



Addition of carboxylic acids modifies phosphate sorption on soil and boehmite surfaces: A solution chemistry and XANES spectroscopy study

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ABSTRACT

Soil acidification is a globally significant agricultural issue, as the plant availability of phosphorus (P) is decreased through increased P sorption onto aluminium (Al) hydroxides and other solid phase binding sites. X-ray absorption near edge structure (XANES) spectroscopy generated new information on the speciation of Al and P in the presence of carboxylic acids on soil and boehmite (γ -AlOOH) surfaces. XANES spectra were acquired in the soft X-ray regime at the P and Al $L_{2,3}$ -edges, and the Al K -edge, respectively. Adding oxalic acid to soil enhanced Al dissolution and exposed previously occluded soil P, while hydroxybenzoic and coumaric acids did not compete with P for surface binding sites. Boehmite strongly adsorbed carboxylic acids in the absence of applied phosphorus. However, when P was applied with carboxylic acids, the carboxylics were unable to compete with P for binding, especially hydroxybenzoic and coumaric acids. Using XANES in both total electron yield and fluorescence yield modes provided valuable information on both surface and near-surface processes of P and Al due to different information depths. The Al K -edge XANES provided baseline information on the solid-phase matrix. XANES in total electron yield mode and at the P L -edge shows promise for speciation of elements on soil surfaces due to enhanced sensitivity for speciation of surface-adsorbed species compared to the commonly used P K -edge XANES.

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1. Introduction

Phosphorus (P) is a key nutrient required for plant growth, with the application of inorganic phosphate fertiliser being a significant annual expense incurred in the production of food crops. However, the availability of this P fertiliser for plant uptake is severely decreased in acid soils due to increased phosphate sorption onto aluminium (Al) hydroxides and other solid phase binding sites [1]. This is a significant problem, as soil acidity affects up to 50% of the potentially arable land throughout the world [2]. In Victoria, Australia, soil acidity limits productivity on over three million hectares of agricultural land.

Phosphate sorption can occur through either solid phase adsorption and complexation reactions, or through precipitation and co-precipitation reactions [3]. There is considerable evidence that naturally-derived organic carbon (C) compounds may influence soil chemical and biological processes, and specifically, enhance P availability [1,4,5]. These compounds may be derived from the

degradation of organic matter, plant root exudation, or microbial metabolism. Previous work has identified that those compounds containing a carboxylic acid group ($-\text{COOH}$, e.g. oxalic acid) are most effective in decreasing P sorption in acid soil [6,7]. These compounds include organic acids, benzoic acids and cinnamic acids. Example compounds from each class are oxalic acid, *p*-hydroxybenzoic acid, and coumaric acid (Fig. 1).

Carboxylic acids increase phosphate availability through changing the surrounding chemical environment via substitution reactions, whereby carboxylic acids bind preferentially with solid-phase cations (including Al), decreasing the number of available P sorption sites [6,8]. However, as the binding affinity of carboxylic acids to solid-phase cations is based on their arrangement of carboxylic and phenolic groups, this will vary between specific compounds. For example, the order of binding affinity to Al for the three carboxylic acids mentioned above decreases in the order of oxalic acid, *p*-hydroxybenzoic and coumaric acid [9].

The following diagram shows a simplified version of these substitution reactions, depicting how the addition of oxalic acid may displace chemisorbed phosphate from an Al hydroxide binding site on a soil surface (Fig. 2). The direct adsorption of an acid functional group on the Al hydroxide (Figs. 2d and 2e) is another reaction

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route that prevents P sorption from occurring. Complexation of oxalic acid and Al hydroxide may also result in Al hydroxide being stripped off the soil surface, and into solution [10].

The proposed interactions between these acids and solid phase binding sites, including Al hydroxides, have been established largely by measuring changes in the chemistry of soil solution, and utilising speciation modelling programs such as GEOCHEM [11]. This is due to a lack of appropriate techniques for solid-phase measurement of these interactions: classical wet chemistry fractionation techniques (e.g. [12]), can only determine gross changes in forms of soil P, while solid-state ^{31}P nuclear magnetic resonance cannot clearly define metal phosphate species due to interference from these paramagnetic ions (e.g. Al, Fe) [13].

Synchrotron-based techniques can add value to these discussions by providing a novel understanding of solid phase processes, with recent research utilising synchrotron X-ray absorption near edge structure (XANES) spectroscopy to characterise phosphate species in soil directly [14–16]. XANES shows promise for the analysis of carboxylic acid reactions at the soil surface, and for determining how addition of these compounds can modify phosphate sorption reactions. At present there are no published reports using XANES for direct measurement of these carboxylic-based reactions. Developing a greater understanding of P sorption reactions at the soil surface, and the role of carboxylic acids in these reactions, may lead to more efficient P fertiliser utilisation with substantial economic and environmental benefits.

The aim of this study was to identify the effects of added carboxylic acids (oxalic, *p*-hydroxybenzoic and coumaric acid) on P surface reactions in an acid soil and a reference mineral

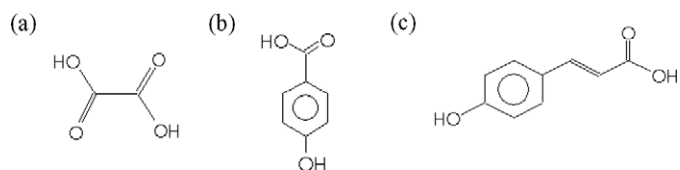


Fig. 1. Example compounds from the organic, benzoic and cinnamic groups: (a) oxalic acid, (b) *p*-hydroxybenzoic acid, and (c) coumaric (or hydroxycinnamic) acid.

