Phosphate Amendments for Chemical Immobilization of Uranium in Contaminated Soil

by

Matthew Robert Baker

(Under the Direction of John C. Seaman)

Abstract

Uranium (U) contamination is a major environmental problem associated with the mining and processing of nuclear materials for both weapons and power production. When possible in situ soil remediation techniques are preferable for reducing the risk associated with diffuse low-level U contamination. Uranium is known to form sparingly soluble phosphate compounds that persist in the environment. Therefore, batch experiments were performed to evaluate the efficacy of three phosphate amendments, hydroxyapatite (HA), sodium phytate (IP6) and sodium tripolyphosphate (TPP), to immobilize U in contaminated sediments. The amendments were added at equivalent phosphorus (P) concentrations and then equilibrated under a range of test conditions, with changes in soluble U and P_{total} monitored at pre-set time intervals. Only HA was effective at reducing soluble U when compared to the control, with IP6 and TPP increasing soluble U. After equilibration, changes in contaminant partitioning in the amended sediments was evaluated using operational extraction methods.

Index words: Uranium, IP6, Hydroxyapatite, TPP, Phosphate, Batch Experiment, Immobilization, Sequential Extraction

PHOSPHATE AMENDMENTS FOR CHEMICAL IMMOBILIZATION OF URANIUM IN CONTAMINATED SOIL

by

MATTHEW ROBERT BAKER

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by

Matthew Robert Baker

Approved:

Major Professor:	John C. Seaman
	Aaron Thompson
	Fanny Coutelot

Electronic Version Approved:

Suzanne Barbour
Dean of the Graduate School
The University of Georgia
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For my Dad, who shared with me his love of science and passion for learning. For my Mom, who is the strongest person I know. Without their support and strength I would not be where I am today.

CONTENTS

List of Figures . . . vi

List of Tables . . . ix

1 Literature Review . . . 1

  1.1 Vadose Zone or Subsurface Environment . . . 1

  1.2 Uranium . . . 6

  1.3 Contaminated Sites Remediation . . . 8

  1.4 Objectives . . . 13

2 The Use of Phosphate Amendments on Uranium Contaminated Soil . . . 14

  2.1 Introduction . . . 14

  2.2 Materials and Methods . . . 17

  2.3 Results . . . 21

  2.4 Discussion . . . 30

3 Effect of Phosphate Amendments on Contaminant Partitioning in Soil . . . 43

  3.1 Introduction . . . 43

  3.2 Materials and Methods . . . 45

  3.3 Results . . . 47

  3.4 Discussion . . . 56

4 Summary and Conclusions . . . 67

References . . . 70

List of Figures

1.1 Diagram showing vertical cross section from the land surface through the vadose zone. 3
1.2 Trace element reactivity in soils. 6

2.1 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g soil) on soluble U in contaminated Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 35
2.2 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g soil) on soluble Ni in contaminated Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 36
2.3 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the pH of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 37
2.4 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the ORP of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 38

2.5 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the DOC of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 39

2.6 Dispersal of organic matter in contaminated Steed Pond sediment amended with HA, IP6, and TPP, and then equilibrated in ARW background solution. 40

2.7 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on soluble P in Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals. 41

2.8 Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on soluble U and Ni in Steed Pond sediment equilibrated in unsaturated batch conditions. Error bars represent 95% confidence intervals. 42

3.1 Toxicity Characteristic Leaching Procedure (TCLP)-extractability of U from contaminated Steed Pond sediment amended with HA, IP6, and TPP and then equilibrated under oxic (a), anoxic (b), and unsaturated (c) conditions. For graphs d, e, and f, the TCLP-extractable U values were corrected for U removal during initial equilibration and reported on a mass basis. Error bars represent 95% confidence intervals. 59

3.2 Toxicity Characteristic Leaching Procedure (TCLP)-extractability of Ni from contaminated Steed Pond sediment amended with HA, IP6, and TPP and then equilibrated under oxic (a), anoxic (b), and unsaturated (c) conditions. For graphs d, e, and f, the TCLP-extractable Ni values were corrected for Ni removal during initial equilibration and reported on a mass basis. Error bars represent 95% confidence intervals. 60

3.3 Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under oxic conditions. 61

3.4 Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under anoxic conditions. 62

3.5 Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP in unsaturated conditions. 63

3.6 Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under oxic conditions. 64

3.7 Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under anoxic conditions. 65

3.8 Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP in unsaturated conditions. 66

List of Tables

2.1 Physical and Chemical Characteristics of Steed Pond Sediment. . . . 17
2.2 Phosphate Amendment Treatments Amount Based on Equivalent PO_4 Contents. 18
2.3 Artificial Rain Water Composition 21
2.4 General data trends observed for the three P treatments. 31

3.1 Sequential extraction procedure for trace element partitioning assessment. (Modified Miller et al. 1986 method) 48

Chapter 1

Literature Review

The following literature review presents the different scientific concepts that are relevant to the current study. This section defines the subsurface environment and the complex and often interrelated processes that occur in that system as they pertain to the mobility of trace elements, including uranium (U). Then follows a brief discussion about U chemistry that focuses on its complex behavior in the subsurface environment. Next, I define what contaminated areas are and touch on the regulatory framework that governs remediation efforts as they apply to the soil environment. This is followed by a discussion of remediation techniques applicable to contaminated areas with a more specific focus on contaminant immobilization using phosphate amendments. The advantages and disadvantages of various phosphate amendments for trace element and U immobilization are discussed with an emphasis on the specific amendments to be evaluated in the current study.

1.1 Vadose Zone or Subsurface Environment

The unsaturated zone (or vadose zone) includes all the soil and sediment materials situated above the water table (Figure 1.1). The unsaturated zone is a three-phase medium consisting of the solid matrix plus the liquid and gaseous phases. The vadose zone functions as the central link between several important environmental compartments i.e., atmosphere, biosphere, and groundwater as seen in Figure 1.1.

