THE FORM AND AVAILABILITY OF SLOWLY AVAILABLE PHOSPHORUS IN DEPLETED VERTOSOLS

Submitted by

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I dedicate this thesis to my grandparents, Ronald and Helen McLaren, and Jim and Olive Nelson.

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Conference presentations

McLaren, T.I., Guppy, C.N., Tighe, M. (2012). Using Colwell and BSES extractable phosphorus to predict Faba bean (*Vicia faba* L.) response. *Grains Research and Development Corporation Research Update (Northern)*, Goondiwindi, Qld

McLaren, T.I., Guppy, C.N., Tighe, M. (2012). Shining synchrotron light on phosphorus (P) minerals in the dark: P forms in Vertosols. *Cotton Science Forum*, Narrabri, NSW

McLaren, T.I., Guppy, C.N., Tighe, M. (2011). Rapid, non-destructive total element analysis using portable X-ray fluorescence (PXRF) on cotton leaf tissue and soybean grain, *12th International Symposium on Soil and Plant Analysis Conference*, Chania, Greece

McLaren, T.I., Guppy, C.N., Tighe, M., Forster, N., Grave, P. (2010). Non-destructive element analysis using portable X-ray fluorescence (PXRF) on Vertosol soils in the northern grains region. *Australasian Soil and Plant Analysis Council Conference*, Canberra, ACT

McLaren, T.I., Guppy, C.N., Tighe, M. (2010). Non-destructive soil and plant analysis using PXRF in cotton systems, *Cotton Science Forum*, Narrabri, NSW

Publications

McLaren, T.I., Bell, M., Rochester, I.J., Guppy, C.N., Tighe, M., Flavel, R.J. (2012). Growth and P uptake of faba bean and cotton are related to Colwell-P concentrations in the subsoil of Vertosols. *Crop and Pasture Science* (under review)

McLaren, T.I., Guppy, C.N., Tighe, M., Moody, P., Bell, M. (2012). Dilute acid extraction is a useful indicator of the supply of slowly available phosphorus in Vertosols. *Soil Science Society of America Journal* (under review)

McLaren, T.I., Guppy, C.N., Tighe, M., Schefe, C.R., Flavel, R.J., Cowie, B., Tadich, A. (2012). Soil phosphate removal by a two-step sequential fractionation procedure and a dilute acid extractant in a Vertosol soil using XANES. *Soil Science Society of America Journal* (submission imminent)

McLaren, T.I., Guppy, C.N., Tighe, M., Forster, N., Grave, P., Lisle, L., Bennett, J. (2012). Rapid, non-destructive total elemental analysis of Vertosol soils using portable X-ray fluorescence. *Soil Science Society of America Journal*, **76**(4), 1136-45

McLaren, T.I., Guppy, C.N., Tighe, M. (2012). A rapid and non-destructive plant nutrient analysis using portable X-ray fluorescence. *Soil Science Society of America Journal*, **76**(4), 1146-53

Abstract

Vertosols are an important soil type used for cotton production in the northern grains region (NGR) of eastern Australia. Historically, cotton has received minimal phosphorus (P) input due to the high fertility of Vertosols. Over the past 30 years, P fertiliser use in the cotton industry has increased six-fold, due to the perceived decline in soil fertility in the NGR. However, when P is applied to cotton systems, the amount of P fertiliser recovered by the crop (PUE) has been low and unpredictable (0 – 67 %), and few studies have investigated why this is so. The unpredictability of PUE in cotton systems refers to the lack of cotton response when P fertiliser has been applied in some soils, which was based on recommendations from the commonly used Colwell soil P test. Long-term field trials suggest the quantity of readily available P measured using the Colwell extractant is being replenished by other soil phosphates not measured by the Colwell extractant. This may be due to the large amounts of Ca phosphates typically found in Vertosols, which may supply or replenish labile soil P pools in the 0 – 10 cm and 10 – 30 cm layers. Recent studies have used a dilute acid test (colloquially referred to as the BSES extractant) to measure Ca phosphates in Vertosols, however, little is known about the P pools removed by this extractant. The aim of this project was to understand the ability of Ca phosphates to supply or replenish plant available P in the cotton systems of the NGR.

In Chapter 2, the response of faba bean and cotton to subsoil P when moisture was limiting in the topsoil was investigated in glasshouse studies. The growth and P uptake of faba bean and cotton was related to Colwell-P concentrations in the subsoil, demonstrating the potential importance of subsoil P pools in crop P uptake under dry topsoil conditions. This study confirms the Colwell soil P test is a good indicator of plant available P in Vertosols of the NGR. The quantity of BSES-P was not related to faba bean and cotton P uptake over one crop cycle, although this was unsurprising give the majority of these soils contained BSES-Ca/P ratios above 74:1 (Chapter 3).

