

SPECIATION AND REACTIVITY OF PHOSPHORUS AND ARSENIC IN MID-ATLANTIC SOILS

by

Audrey Gamble

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ABSTRACT

Phosphorus (P) and arsenic (As) are chemically similar elements with widely different impacts on the environment. Phosphorus is an essential element for crop growth and a widely-applied fertilizer to agricultural soils, but can act as a pollutant when excess P erodes or leaches into water sources, adversely affecting water quality. Arsenic is a known carcinogen that occurs naturally and anthropogenically in soils and can pose significant risk to human health. An understanding of fundamental soil P and As chemistry is necessary to understand cycling and bioavailability of these elements in the environment. Synchrotron-based X-ray absorption near edge spectroscopy (XANES) and X-ray fluorescence (XRF) techniques are used in the current study to determine speciation of P and As in soils from the Mid-Atlantic. This paper has three primary objectives: 1) examine soil P speciation (chemical forms) using novel synchrotron-based micro-focused XANES (μ -XANES) techniques; 2) comparatively assess P desorption potential in Mid-Atlantic soils based on soil chemical and physical properties; and 3) assess the toxicity and bioavailability of As in historically-contaminated orchard soils, where lead arsenate was applied. In this study, XAS and XRF techniques (objective 1) have identified calcium phosphates, Fe phosphates, Al-sorbed P, and Fe-sorbed P in soils. Our study demonstrates the value in pairing XRF and XAS studies to evaluate P speciation *in situ* for soils. Sequential extractions indicate that P is primarily associated with iron (Fe) and (Al) in the evaluated soils, and batch desorption demonstrates that soils with high amorphous Fe- and Al-oxide content are less vulnerable to desorption (objective 2). Results from sequential extracts were not representative of major species identified with XAS techniques, and could signify that P speciation is more easily detected for discrete, P-rich particles with μ -XANES. Bioavailability and speciation

studies to assess soil As toxicity in legacy orchard soils (objective 3) indicate less than 22% of total As is bioavailable at all previous orchard locations. All As appears to be in the less-toxic As(V) form based on XAS analysis. Arsenic is relatively immobile in background electrolyte solutions, but phosphate concentration increases As mobility in contaminated soils. These studies demonstrate the importance of synchrotron-based methods to evaluate P and As speciation in soil.