The liquid phase is situated in the pores of the solid matrix and plays a key role in the transfer of soluble substances in the geologic profile. Indeed, reactions within the vadose zone are quite complex due to both temporal and spatial variations in saturation, with the pores partially filled with water and air. It is expressed by the saturation level and controls the flow in the soil. The vadose zone has two specific aspects in term of element transfers. First, this area can store water and dissolved substances. Secondly, rapid deep drainage of the mobile portion of the water is possible, determining groundwater recharge, and depending on its composition, the contamination of groundwater reserves.

In some cases, the soil can have a high concentration of contamination comprised of either organic or inorganic (or both) contaminants. Soil materials can act as reactive filters for preventing groundwater contamination and protecting groundwater quality. An understanding of the mechanisms controlling contaminant transfer is essential to preserving drinking water resources. The study focuses on the inorganic contaminant element and more specifically trace element (TE) contamination.

1.1.1 Trace Elements in the Vadose Zone

Chemical elements are generally separated into "Major" and "Trace" elements based on their relative concentrations in un-impacted systems. Trace elements are generally found at concentrations below 0.1% of geologic materials, or less than 100 $mg\ kg^{-1}$ of dry matter for living organisms.

Trace elements can be metals, metalloids, or actinide elements that are present naturally in soil (i.e., As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se). TEs are largely derived from the weathering of the parent rock. However, the most important TEs in soil have some relationship to anthropogenic activity.

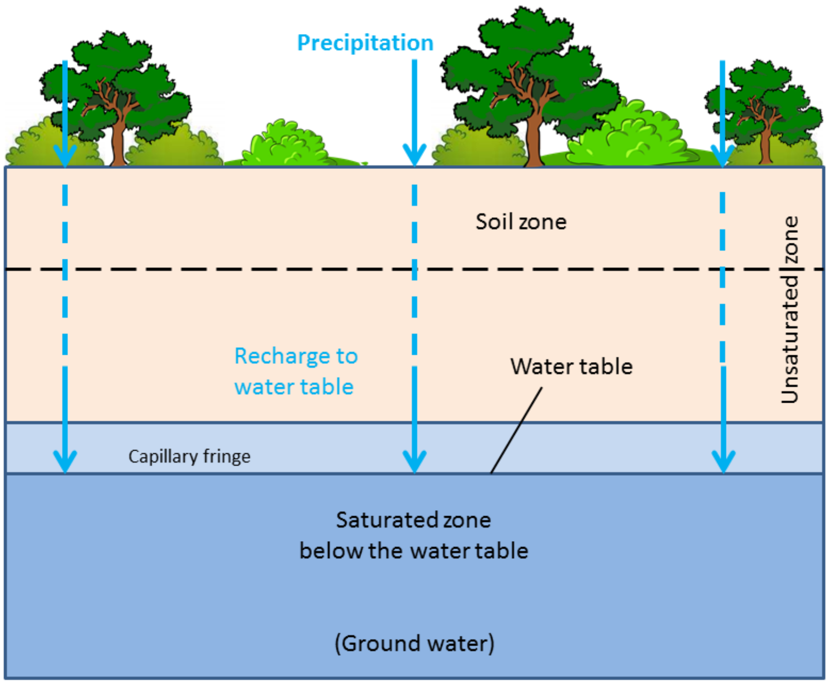

Figure 1.1: Diagram showing vertical cross section from the land surface through the vadose zone.

Trace elements are associated with different soil compartments or fractions, and they can exist in a variety of chemical forms (Figure 1.2). In the soil solution, dissolved TEs can exist in their simplest form (hydrated cations or oxyanions), but also in the form of organic and inorganic complexes. In addition to the dissolved element, colloidal and fine suspended particulates may also contain a large fraction of TEs in the soil solution. A significant fraction of the total TE content is usually associated with the solid phase (organic or mineral). For example, the cadmium (Cd) level in uncontaminated soils is $\approx 0.8\ mg\ kg^{-1}$, while the Cd concentration in soil solution typically ranges from 0.01-5 μg L^{-1}, which represents less than 0.00003% of the total Cd (68). Yet, the soluble fraction can have a significant impact on the environment. In the solid phase of the soil, TEs can be adsorbed or complexed on the surface of solid materials. They can also be included in either the crystal lattice or in an amorphous structure. The TEs that are surficially adsorbed by solid components (i.e., clay minerals, iron (Fe) and manganese (Mn) oxides, organic matter, etc.) are sorbed via several complex mechanisms (described below), and may become more or less mobile with changes in the chemical environment. In contrast, TEs structurally incorporated into soil minerals are far less susceptible to becoming mobile and/or bioavailable, and may be slowly released over time as the minerals are progressively altered.

Physical, chemical and biological processes control TE speciation, redistribution and mobility in soil. Trace elements can adopt different forms when in solution, and their chemical speciation may control the way they interact in the environment. A better understanding of TE speciation in soil systems can improve our ability to predict contaminant transfer and develop management strategies that reduce transfer from the vadose zone to fragile groundwater resources.

Figure 1.2 shows the main interactions between an atom and/or molecule and a solid in soils. The physico-chemical processes at the solid- liquid interface that control TE partitioning include the following: (1) ion exchange (or electrostatic nonspecific adsorption); (2) surface complexation (adsorption specific to the mineral phase) with organic matter; and (3) precipitation / co-precipitation (1; 35). Soil constituents responsible for TE partitioning include clays, carbonates, metals, (hydr)oxides (mainly those from Fe and Mn), silica, and organic matter (Figure 1.2). The main mechanisms affecting liquid-solid TE partitioning are:

- **Sorption:** a term used generally to describe the loss of an element from the aqueous phase without implying the underlying mechanisms. Non-specific adsorption is a process that balances the charge of the ions on the soil particles by electrostatic attraction (also called chemisorption), while the specific adsorption involves the formation of chemical bonds between the ions and the sorption sites on the surface of minerals (also called physisorption). In soil, the main sorption phases are the clay minerals, carbonates and silicates.