This study confirmed that cotton is well suited to low soil P environments. Cotton was less responsive to increasing subsoil Colwell-P concentrations when compared to faba bean. It is possible that the concentration of P in the soil solution needed to trigger cotton root proliferation is low in comparison to other crop species. This is also supported by the lack of cotton response to increasing volumes of soil P enrichment in the subsoil. However, caution is needed applying these results to cotton systems as the majority of cotton is irrigated and this would increase the amount of P sourced from topsoils. We recommended that Colwell-P be measured in both the topsoil and subsoil layers, and BSES-P used periodically (e.g., every ~ 10 years) to monitor soil P rundown in Vertosols.

In Chapter 3, this study demonstrated the ability of BSES-P to supply Colwell-P in the Vertosol soils of the NGR. In approximately half the Vertosols tested Colwell-P was being replenished by BSES-P and this occurred when soils contained BSES-P concentrations greater than 61 mg P/kg. This experiment also found that BSES-P was more likely to supply Colwell-P when the ratio of Ca (mg/kg) to P (mg/kg) in the BSES extract was greater than 74, suggesting the presence of Ca phosphates of low solubility.

In Chapter 4, the soil phosphates removed by the 0.1 M NaOH and 1 M HCl extractants were investigated using P K-edge X-ray absorption near-edge structure (XANES). This study aimed to understand the difference between the soil phosphates removed by the 1 M HCl and BSES extractants (Chapter 4). An important aspect of this study was the application of P K-edge XANES for soil P studies in untreated soils, although the high method detection limit of the Soft X-ray beamline at the Australian Synchrotron made accurate identification of soil phosphates difficult.

There was supporting evidence that the 0.1 M NaOH and 1 M HCl extractants remove soil phosphates according to the solubility of the P minerals that the reagent is likely to dissolve. Calcium phosphates were the dominant soil P pool in Vertosols, and XANES spectra characteristic to Ca phosphate reference materials were removed after 1 M HCl extraction. However, P K-edge XANES spectra on the soil residue after 0.1 M NaOH and 1 M HCl extraction lacked pre- and post-edge features because of the high method detection limit of the Soft X-ray beamline, and it is possible that other soil phosphates may have been removed in addition to Ca phosphates. This study suggests that the method detection limit of the Soft X-ray beamline at the Australian Synchrotron is ~ 2200 mg total P/kg, and further difficulties were found in attempting to identify and quantify the soil phosphates removed by the BSES extractant.

A comparison of the solution extracts removed by the 1 M HCl and BSES extractants indicate approximately 80 % of the P removed by the 1 M HCl extractant is removed by the BSES extractant. The amount of Ca phosphates removed by the BSES extractant is likely to be lower when compared to those removed by the 1 M HCl extractant because the later reagent has a lower pH and could potentially dissolve more thermodynamically stable Ca phosphates. However, it was unclear from this study what soil phosphates constitute BSES-P and further research is needed to investigate this.

This project significantly advances our understanding of the slowly available P pool in Vertosols, and demonstrates the ability of the BSES extractant to predict the supply of Ca phosphates to supply or replenish plant available P in Vertosols of the NGR. Further research is needed to understand the form and availability of Ca phosphates at differing BSES-P concentrations and BSES-Ca/P ratios.

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Abbreviations

Al	Aluminium
AMF	Arbuscular mycorrhizae fungi
ANOVA	Analysis of variance
AR	*Aqua regia*
As	Arsenic
ASPAC	Australasian Soil and Plant analysis Council
Ca	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcite
CCRMP	Canadian Certified Reference Materials Project
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
DCP	Dicalcium phosphate
DCPD	Dicalcium phosphate dihydrate
DL	Definitive level
DM	Dry matter
ECEC	Effective cation exchange capacity
FA	Fluorapatite
Fe	Iron
FeO	Iron oxide
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HA	Hydroxyapatite
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
He	Helium
HF	Hydrofluoric acid
HNO_3	Nitric acid
ICP-OES	Inductively couple plasma optical emission spectroscopy
IRMM	Institute for Reference Materials and Measurements
K	Potassium
KH_2PO_4	Potassium dihydrogen orthophosphate

LCF	Linear combination fitting
LXRF	Laboratory X-ray fluorescence
MDL	Method detection limit
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
NAA	Neutron activation analysis
$Na_4P_2O_7$	Sodium pyrophosphate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NGR	Northern grains region
NHHF	HNO_3, H_2O_2, and HF acid digest
Ni	Nickel
NIST	National Institute of Standards Technology
OCP	Octocalcium phosphate
OVD	Open vessel digest
P	Phosphorus
Pb	Lead
PUE	Phosphorus use efficiency
PXRF	Portable X-ray fluorescence
Qual	Qualitative screening
Quant	Quantitative screening
Rec	Elemental recovery
Rh	Rhodium
RSD	Relative standard deviation
S	Sulfur
SCD	Sealed chamber digest
Si	Silica
SiO_2	Silica dioxide
TCP	β-Tricalcium phosphate
TFY	Total fluorescence yield
Ti	Titanium
USEPA	United States Environmental Protection Agency
XANES	X-ray absorption near-edge structure
XRF	X-ray fluorescence
Zn	Zinc