Investigating phosphate sorption reactions in acid soils through solution, NMR, and L- and K-edge XANES analyses

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Abstract

The plant availability of phosphorus (P) is decreased in acid soils through increased P sorption onto solid-phase binding sites. This is a significant problem in Victoria, Australia. This research utilised a suite of complementary techniques, including classical solution analysis, nuclear magnetic resonance (NMR) and synchrotron-based X-ray technologies (X-ray Absorption Near Edge Structure, XANES; micro X-ray fluorescence spectroscopy, μ-XRF) to investigate the forms of sorbed P in acid soils. The addition of carboxylic acids modified sorption of applied P, with oxalic acid being most effective in competing with P for binding sites. Solid state ^{31}P NMR showed that inorganic P, as PO_4 was the dominant species present in the bulk soil, while XANES provided information on reactions occurring at (P L-edge XANES) or near (P K-edge XANES) the soil surface. For example, the addition of oxalic acid resulted in dissolution of surface-bound Al, exposing previously occluded P.

Key Words
Synchrotron techniques, carboxylic acids, acid soil.

Introduction
Phosphorus (P) is a key nutrient required for plant growth, with inorganic phosphate fertiliser extensively used in the production of food crops in Australia. However, the availability of this P fertiliser for plants is severely reduced in acid soils due to phosphate sorption onto aluminium (Al) hydroxides and other mineral binding sites. This is a significant problem in some areas of Victoria, Australia.

The degree to which applied P is bound onto soil surfaces in acid soils is influenced by many factors, including the type of fertiliser applied, and the presence of competing anions, such as carboxylic acids. However, most of the evidence supporting the interactions between fertiliser type and/or carboxylic acids and solid phase P binding sites has been established through measuring changes in the chemistry of soil solution, and utilising speciation modelling programs. A limitation of this approach is that these solution-based techniques can only determine gross changes in forms of soil P, without improving our understanding of solid phase processes. Therefore, in order to directly investigate P sorption reactions on soil particles, techniques such as solid-state ^{31}P nuclear magnetic resonance (NMR) and X-ray absorption near edge structure (XANES), may add value.

The application of synchrotron-based techniques in soil science is relatively new, with P K-edge XANES being the technique of choice in determining 'averaged' P speciation throughout a soil sample (Hesterberg *et al.* 1999), while recently, the P L-edge XANES technique has been used to determine P speciation on soil surfaces (Ajiboye *et al.* 2007a).

The aims of this research were therefore to determine the effect of carboxylic acid addition on P sorption reactions in acid soil, utilising a range of techniques, and (ii), evaluate the sensitivity of the P L-edge XANES technique in determining P speciation on soil surfaces upon the addition of different inorganic phosphate fertilisers.

Methods
Soil collection
The selected soil was a Bleached, Eutrophic, Yellow Dermosol (Isbell, 2002) sourced from the Department

of Primary Industries – Rutherglen Centre, Victoria, Australia. A single soil sample was collected from the 0-0.10 m depth, air-dried, and passed through a 2-mm sieve before use. (Soil pH_{CaCl2} 4.6).

Effect of carboxylic acid addition on P reactions in acid soil
Samples were prepared by weighing out 2.5 g samples of soil in triplicate for each treatment. Solutions of 1 mM carboxylic acids (oxalic, p-hydroxybenzoic and coumaric acids) and/or 100 mM P (as KH_2PO_4) were added to the soil in a 1:10 w/w soil:solution ratio and shaken for 17 h. After shaking, solution pH was measured, samples were centrifuged for 12 min and the centrifuged supernatant of all samples filtered through a 0.22 μm filter. The solution was then analysed for total solution P and Al by inductively coupled plasma-atomic emission spectrometry (ICPAES), carboxylic acid concentrations by high pressure liquid chromatography (HPLC), and solution P speciation by ^{31}P NMR. The remaining solid phase was further centrifuged to remove trace amounts of solution and dried in desiccators for 10 d. The dried samples were then finely ground using an agate mortar and pestle and stored in sealed vials prior to total soil P, solid-state ^{31}P MAS NMR and XANES analysis.