- **Complexation:** a chemical bond between a dissolved ion and an organic molecule (R-COOH for example). The resulting association, named "complex", remains in a dissolved form. A complexation reaction occurs when a cation reacts with an anion having a ligand function (atom possessing a pair of free electrons). In soils, the major complexing agent is the organic matter.
- **Precipitation-dissolution:** Precipitation and dissolution play a major role in soil chemistry, especially on the regulation of major elements (e.g., calcium, carbonates and silicate) and also in the retention of TEs. Precipitation is defined as the passage of a solute solution into a solid state (dissolved product is transformed into solid state) depending on the equilibrium:

$$nM_{aq}^{m+} + mX_{aq}^{n-} = M_nX_m(aq) = M_nX_m(s)$$

The mobility of an element in the soil designates the ability of it to pass from a form where it is retained with some energy into another where it is held with less energy (29). Thus, a TE can pass successively through forms where it is less and less energetically bonded leading into the soil solution. The main environmental factors influencing TE mobility in soils are pH, redox potential (pe) and cation exchange capacity (CEC) (12; 30; 55). A TE present in the soil in sorbed form is generally more mobile than an element held within the soil mineral crystal lattice.

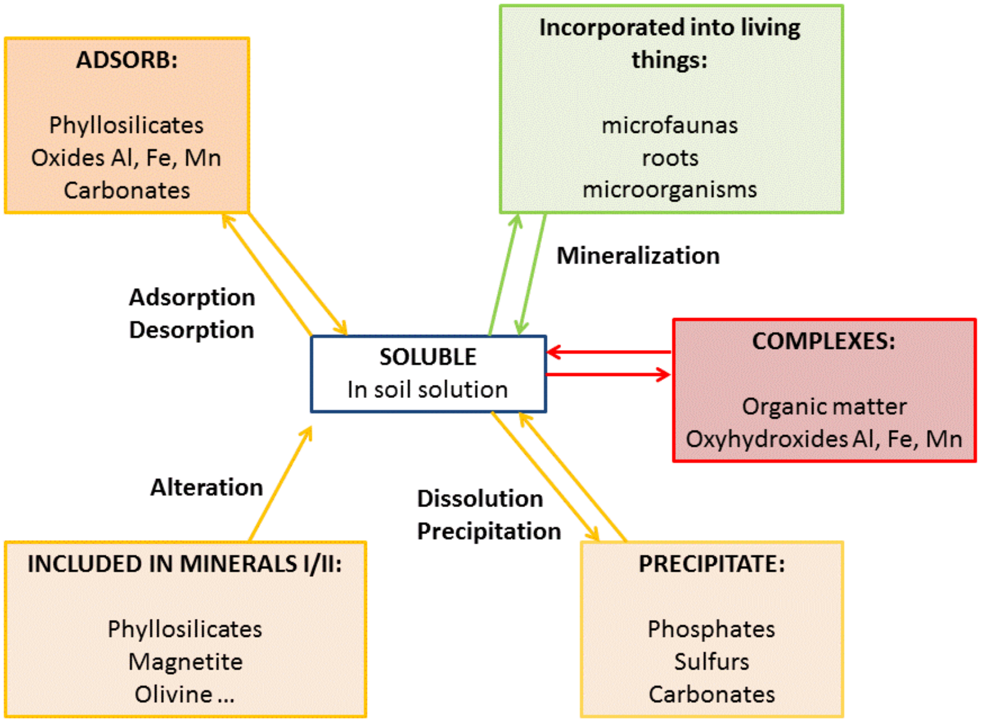

Figure 1.2: Trace element reactivity in soils.

1.2 URANIUM

Uranium (U) is an actinide, atomic number 92, and naturally consists of three isotopes: ^{238}U (99.3% and 4.47 x 10^9 half-life), ^{235}U (0.7% and 7.04 x 10^8 half-life), and ^{234}U (0.005% and 2.46 x 10^4 half-life). Uranium can be found in four oxidation states in aqueous systems (+3, +4, +5, and +6), but only the +4 and +6 states are common. All U isotopes are radioactive and ^{238}U is the most prevalent isotope in U bearing ore materials. Uranium-235 (^{235}U) is a naturally occurring fissile isotope that (through enrichment) is used in nuclear weapons and power reactors in the form of uranium dioxide (UO_2) (11). U.S. civilian power plants typically use 3-5% enriched ^{235}U while weapons use “highly enriched uranium” (HEU) with over 90% ^{235}U. HEU is used by all U.S. naval reactors and also some research reactors.

Uranium-235 (^{235}U) and ^{238}U are two of the most abundant naturally occurring radionuclides, and average U concentrations in groundwater range from < 0.1 (reducing) to 100 $\mu g\ L^{-1}$ (oxidizing) (10). Uranium has traditionally been obtained from mining ores like uranite (formerly pitchblende (UO_2)) and autunite ($Ca(UO_2)_2(PO_4)_2 * 10 - 12(H_2O)$), but it can also be obtained from phosphate rock ($Ca_3(PO_4)_2$). Since phosphate rock contains small amounts of naturally occurring radionuclides including U, it often ends up in waste products during fertilizer processing and manufacture. The milling and enriching of U-containing ores for nuclear material and weapons, the large scale use of phosphate rocks as fertilizers, and early lack of regulation for radioactive mill tailings and waste have led to widespread environmental U contamination in soils, sediments and groundwater.

1.2.1 BEHAVIOR IN SOILS, REACTIVITY: SOLID PHASE -LIQUID PHASE::

Uranium partitioning and mobility in the soil environment is complex and depends on many interrelated mechanisms and factors including the U concentration, pH, redox potential, dissolved CO_2 concentrations, organic matter content, and the presence and concentration of complexing anions (such as carbonate, CO_3^{2-}) (57). The reduced oxidation state, U(IV), is orders of magnitude less soluble than the oxidized state, U(VI). The most common and mobile form of U exists as uranyl cation (UO_2^{2+}), which shows similar cation exchange reaction behavior to Ca^{2+} (60). At neutral pH, U primarily exists as soluble U(VI)-bearing species under oxidizing conditions or as less soluble U(IV)-bearing species under reducing conditions (48). Under oxidizing conditions and neutral pH, U(VI) species can be immobilized by adsorption to iron minerals (33). Uranyl can be chemically reduced to the immobile U(IV) by reduced iron or sulfur species (15; 27) and/or biologically by native anaerobic microbial communities (70).

