

**THE EFFECTS OF IRON(II) ON ARSENIC(III) OXIDATION AND
ARSENIC SORPTION/DESORPTION ON MANGANESE OXIDES**

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

Summer 2014

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ABSTRACT

Arsenic contamination of groundwater and soils is a major global environmental challenge and poses a significant health risk to millions of people throughout the world. Both As(III) and As(V) are carcinogens, but As(III) is more toxic and more mobile. Thus, oxidation of As(III) to As(V) is an effective way to reduce As toxicity. As(III) oxidation by Mn-oxides has been extensively studied in the laboratory, however, the oxidation/sorption kinetics and mechanisms of As(III) under natural heterogeneous environments remains unclear. As(III) and Fe(II) coexist in many As contaminated environments and the presence of Fe(II) can influence the behavior of As(III) on Mn oxides. In this study, As(III) oxidation by a poorly-crystalline phyllosulfate (δ -MnO₂) in the presence and absence of dissolved Fe(II) was investigated using stirred-flow and batch experiments. The solids after reaction are characterized by X-ray absorption spectroscopy (XAS), Mössbauer spectroscopy and transmission electron microscope coupled with energy-dispersive X-ray spectroscopy (TEM-EDS). Results showed that in the presence of Fe(II), As(III) oxidation was inhibited due to the competitive oxidation of Fe(II) as well as the formation of Fe(III)-(hydr)oxides on the δ -MnO₂ surface. However, the sorption of As(III), As(V) and Mn(II) increased, since the newly formed Fe(III)-(hydr)oxides provided additional sorption sites. XAS analysis revealed that at low Fe(II) concentration, As(V) was the predominant As species on the solid phase, while at high Fe(II) concentration, both As(III) and As(V) were sorbed on the solid phase. As preferred to bind with the newly formed Fe(III)-(hydr)oxides through a bidentate

binuclear corner-sharing complex. Fe(III)-(hydr)oxides formed during Fe(II) oxidation by δ -MnO₂ were predominantly ferrihydrite and goethite as well as a small amount of lepidocrocite. The adsorbed As can be desorbed from the Fe/Mn-oxides surface, to some extent, and more As(III) is desorbed than As(V), due to the weaker binding of As(III) with Fe/Mn-oxides. This study suggests that the oxidation of As(III) by δ -MnO₂ in the presence of Fe(II) is very complex, involving several simultaneous reactions. A comprehensive understanding of the As(III) oxidation and As sorption on Mn-oxides as impacted by Fe(II) is essential and will provide significant information that can be used to better predict the toxicity and mobility of As in the environment as well as to develop strategies for remediation of As-contaminated waters and soils.