

# The Effect of Organic Ligands on Phosphate Sorption in Soil: Detection by P/Al $L_{2,3}$ -edge and Al $K$ -edge XANES

C.R. Scheffe, P. Kappen (1), P.J. Pigram (1), L. Zuin (2), C. Christensen (3)

(1) Department of Physics and Centre for Materials and Surface Science, La Trobe University, Victoria 3086, Australia

(2) Canadian Light Source, Inc.

(3) College of Agriculture and Bioresources, University of Saskatchewan

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## PRINCIPAL CONTACT:

**C.R. Scheffe**

Research Scientist,  
Future Farming Systems  
Research Division,  
Department of Primary Industries,  
Rutherglen Centre,  
Victoria 3685, Australia  
cassandra.scheffe@dpi.vic.gov.au

## Introduction

X-ray absorption near edge structure (XANES) spectroscopy at the phosphorus (P)  $K$ -edge is becoming widely utilised for speciation of P in soil [1], with some preliminary results reported using P  $L_{2,3}$ -edge XANES [2]. Studies of soil aluminium (Al) speciation by XANES are rare [3], although Al is an important factor in soil P speciation. The VLS-PGM beamline 11ID-2 [4] and SGM beamline 11ID-1 [5] at the CLS were used to obtain complementary information on soil P and Al speciation, through measurement of the P and Al

$L_{2,3}$ -edge (VLS-PGM) and the Al  $K$ -edge (SGM).

## Science

Phosphorus (P) fertiliser availability is severely reduced in acid soils due to increased P sorption onto Al hydroxides and other solid-phase binding sites. The addition of organic ligands (organic and benzoic acids) may modify P sorption through competitively binding to phosphate sorption sites (including Al hydroxides) on the soil surface [6].

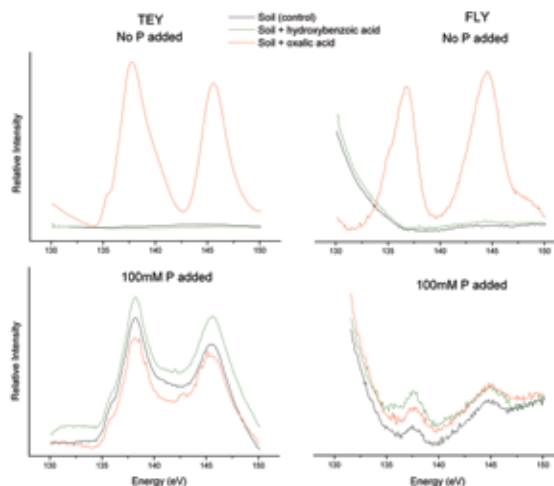
The objective of this research was to determine the ability of XANES to detect modified phosphate surface reactions in the presence of organic ligands. An increased understanding of these processes will contribute towards enhanced P fertiliser efficiency through better soil management and potentially, to modified fertiliser formulations.

Solutions containing 100 mM P (as  $\text{KH}_2\text{PO}_4$ ) and/or 1 mM carboxylic acids (oxalic or hydroxybenzoic acid) were added to a highly acidic soil (pH<sub>Ca</sub> 3.8) from south-eastern Australia. After mixing for 17 h, the solution was decanted and the soil retained. The dried soil was finely ground and presented to the VLS-PGM and SGM beamlines at the CLS, mounted on carbon tape. Al and P  $L$ -edge data were collected in both the Total Electron Yield (TEY) and Fluorescence Yield (FLY) modes over the ranges of 74–92 eV and 130–155 eV, respectively, while Al  $K$ -edge data was collected in the TEY mode over the range of 1485–1685 eV.