Much of the U environmental remediation research has focused on reducing the more mobile U(VI) to the less mobile U(IV) (9; 16; 17; 24; 36; 37; 41; 57; 56; 63; 64; 59; 71). As U is the most common contaminant found throughout the DOE complex (15; 53), remediation methods must be developed in order to limit the contamination spread.

1.3 CONTAMINATED SITES REMEDIATION

A site is considered contaminated when old waste deposits or the introduction of polluting substances will likely cause a nuisance or a perennial risk to people or the environment at levels above the background concentration (EPA Guidelines 2009). Currently, there is not a specific legal framework or threshold for defining U pollution in soil in the U.S. and U contamination is covered under multiple regulatory agencies. Radioactive waste storage and the mill tailing regulation are both regulated by the U.S. Nuclear Regulatory Commission (NRC), and the drinking water standards are regulated by the U.S. Environmental Protection Agency (EPA). The EPA has established a maximum contaminant level (MCL) for U of 30 micrograms per liter ($\mu g\ L^{-1}$) in drinking water. The MCL is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system, but there is still no framework in the case of soil contamination.

1.3.1 REMEDIATION TECHNIQUES

In some cases, the TE concentration in groundwater is above the set threshold level due to vadose zone contamination. In such case, measures must be taken in order to limit further contaminant transfer from the vadose zone to the groundwater. The aim of soil remediation is to make a site suitable for a potential end use. Thus, a remediation plan needs to define appropriate metrics to assess when clean-up is warranted and complete.

Remediation efforts may require the complete removal of the contaminant or may seek to leave the residual contaminant in a form that is considered less of a potential hazard. The choice of a remediation strategy is generally based on the nature and extent of contamination, soil type, and characteristics of the contaminated site (30). Unlike other soil contaminants (i.e., anthropogenic organic compounds), TEs and long-lived radionuclides cannot be eliminated or degraded by decomposition-mineralization, and thus persist, regardless of the form in which they are present in the soil.

The remediation technique most often used for TE contamination is excavation of soils and sediments (i.e., removal) followed by *ex-situ* processing or isolation within a landfill. In contrast, *in-situ* remediation strategies focus on altering the chemical form of the contaminant in an effort to reduce its mobility and availability. Excavation is a fast and relatively simple method. It involves removing contaminated materials and shipping them to a treatment center or disposal site depending on the concentration and types of pollutants they contain (31). Costs are proportional to the volume of material processed and can quickly become prohibitive when considering large areas of diffuse contamination. This technique is applicable to all kinds of pollutants and may be subject to acceptance criteria for subsequent treatment and disposal. Clearly this technique is limited to relatively surficial materials. Excavated soils can be treated by soil washing, containment, stabilization and solidification, and heat treatments prior to eventual disposal.

Conversely, in situ treatments do not require soil excavation and disposal. Such techniques are generally used when the contaminated area is quite extensive. In such cases the costs are generally lower than treatments that involve excavation and disposal. In-situ remediation techniques include:

- **Phytoremediation** - extracting soil contaminants through the use of plants that can withstand/tolerate the contaminant, extract significant quantities of the target contaminant, and produce sufficient biomass to make removal economical.

- **Immobilization** – introduction of targeted adsorbent and/or chemical modification to enhance target contaminant partitioning to a less mobile/bioavailable phase.

1.3.1.1 In Situ Immobilization

In-situ immobilization covers a wide range of soil remediation strategies, and aims to reduce the TE labile fraction (the fraction that can be easily released in solution) by adding a binding agent (amendment) to the soil while leaving the soil structure and function generally intact (32). This technique consists of changing the chemical state of the target contaminant by adding mineral or organic phases to the soil surface. Added phases are able to adsorb, complex or co-precipitate TE in situ. This technique does not eliminate contaminants from the soil, but can greatly reduce their ability to transfer to the soil solution. Thus, in-situ immobilization presents both a more cost effective option, and a better environmental balance for stabilizing larger areas of contamination when compared to conventional excavation techniques (38).

Naturally occurring or artificial soil amendments such as liming materials, phosphates, zeolites, bentonite, clay, Fe metal, Fe and Mn oxides, and organic matter, may be used to mitigate the mobility of TEs (23; 32). These amendments effectively reduce TE mobility by promoting the formation of insoluble precipitates or by enhancing the soil's capacity to bind the contaminant via a more stable sorption mechanism. Immobilization studies often intend to limit transfer to plants. Limited attention has been given to U leaching to groundwater (22; 25; 26; 49; 54). However, reducing U leaching could reduce U dispersion and play a significant role in the protection of groundwater resources (54).

1.3.1.2 PHOSPHATE AMENDMENTS

Soil phosphorus (P) exists in both organic and inorganic forms, and can be rapidly fixed in somewhat insoluble forms depending on many soil and environmental factors, including soil type (i.e., mineralogy, texture, OM content, etc.) and pH (61). Orthophosphate, the simplest phosphate, has the chemical formula PO_4^{3-}. Polyphosphates are mixtures of long-chain phosphate ions (i.e., pyrophosphate $(HP_2O_7)_3^-$) and orthophosphates. Chemical immobilization using phosphate amendments, such as mineral apatite, hydroxyapatite (HA), and phosphate salts, has proven effective in reducing TE mobility by the formation of TE–phosphate precipitates (3; 7; 40; 47; 58; 59; 65). Many TEs form poorly soluble precipitates with orthophosphate (PO_4), and the addition of phosphorus containing materials has been proposed as a means of limiting TE mobility, including U and nickel (Ni) (2; 58; 59). Application of the phosphorus-containing material for the immobilization of TE in soils is based on the tendency of phosphates to precipitate TEs by forming stable solid phases. Various phosphate sources were tested to immobilize TEs in soils (32). Arey et al. (1999) used HA to immobilize U in sediments with varying organic matter contents. Hydroxyapatite additions significantly reduced U mobility and the use of electron microscopy (TEM) combined with micro-analytical techniques (EDX) suggests the formation of secondary Al/Fe-phosphates that sequester U in a form that is less soluble than autunite, $(Ca(UO_2)_2(PO_4)_2 \cdot 10 - 12H_2O)$.