The XANES experiments at the P L-edge were performed at the Canadian Light Source, Saskatoon, Canada, using the VLS-PGM beamline. Samples were presented to the beamline on double-sided carbon tape. Micro-X-ray fluorescence (μ-XRF) and micro-XANES (μ-XANES) experiments at the P K-edge were performed at the LUCIA beamline of the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland, with samples prepared on thin-sectioned epoxy resin.

Use of P L-edge XANES to determine P speciation on soil surfaces upon addition of different fertilisers
The same soil was used as that detailed above. Solutions of potassium dihydrogen phosphate (KH_2PO_4), triple superphosphate ($Ca(H_2PO_4)_2.H_2O$; TSP) and di-ammonium phosphate (($NH_4)_2HPO_4$; DAP) were added to the soil at a range of concentrations (0, 0.5, 1, 25, 50, 100 mM) in a 1:10 w/w soil:solution ratio. Samples were shaken for 17 h. After shaking, solution pH was measured and samples were centrifuged for 12 min. The supernatant was filtered through a 0.22 μm filter and analysed for total solution P and Al by ICPAES. The remaining solid phase was further centrifuged to remove trace amounts of solution and dried in desiccators for 10 d. The dried samples were then finely ground using an agate mortar and pestle and stored in sealed vials prior to total soil P and P L-edge XANES analysis. The XANES experiments were performed on the VLS-PGM beamline at the Canadian Light Source. Beamline set-up and sample presentation was the same as that used above.
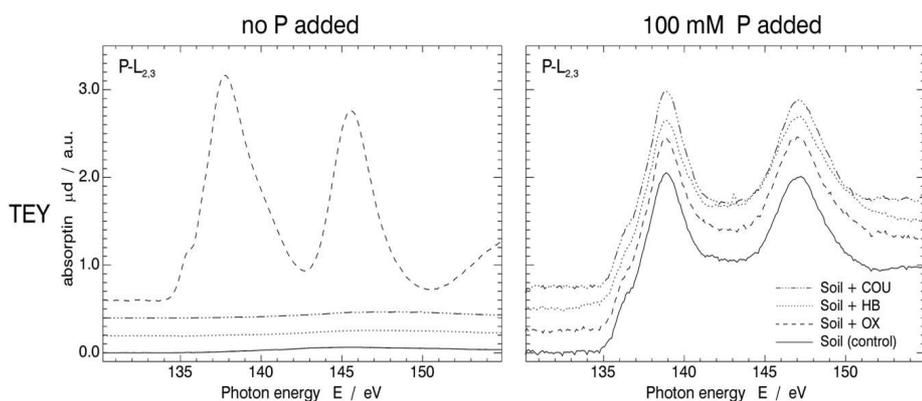
Results
Effect of carboxylic acid addition on P reactions in acid soil
Addition of the various carboxylic acids had different effects on the chemistry of P and Al in soil (Table 1). When no P was added, oxalic acid (OX) addition significantly increased the concentration of endogenous P in solution ($P<0.005$) compared to the other treatments. Solution Al concentrations were also increased in the OX treatment compared to the untreated soil (0P) ($P<0.001$), while solution Al was reduced in the hydroxybenzoic acid (HB) and coumeric acid (COU) treatments ($P<0.001$). The addition of P resulted in sorption of about 5.5 mM of added P (1.7 g kg^{-1}) (Table 1), with no significant differences in sorption between the various treatments (100P, OX+P, HB+P, COU+P). Increased concentrations of Al in solution, compared to the untreated soil ($p<0.001$; Table 1), suggest that the high concentrations of P applied may also have had an extraction effect, resulting in the solubilisation of endogenous soil Al and P (Rajan 1975).

Strong treatment effects were observed in the P L-edge XANES spectra (Figure 1). The endogenous concentration of P on the solid phase was below the detection limit, as were the coumeric and hydroxybenzoic treatments. However, a strong P signal was observed in the oxalic acid treatment, which could only have come from endogenous P (as no P added). Therefore, it is proposed that oxalic acid-mediated dissolution of Al species from the soil surface resulted in the exposure of previously occluded phosphorus.