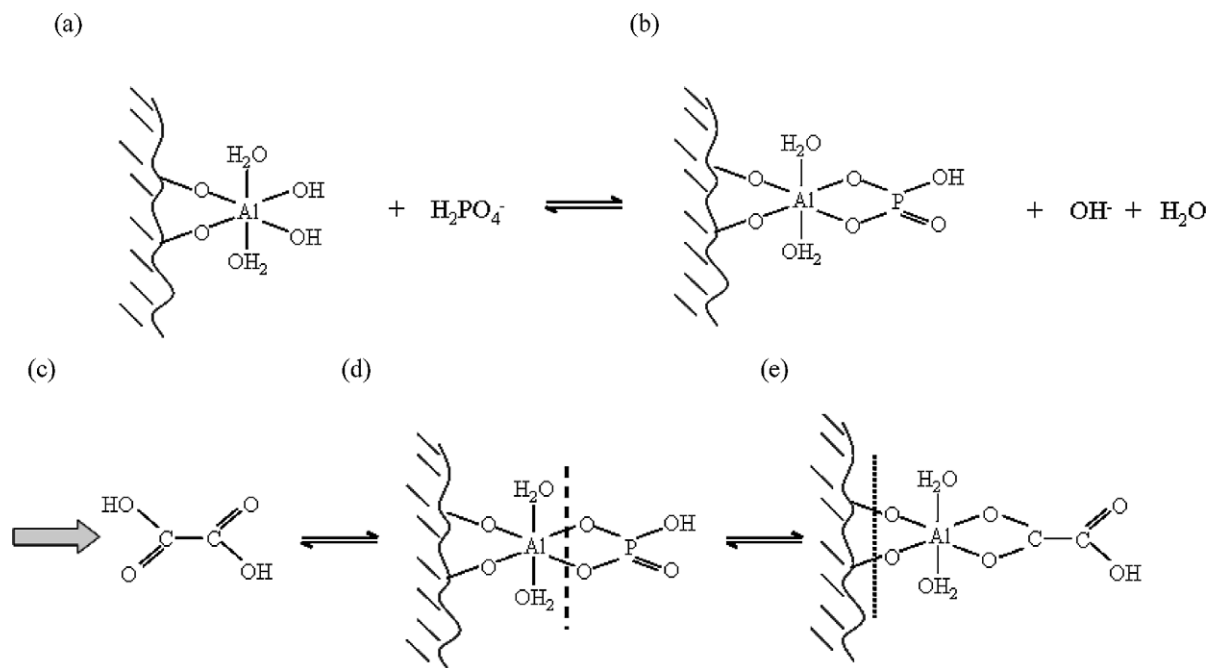


Fig. 2. Diagram showing the complexation and displacement of phosphate from an Al hydroxide binding site in the following stages: (a) Al hydroxides are present on the soil surface, (b) the complexation of H_2PO_4^- by a surface-bound Al hydroxide, (c) the addition of oxalic acid, (d) the breaking of the Al-phosphate bond, and (e) the substitution of phosphate with oxalic acid. The dotted line in (e) denotes the potential for oxalic acid to actually extract the Al hydroxide off the soil surface.

(Boehmite, $\gamma\text{-AlOOH}$). XANES data of the P and Al *L*-edges were used to provide new information on the chemistry and structure of P and Al on soil and boehmite surfaces, and near-surfaces, and how these arrangements are modified in the presence of carboxylic acids. Additional Al *K*-edge XANES data of soil and boehmite were obtained to provide supporting evidence on the effect of carboxylic acids on Al chemistry.

2. Materials and methods

The selected soil was a bleached eutrophic yellow Dermosol [17] sourced from the Department of Primary Industries, Rutherglen Centre, Victoria, Australia. This soil had been under a phalaris-based (*Phalaris aquatica*) pasture for the past 15 years, receiving annual additions of superphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) fertiliser. A Dermosol was selected as it is the dominant soil type within the strongly acidic agricultural zone in Victoria [18]. This particular soil has been extensively characterised in respect to its P sorption and Al solubility properties [19,20]. X-ray diffraction analysis (XRD; Philips PW1710) showed the soil to contain dominant (>60 wt%) quartz, minor (5–20 wt%) kaolin and k-feldspar (orthoclase), and trace (<5 wt%) sodium–calcium (Na–Ca) feldspar (albite), anatase and mica (illite). A single soil sample was collected from the 0–0.10 m depth, air-dried, and passed through a 2-mm sieve before use. Boehmite was selected as a reference mineral as it is a common constituent of soils and sediments, and has been used previously in XANES P sorption experiments [15,21]. Analytically pure boehmite (as determined by XRD) was obtained from BASF Catalysts LLC, USA.

The experimental treatments are listed in Table 1. Samples were prepared by weighing out 2.5 g samples of soil and boehmite 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 and boehmite in a 1:10 (w/w) soil:solution ratio. Boehmite samples were pH-adjusted to 6.4 ± 0.2 and samples were shaken end-over-end at 29 r.p.m. for 17 h. This extraction time was selected based on previous sorption studies (data not shown) which showed 17 h to be sufficient for the

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