However, phosphates should be used with caution because their addition can alter pH and enhance release of certain TEs (38). Phosphate amendments may also migrate from the treatment area and contaminate ground or surface waters

(43), possibly resulting in surface water eutrophication. Additionally, this approach is limited to surficial areas of contamination where relatively insoluble phosphate-based reactants can be readily mixed with the contaminated material. To overcome such limitations, researchers have investigated a range of soluble PO_4-containing materials with limited success, including inositol hexaphosphate (IP6).

Inositol phosphates are a group of organic phosphorus compounds that exist in the natural environment as inositols in various states of phosphorylation (1-6 phosphate groups linked by an ester bond). IP6 has nine different sterio-isomers that differ only in the orientation of the six phosphate groups, with the myo stereoisomer being the most common in nature (62). Phytate and phytic acid are also commonly accepted names for various forms of myo-inositol hexakisphosphate, and phytate has been noted as being the most studied form of organic P that persists in soils (21; 62; 72).

Sodium tripolyphosphate (TPP), like IP6, is a water-soluble long-chain phosphate compound which has been found to reduce soluble U concentrations when applied to contaminated sediments (74). IP6 and TPP will generally migrate through soils and sediments to a greater degree than orthophosphate, and eventually yield orthophosphate through various degradation reactions which can then precipitate with the target contaminant. When added to sediments as the soluble Na form, both IP6 and TPP can serve as weak bases and increase soil pH. Like orthophosphate, IP6 forms strong bonds with oxy-hydroxide minerals that can limit its mobility, and induce surface charge reversal that may induce clay dispersion. In addition, IP6 can also act as strong metal chelate, with the potential to actually increase the solubility and mobility of the target contaminant depending on the specific chemical conditions in question (13; 14; 56). It is generally thought that the contaminant TEs sorb to the IP6 precipitate and/or replace Ca to some degree within the precipitate (43; 44; 45).

The strong adsorption of IP6 to hydrous Al and Fe oxides and/or complexation followed by precipitation with polyvalent cations has been invoked to explain the persistence and accumulation of IP6 in the soil environment (6; 13; 14; 46).

1.4 OBJECTIVES

The use of inositol hexaphosphate (phytate; IP6) and TPP has been proposed as more soluble PO_4 sources (PO_4s like HA) for treating metal (Pb) and actinide (U, Pu, etc.) contaminated soils and sediments where the use of sparingly soluble PO_4 sources is impractical. This study proposes to evaluate the effectiveness of more soluble PO_4 sources compared to HA in immobilizing U and Ni under aerobic and anaerobic conditions. We also want to improve our understanding of the effect more soluble PO_4 sources have on U and Ni solid-phase distribution in Steed Pond sediments and whether the different amendment levels or batch conditions effect their distribution or mobility in the environment as compared to commonly used HA. The objectives of the current study were to: (1) evaluate the effectiveness of three phosphate amendments, HA, IP6 and TPP, to immobilize U and other contaminant metals (i.e., Nickel (Ni)) in highly weathered Atlantic Coastal Plain sediments as a function of redox status and degree of saturation; and (2) to use both regulatory (i.e., EPA Toxicity Characteristic Leaching Procedure (TCLP)) and operationally-based selective extraction methods (i.e., Miller et al. (1986) sequential extraction method) to evaluate changes in the solid-phase speciation of U and Ni in amended sediments that are indicative of changes in contaminant bioavailability and migration potential.

CHAPTER 2

THE USE OF PHOSPHATE AMENDMENTS ON URANIUM CONTAMINATED SOIL

2.1 INTRODUCTION

Uranium (U) is the most common contaminant found throughout the Department of Energy (DOE) complex (53). Uranium is a concern for its radiological and chemical toxicity and can persist in the environment as its three main isotopes have long half-lives, i.e., ^{238}U = 4.5 x 10^9 years, ^{235}U = 7.04 x 10^8 years, ^{234}U = 2.5 x 10^5 years. The presence and accumulation of U in groundwater and sediments has been noted as a problem in several areas on the Savannah River Site (SRS), a DOE facility once used for the production of plutonium (Pu) and tritium (^{3}H) for nuclear weapons. Contamination resulted from both accidental and intentional releases from the 1950s through the 1980s when several U processing facilities were operating (18; 33).

One example is the Tims Branch stream corridor on the SRS. Tims Branch is a second-order stream and a tributary of Upper Three Runs Creek draining approximately 16 km^2 and eventually feeding into the Savannah River. Between 1954 to 1984, Tims Branch received approximately 44,000 kg of depleted U from the M Area fuel and target assembly fabrication facility, which accounts for approximately 97 percent of the gross alpha activity released from SRS facilities. Monitoring surveys suggest that seventy percent of the U released to Tims Branch was deposited in Steed Pond, a former farm pond approximately 4.5 hectares in area that acted as a settling basin for contaminants (19; 66). In addition to significant amounts of U, the

Tims Branch-Steed Pond watershed also received large amounts of nickel (Ni), lead (Pb), and other contaminants associated with nuclear materials production (51).

Once the Steed Pond dam was removed, the contaminated sediments were exposed and subjected to frequent erosion, with particulates mobilized during storm events serving as a significant vector for U transport (4). Initially revegetation of the exposed sediments in the drained pond was somewhat stunted due to metal toxicity (52). However, Steed Pond has since revegetated, with current flow restricted to a shallow braided stream feeding through to Tims Branch.