Micro-beam techniques (μ-XRF/μ-XANES) were used to determine the P distribution and speciation in the nil-P treatments, due to the low concentrations of endogenous soil P present (165-176 mg P kg^{-1}). In the 0P treatment, a slight pre-edge shoulder in the μ-XANES spectrum (Figure 2) suggests that the P may be present as phosphosiderite (Ajiboye *et al.* 2007b). The poorly-defined post-edge structure in the μ-XANES spectrum for OX (Figure 2) indicates that this P may not have been bound to an aluminosilicate mineral. The P present

in the HB treatment was either adsorbed onto an Al hydroxide (Toor *et al.* 2006), or present as variscite (Ajiboye *et al.* 2007b). Low P concentrations meant little information could be gained from the COU spectra (Figure 2).


**Table 1. Solution chemistry results**

Sample	Solution P (mM)	Solution Al (mg/L)
0P	0.006	7.92
OX	0.011	15.64
HB	0.003	0.68
COU	0.004	1.06
100P	94.46	15.82
OX+P	94.53	24.95
HB+P	94.45	36.69
COU+P	94.67	5.17

Figure 1. P L-edge XANES spectra of no P and added P soil treatments, as measured by total electron yield (TEY).

Micro-XANES analysis of 100P was analysed at two discrete locations. The first (100P I) was located on the edge of an Al structure, with the P adsorbed to an Al mineral, likely gibbsite (Toor *et al.* 2006). The second P location (100P II) was co-located with both Al and Mg, although the μ-XANES results are somewhat inconclusive due to noise (Figure 2). A unique pre-edge shoulder and post-edge widening at the base of the white-line of the OX+P μ-XANES is proposed to be due to the P being present as an ammonium phosphate compound (Ajiboye *et al.* 2008), or P adsorption onto a Mg compound, of composition not yet defined (Figure 2). The μ-XANES spectra of HB+P and COU+P indicate that the phosphate in both samples is adsorbed onto an Al mineral, likely gibbsite (Figure 2) (Hesterberg *et al.* 1999).
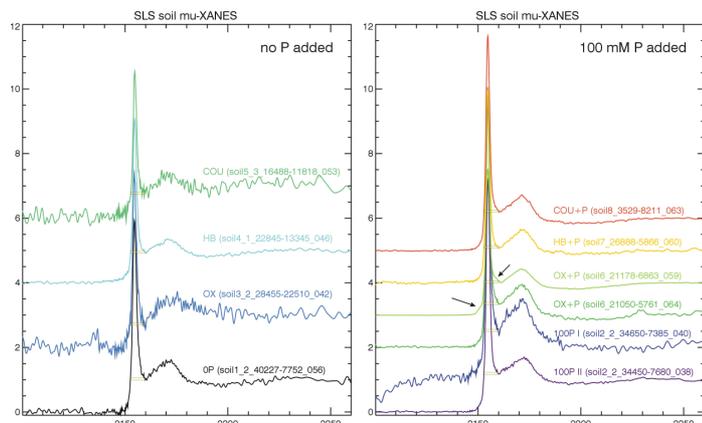
Figure 2. P K-edge μ-XANES spectra of P hotspots
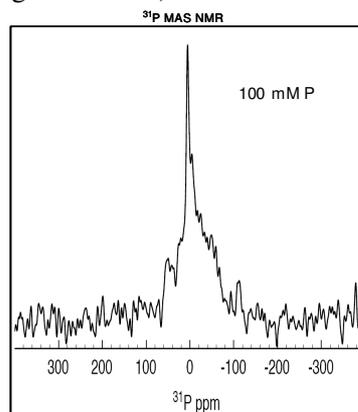
Figure 3. ^{31}P MAS NMR for the 100P treatment

The amount of P present in the 0P treatments was below the detection limit for ^{31}P MAS NMR. Phosphorus was detected in the added P treatments, with PO_4 being the dominant species (Figure 3, only 100P treatment displayed).

This research has shown that the addition of oxalic acid to an acid soil enhanced Al dissolution and exposed 'hotspots' of previously occluded P. Hydroxybenzoic and coumeric acids could not compete with P for solid phase binding sites. The amount of P sorbed did not change in the presence of carboxylic acids. This is likely due to the disparity in the P and carboxylic concentrations used (100 mM and 1 mM respectively), which were designed to reflect the likely concentrations around a dissolving fertiliser granule.

