com.au
W soilcrc.com.au

Australian Government
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