In addition to the inherent complexities of the Tims Branch-Steed Pond system, U partitioning in the environment and availability in soils is complex and depends on many interrelated mechanisms and factors, including the U concentration, pH, redox status, dissolved CO_2, organic matter content, and the presence and concentration of complexing anions (such as carbonate, CO_3^{2-}) (57). The most common and mobile form of U exists as the uranyl cation (UO_2^{2+}) (60). Under oxidizing conditions and neutral pH, U(VI) species can be immobilized by adsorption to iron minerals (33). The reduced oxidation state, U(IV), is orders of magnitude less soluble than the oxidized state, U(VI). Under reducing conditions, U(VI) can be chemically reduced to immobile U(IV) by reduced iron [(Fe(0), Fe(II)] or sulfur (S^{2-}) species (15; 27) and/or biologically by anaerobic microbial communities (70).

Due to the expansive area that is impacted, in situ immobilization is the preferred remediation approach for addressing U contamination in the Tims Branch-Steed Pond system. In-situ immobilization covers a wide range of soil remediation strategies, and aims to reduce the contaminants labile fraction (the fraction that can be easily released in solution) by adding a reactive binding agent (amendment) to the soil while leaving the soil structure and function generally intact (32). Such techniques generally focus on reducing the mobile fraction of the target contaminant through the addition of a reactive phase, such as liming materials (e.g., $\mathrm{CaCO_3}$,

$CaOH_2$, etc.), phosphates, zeolites, bentonite clays, Fe metal, Fe and Mn oxides, and organic matter, to mitigate the toxic effects of a range of soil contaminants (23; 32). Thus, in-situ immobilization is generally less expensive than conventional soil excavation and disposal and far less disruptive to functioning, albeit contaminated, ecosystems, especially when applied to expansive areas that are only marginally contaminated (38). However, the immobilized contaminant remains in place with the potential to be a future hazard if chemical conditions change. This limitation necessitates a more thorough understanding of the underlying mechanisms controlling contaminant partitioning in treated systems.

Chemical immobilization using phosphate amendments, e.g., hydroxyapatite ($Ca_5(PO_4)_3(OH)$; HA), has proven effective in reducing the mobility of trace elements (Pb, As, Zn, Cu) and radionuclides (U and others) (3; 7; 40; 47; 58; 59; 65). However, this approach is limited to surficial areas of contamination where relatively insoluble reactants can be readily mixed with the contaminated material. To overcome such limitations, researchers have investigated a range of soluble PO_4-containing materials with limited success, including inositol hexaphosphate ($C_6H_{18}O_{24}P_6$; IP6), depending on the material's compatibility with the geology and groundwater chemistry of a given site (2; 58; 59; 56). Sodium tripolyphosphate ($Na_5P_3O_{10}$; TPP), like IP6, is a water-soluble phosphate compound which has been found to reduce soluble U concentrations when applied to contaminated sediments (74). IP6 and TPP are generally more mobile in the soil environment than orthophosphate, and eventually yield orthophosphate through degradation reactions, which can then precipitate with the target contaminants.

The Steed Pond/Tims Branch watershed on the SRS is a complex system that is subject to changing degrees in saturation and episodic erosion events that are complicated by changes in site management policies that affect the amount of drainage water passing through the system. Therefore, the primary objective of the current study is to evaluate the effectiveness of IP6 and TPP compared to commonly used HA in immobilizing U and Ni from Steed Pond sediments as a function of redox status and the degree of saturation.

2.2 Materials and Methods

Table 2.1: Physical and Chemical Characteristics of Steed Pond Sediment.

Parameter	
Particle Size Distribution[1]	
Sand (%)	19.2
Silt (%)	45.2
Clay (%)	35.6
Texture Classification[2]	Silty Clay Loam
pH[3]	4.1
CDB ext. Fe[4] (mg/gm)	3.2
CDB ext. Al (mg/gm)	2.2
Organic Carbon[5] (g/kg)	49
Clay Mineralogy[6]	kaol, HIV, gibb, goe, q
Metal Concentrations (mg/kg)	
U	2040 (2)[7]
Ni	902 (10)[7]

[1] PSD: Particle Size Distribution ((20)).

[2] Textural classification based on the USDA classification scheme.

[3] pH in deionized water (DIW), 2/1 solution to soil ratio

[4] CDB ext. Fe: citrate dithionite bicarbonate extractable Fe ((28)).

[5] Catalytically aided combustion at 900 °C

[6] Clay mineralogy of the ≤ 2 μm fraction; kaol = kaolinite, HIV = hydroxyl-interlayered vermiculite, gibb = gibbsite, geo = goethite, and q = quartz.

[7] Numbers in parentheses are background levels for soils on SRS ((50))

The effectiveness of IP6, TPP, and HA at immobilizing U and Ni in contaminated sediment was tested in batch experiments under two redox conditions. Steed Pond sediments are acidic (pH 4.0-4.5) highly weathered Atlantic Coastal Plain sediments, and the test sample is a Silty Clay Loam (based on USDA classification (Table 2.1)). The U (2,040 mg kg^{-1}) and Ni (902 mg kg^{-1}) concentrations in the test sediment are many times higher than non-impacted soils on the SRS (Table 2.1) (4; 50; 58).

Table 2.2: Phosphate Amendment Treatments Amount Based on Equivalent PO_4 Contents.