Use of P L-edge XANES to determine P speciation on soil surfaces upon addition of different fertilisers
Solid-phase P was detectable on soil surfaces by P L-edge XANES when 25 mM P was added as TSP and DAP, which equated to *ca.* 920 mg P kg^{-1} (Figure 4). The poor detection with 25 mM KH$_2$PO$_4$ addition indicates that 860 mg P kg^{-1} is on the detection limit. According to the XANES spectra, the speciation of surface-bound P does not appear to vary significantly according to P source (Figure 4). As all P sources were in the form of PO_4, this was not unexpected. However, the quality of the spectra varied significantly between

P sources at each of the rates of P addition, with DAP addition consistently producing spectra of the highest quality and intensity.
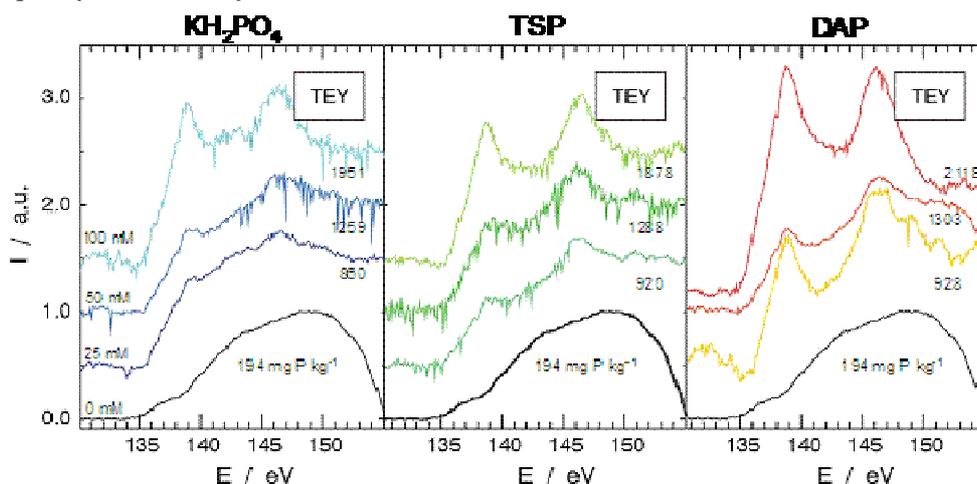
Figure 4. P L-edge XANES spectra (TEY mode) for each P source at each rate of P addition. Only 25, 50 and 100 mM P additions are shown due to lack of detection at lower levels. The values against each spectra are the soil P concentrations (mg P kg^{-1}) for each sample. Spectral 'noise' is due to sample charging, an effect often observed when data is collected in TEY mode.

This experiment has definitively demonstrated that the detection limit of soil P for the P L-edge XANES technique is significantly less than that required for P K-edge XANES (920 *vs* 1800 mg P kg^{-1}). Ongoing data acquisition will determine if this detection limit varies with different soil types, and further spectral interpretation will identify the dominant P species present in each treatment.

Conclusion

Synchrotron-based techniques can add value to soil P investigations as solid-state analysis can be conducted to detection limits beyond that possible using established techniques such as solid-state ^{31}P NMR. In particular, the P L-edge XANES is of benefit in determining changes in soil P chemistry on soil surfaces, as the penetration depth has been estimated to be less than 30 nm, based on Al_2O_3 data. This research has demonstrated the ability of P L-edge XANES to identify changes in the soil surface P chemistry due to the addition of carboxylic acids and/or phosphate. Due to the higher detection limit of P K-edge XANES, a micro-probe is useful in locating areas of high P concentrations, from which to gather spectra. However, a downside of using P K-edge μ-XANES is that as areas of high P concentration are preferentially measured, it is thus difficult to ascertain any treatment effects across the soil sample.

This work highlights the potential for organic C compounds to modify soil P reactions. A greater understanding of these 'functional components' of soil organic matter may contribute to more efficient organic matter management, resulting in enhanced P efficiency in acid agricultural soils.

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