

**ON THE USE OF EXTENDED X-RAY ABSORPTION FINE STRUCTURE  
SPECTROSCOPY TO DETERMINE THE BONDING CONFIGURATIONS OF  
ORTHOPHOSPHATE SURFACE COMPLEXES AT THE  
GOETHITE/WATER INTERFACE**

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences

Fall 2012

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## ABSTRACT

Phosphate transport, cycling and availability in soils are strongly affected by sorption reactions with Al- and Fe- (hydr)oxides, 1:1 silicate clays and with some components of soil organic matter. The importance of these reactions lies in the fact that phosphorus (P) can be a limiting nutrient in terrestrial ecosystems, and sorptive removal of natural or fertilizer P can impact the health and the production levels of agriculture. Notwithstanding, sorption/desorption reactions controlling excess P concentrations in soils, particularly as a result of anthropogenic activity, are also important to ensure soil and water quality. A great deal of research on P retention mechanisms in soils and soil components has been conducted over the last decades. However, in spite of the large amount of literature garnered from the decades of research on this subject, studies addressing P sorption mechanisms, particularly on goethite, have resulted in countless conflicting interpretations of binding mechanisms. With the advent of more sophisticated molecular-scale techniques, such as Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy, one is now able to measure interatomic distances between an X-ray absorbing atom and its nearest neighbors and to assign sorption mechanisms based on the bonding distances between the two entities. In this study, we employed EXAFS spectroscopy to examine the effects that some environmental conditions impart on P surface complexation at the goethite/water

interface. Three sets of experiments were performed in order to obtain detailed structural information on the P structures formed on goethite as a function of (i) surface loading, (ii) pH and (iii) residence time. The first set of experiments (chapter 2) was intended to address the surface loading effects of P on the sorption mechanisms in which goethite was reacted with orthophosphate at P concentrations of 0.1, 0.2, and 0.8 mmol L<sup>-1</sup> at pH 4.5 for 5 days. EXAFS analysis revealed a continuum between adsorption and surface precipitation, with bidentate mononuclear (<sup>2</sup>E), bidentate binuclear (<sup>2</sup>C) and monodentate mononuclear (<sup>1</sup>V) surface complexes as well as surface precipitates forming at the goethite/water interface under the studied conditions. It was also shown that the coexistence of different surface complexes or the predominance of one sorption mechanism over others was directly related to surface loading. The second and third sets of experiments (chapter 3) were carried out to provide information on how the local chemical environment of sorbed P changes as an effect of pH and time. Goethite was reacted with orthophosphate at a P concentration of 0.8 mmol L<sup>-1</sup> P at pH 3.0, 4.5 and 6.0. The residence time effect on the mechanisms of P sorption on goethite was also evaluated for two different reaction times, 5 and 18 days, on goethite suspensions reacted at pH 4.5. The monodentate surface complex was shown to be the predominant mechanism by which P sorbs at the goethite surface under the experimental conditions. The lack of a discrete Fe – P shell and the presence of highly disordered structures, particularly, at R-space ≥ 4 suggested the formation of P surface precipitates at the goethite/water interface.

In the last set of experiments, soils from a field-scale experiment were sampled and analyzed in order to assess the long-term effects of consecutive application of swine and cattle manures (M) on P reactivity and distribution in highly weathered agricultural lands of Paraná state, Brazil. Phosphorus K-edge spectroscopy was employed along with sequential P chemical fractionation and desorption kinetics experiments to provide macro and micro-scale information on the long-term fate of M application on those soils. The M rates applied to those soils over the years were typical of intensive agricultural areas in Brazil, varying from approximately 25 to 90 ton ha<sup>-1</sup> year<sup>-1</sup> on a dry weight basis. The soils have been cropped year round for 10, 20 and 40 years with different land managements, namely Tifton pastureland, no-tillage and conventional agriculture, respectively.

Soil test P (STP) values ranged from 3.7 up to 4.3 times as much higher than the reference soil. A sharp increase in amorphous Fe and Al amounts were observed as an effect of the consecutive application of M. Whereas our results showed that the P sorption capacity of some manured soils remained unchanged, P risk assessment indices such as DPS<sub>M-3</sub>, DPS<sub>Ox</sub>, PSS and PSR-II indicated that P losses should be expected, likely due to the excessive M rates applied to those soils. The much higher contents of amorphous Fe and Al (hydr)oxides in manured soils seem to have counterbalanced the inhibiting effect of SOM on P sorption by creating additional P sorbing sites. Accordingly, the newly created P sorbing surfaces were important to prevent an even larger P loss potential. This observation was in good agreement with desorption kinetics data, which showed that higher half-lives of P in manured soils

might have been due to an enhanced P sorption due to higher amorphous Fe and Al (hydr)oxide contents. Additionally, P in manured soils was shown to be associated with less labile pools. The shortest half-life and thus fastest P turnover in the adjacent forest soil might have been related to more labile P pools in the untreated soil. Although manure application led to an overall enlargement of P pools, reactive P was mainly associated with the less bioavailable ones, as evidenced by sequential P fractionation data. The consecutive application of animal manures was shown to have an effect on the transformation of crystalline into amorphous Fe- and Al-containing minerals, as evidenced by ammonium oxalate extractions of Fe and Al and confirmed by visual inspection of XANES spectra, showing the presence of the diagnostic pre-edge feature of crystalline Fe(III)-minerals in the adjacent area and its absence in manured soils. Accordingly, the highly reactive non-crystalline Fe-containing minerals formed are presumably the main surfaces to which P from the animal manures is held.