% Hydroxyapatite (HA)	**(g) HA by 100g soil**	**(g) IP6 by 100g soil**	**(g) TPP by 100g soil**
0	0	0	0
0.5	0.5	0.46	0.37
1.5	1.5	1.38	1.10
2.5	2.5	2.30	1.83

2.2.1 Batch Equilibration Experiment

Twenty grams (dry weight) of Steed Pond sediment were placed in a series of 250 mL batch vessels with duplicates for each treatment. Four treatment levels of three different P sources were added to each vessel corresponding to 0, 0.5, 1.5, and 2.5 percent of HA equivalent based on soil mass (Table 2.2) in 200 mL of artificial rain water (ARW) as the background solution (Table 2.3). The ARW was used to simulate the low ionic strength solution that the Steed Pond sediment would be typically exposed to during rain events. The salts were combined in a 1 L volumetric flask and filled to volume with ultrapure water to create an ARW stock solution. The ARW treatment solution was made by diluting 1 mL of the concentrated ARW stock solution (Table 2.3) in 1 L of DIW. The dry additive phosphate treatment (i.e., HA, Sigma Aldrich; IP6, Sigma Aldrich; and TPP, Alfa Aesar) levels were based on equivalent masses of P for all three source materials,i.e., 0.0, 0.09, 0.28, and 0.46 g of P by 100 g dry sediment (Table 2.2). To identify the effect of O_2 on U immobilization, batches were run in both oxic and anoxic environments. Oxic samples were equilibrated on the lab bench open to the atmospheric O_2(g) while anoxic samples were equilibrated in an anaerobic chamber ($98\%N_2/2\%H_2$). Both oxic and anoxic samples were equilibrated on an orbital shaker for 30 days at 25 °C. Aliquots for chemical analysis, pH, and ORP measurements (SevenExcellence pH/ORP, Mettler Toledo) were collected at 24 h, 3 d, 7 d, 15 d, and 29 d time intervals. Aliquots were limited to $\leq$ 2.8 mL per sampling interval (for a maximum of 14 mL or 7 percent of total solution) to limit the impact on the continuing vessel equilibration. Aliquots were filtered through a polycarbonate membrane filter (0.22 μm pore size) and a fraction of each aliquot was set aside for analysis of dissolved organic carbon (DOC) using the combustion catalytic oxidation method following acidification and sparging to remove inorganic carbon (Shimadzu TOC-5000A). Orthophosphate levels were determined using the molybdate blue colorimetric method (42). The remainder of the filtered fraction was acidified (2% HNO_3) for preservation and analyzed for U and Ni by inductively coupled plasma mass spectrometry (ICP-MS) (NexION 300X, Perkin-Elmer Corp.) according to the QA/QC protocols outlined in EPA Method 6020B. Total P in solution was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 4300 DV, Perkin-Elmer Corp.). After the remaining solution was drained, residual sediment samples were homogenized and air-dried for subsequent solid-phase characterization, the details of which are described in Chapter 3.

2.2.2 Unsaturated Equilibration Experiment

The unsaturated batch test consisted of the same soil and amendment ratios as the oxic and anoxic batches. The soil and the amendment were mixed together and ultra-pure water was added to reach 60 percent of the water retention capacity of the soil by recorded weight. The batch treatments were equilibrated for 3 weeks at room temperature and maintained at a constant water level, i.e., 60 percent of the water retention capacity. After the equilibration period, pore water was extracted using centrifugation (J6-MI, Beckman Coulter) (3,000 rpm for 30 minutes). Pore solutions from the unsaturated treatments were acidified (2% HNO_3) and analyzed for U and Ni by ICP-MS. Residual sediment samples were air dried, homogenized, and split into subsamples. Contaminant partitioning was evaluated on the air dried samples using the TCLP (EPA Method 1311 (73)) extraction and a commonly used sequential extraction method (39) which are described in more detail in Chapter 3.

Table 2.3: Artificial Rain Water Composition

Component	**mg L^{-1}**
SO_4	1.34
NO_3	0.71
Cl	0.35
Na	0.75
NH_4	0.14
Ca	0.10
K	0.04
Mg	0.03
(Adapted from Strom and Kaback, 1992) (67)	

2.3 RESULTS

Figure 2.1 shows the concentration of soluble U in mg kg^{-1} of dry sediment versus the time (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP amended [(c) and (f)] sediment samples as well as the different P levels as outlined in Table 2.2 under oxic and anoxic conditions. For the no-amendment control samples, the soluble U concentration marginally increased over the equilibration time from 0.71 ± 0.02 to 3.4 ± 0.82 mg kg^{-1} of dry sediment. At all treatment levels, HA was effective at reducing the amount of U in solution under oxic conditions (Figure 2.1a), from 3.4 ± 0.82 mg kg^{-1} U for the no amendment control to 0.07 ± 0.002 mg kg^{-1} U at the highest HA treatment level. The lowest concentrations (0.09 g P per 100 g soil) of IP6 and TPP amendments (Figure 2.1b and c) both decreased soluble U levels over time; from 2.59 ± 0.08 to 0.07 ± 0.007 U of dry sediment for IP6 amended and from 3.43 ± 0.26 to 2.38 ± 0.30 mg kg^{-1} U of dry sediment for TPP amended sediment.

Neither IP6 nor TPP were effective at reducing the amount of U in solution at higher (0.28 g P and 0.46 g P per 100g soil) P concentrations under oxic conditions. Soluble U for IP6 amended samples increased from 10.31 ± 3.39 to 19.29 ± 1.13 and 11.19 ± 0.58 to 34.87 ± 2.61 mg kg^{-1} of sediment while U in solution for TPP amended samples increased from 11.61 ± 0.28 to 22.73 ± 0.41 and 20.52 ± 0.31 to 58.31 ± 1.87 mg kg^{-1} of sediment.

Unlike the oxic control samples in which the soluble U increased over time, the anoxic control decreased from 1.29 ± 0.23 to 0.19 ± 0.06 mg kg^{-1} of sediment. Figure 2.1d shows all HA amendment levels slightly increased the soluble U concentration under anoxic conditions; 0.04 ± 0.0004 to 0.34 ± 0.026 mg kg^{-1}, 0.06 ± 0.01 to 0.33 ± 0.05 mg kg^{-1} U, and 0.05 ± 0.006 to 0.45 ± 0.017 mg kg^{-1} for the lowest to highest HA amendment concentration. However, these levels were still lower than observed throughout equilibration for the no-amendment oxic controls, suggesting that HA addition is still effective at reducing U solubility, even in systems that may undergo seasonal and episodic changes in redox conditions.