The P  $L$ -edge XANES spectra for each of the soil treatments are shown in Figure 1. When no P was added, the addition of oxalic acid had a significant effect on soil P detection, as determined

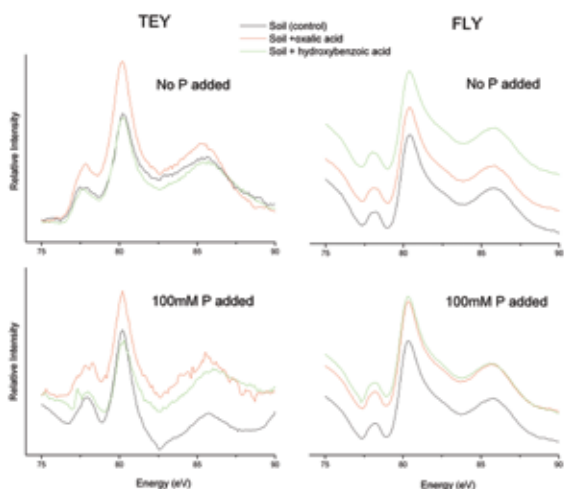
by both TEY and FLY modes (left hand panels, red curve). Soil P was not detected in other nil P treatments. The addition of P resulted in strong detection of P in all added P treatments, as measured by TEY. Measurement in the FLY mode resulted in poor detection of added soil P. The discrepancies observed between the TEY and FLY data are likely due to different photoelectron attenuation lengths between the TEY and FLY modes, a result still under discussion.

The different intensities of P signals in the TEY and FLY modes indicate that the soil P detected by TEY in the oxalic acid (no P) treatment may have been previously occluded at a depth beyond detection in the nil P control, only becoming accessible after dissolution of surface-bound moieties (e.g. Al) by oxalic acid. The greater spectral intensity of soil P in the added P treatments by TEY also indicates that the P is surface-adsorbed.



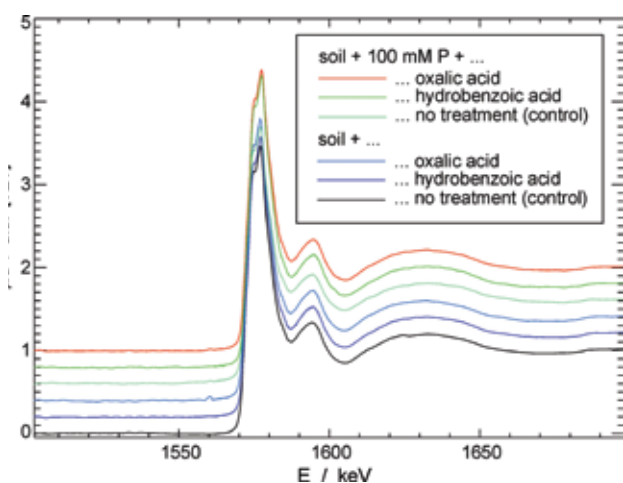
**Figure 1:** P  $L$ -edge XANES spectra of nil P and added P soil treatments, measured in both TEY and FLY modes.

The variation of spectral features observed in the Al  $L$ -edge TEY indicates that organic ligand addition had some effects on surface Al arrangement, particularly in the added P treatments, compared with the added P control (Figure 2; black curve), which are not evident in the FLY mode.



**Figure 2:** Al L-edge XANES spectra of nil P and added P soil treatments, measured in TEY and FLY

The P and Al L-edge spectra have demonstrated the surface-specificity of P and Al-organic ligand reactions. Therefore, it is not surprising that there were no discernable treatment effects measured in the depth-averaged Al K-edge XANES results (Figure 3). The Al present in these soil samples was identified as gibbsite-like, based on comparison with published spectra [3].



**Figure 3:** Al K-edge XANES spectra of all soil treatments, measured by TEY.

## Discussion

This study supports the work previously published by Ajiboye et al [2], who demonstrated the feasibility of P L-edge XANES for speciation of soil P. Assignment of the P XANES spectra obtained in the present study to specific chemical forms is not yet possible due to a lack of published reference spectra, a knowledge gap which will be addressed in future XANES experiments.

The application of P L-edge XANES for speciation of soil and environmental samples shows significant promise due to the increased sensitivity (i.e. lower limits of detection) of surface-bound P, compared with that achieved with the more widely accepted P K-edge XANES technique. In addition, the increased detection of P L-edge XANES can be even further exploited by collection of both TEY and FLY data.

## Conclusion

The use of P and Al L-edge XANES has demonstrated that the addition of organic ligands, especially oxalic acid, has a significant effect on P and Al surface reactions. The increased exposure and detection of soil P with oxalic addition may reflect a potential increase in plant-available phosphorus. Future research is aimed at identifying the forms of P present on soil surfaces, and the mechanisms by which organic ligands may modify surface P reactions.

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