The level of soluble U for anoxic IP6 amended samples (Figure 2.1e) increased from 3.16 ± 0.13 to 4.96 ± 0.56, 20.54 ± 0.58 to 27.05 ± 3.29, and 31.64 ± 0.57 to 40.07 ± 0.06 mg kg^{-1} of dry sediment for the lowest to highest IP6 amendment levels. In a similar fashion, the soluble U levels in TPP amended samples (Figure 2.1f) increased from 3.52 ± 0.08 to 4.51 ± 0.09, 13.26 ± 0.09 to 27.43 ± 1.54, and 30.98 ± 1.69 to 58.11 ± 0.83 mg kg^{-1} of dry sediment from lowest to highest amendment concentration.

Thus, both IP6 and TPP were ineffective at reducing the amount of U in solution at any P concentration in either oxic or anoxic conditions, resulting in the increased solubility of U when compared to the control. In contrast to the oxic environment, where soluble U levels for the control marginally increased throughout the course of equilibration, the soluble U levels for the anoxic controls generally decreased with continued equilibration, suggesting that labile U(VI) is possibly being reduced to U(IV), the less-soluble valence state, in the anoxic chamber.

Figure 2.2 shows the concentration of soluble Ni in mg kg^{-1} of dry sediment over the course of equilibration (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP-amended [(c) and (f)] sediment samples at the different P levels outlined in Table 2.2 under oxic and anoxic conditions. The level of soluble Ni in the oxic control samples increased over time from 7.8 ± 0.42 to 56.7 ± 17.74 mg kg^{-1} of dry sediment. All P treatments generally reduced the amount of Ni in solution as compared to the controls under oxic conditions. However, there were small increases in soluble Ni over the course of equilibration for all P amendments at all treatment levels. HA amended treatments (Figure 2.2a) had a higher Ni concentration in solution at lower amendment levels with treatments increasing from 4.3 ± 0.29 to 25.7 ± 4.01, 2.6 ± 0.17 to 11 ± 0.02, and 1.9 ± 0.06 to 5.2 ± 0.60 mg Ni kg^{-1} of dry sediment from lowest to highest amendment addition. IP6 amended treatments (Figure 2.2b) increased over time from 0.7 ± 0.05 to 6.3 ± 0.11, 1.3 ± 0.02 to 5.5 ± 0.29, and 1.8 ± 0.03 to 10.3 ± 0.92 mg Ni kg^{-1} dry sediment from lowest to highest amendment concentration. TPP amended treatments (Figure 2.2c) increased over time from 1.5 ± .011 to 5.8 ± 0.05, 3.6 ± 0.10 to 9.3 ± 0.09, and 4.3 ± 0.01 to 14.2 ± 0.43 mg Ni kg^{-1} dry sediment from lowest to highest amendment addition.

The anoxic control initially increased the amount of Ni in solution over the first seven days from 20.9 ± 1.3 to 25.1 ± 1.2 mg Ni kg^{-1} dry sediment before the amount of Ni in solution began decreasing over the remaining 22 days down to 1.9 ± 0.59 mg Ni kg^{-1} dry sediment. Under anoxic conditions, HA was the only P amendment effective at reducing the amount of Ni in solution over time (Figure 2.2d). Nickel concentration in solution was reduced from 8.1 ± 0.21 to 2.3 ± 0.12, 5.4 ± 1.01 to 1.9 ± 0.05, and 4.4 ± 0.45 to 1.8 ± 0.001 mg Ni kg^{-1} dry sediment from lowest to highest concentration of HA amendment addition. Both the IP6 and TPP amendments (Figure 2.2e and f), while more effective than the control for most of the experiments duration, increased the amount of Ni in solution over time. IP6 amended samples increased from 0.9 ± 0.03 to 2.9 ± 0.14, 3.1 ± 0.22 to 8.3 ± 0.72, and 4.6 ± 0.10 to 12.4 ± 0.12 mg Ni kg^{-1} dry sediment from lowest to highest amendment concentration. Soluble Ni for TPP amended samples increased from 0.9 ± 0.25 to 2.9 ± 0.04, 3.2 ± 0.21 to 8.4 ± 0.92, and 6.7 ± 0.71 to 13.8 ± 0.67 mg kg^{-1} dry sediment from lowest to highest amendment addition concentration.

HA amended treatments increased Ni in solution over time under oxic conditions, and was only effective at reducing the Ni concentration in solution under anoxic conditions. Both IP6 and TPP treated amendments increased the amount of Ni in solution over time under both oxic and anoxic environments.

Figure 2.3 shows the pH level versus the time (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP amended [(c) and (f)] sediment samples at different P_{Total} levels as outlined in Table 2.2 under oxic and anoxic conditions. Under oxic conditions, the initial control pH starts at 4.6 ± 0.3 and decreases to pH 3.9 ± 0.1 over the course of equilibration. The addition of HA (Figure 2.3a) increased the pH of each of the HA amended batches 0.5 to 1 pH units as compared to the control. However, all HA amended treatments decreased marginally over the course of equilibration. All HA treatment levels started around pH 5.2-5.3 ± 0.1 and after slightly increasing over the first week, dropped back down to either at or below the original pH readings. Both IP6 and TPP amended (Figure 2.3b and c) treatments showed increases in pH levels over the control and HA amended treatments. The highest initial pH was 8.6 ± 0.1 for IP6 (0.46 g P per 100 g soil) amended sediment and 8.1 ± 0.1 for TPP (0.46 g P by 100 g soil) amended, which decreased over time to 7.1 ± 0.1 (IP6 amended) and 6.9 ± 0.1 (TPP amended). The lowest amendment level (0.09 g P by 100 g soil) for both IP6 and TPP showed the greatest decrease over time with final pH of 4.6 ± 0.1; the IP6 amended sample had an initial pH of 6.8 ± 0.2 while the TPP amended sample had an initial pH of 7.3 ± 0.1.

Under anoxic conditions, the pH of the control samples increases from 4.2 ± 0.1 to 6.6 ± 0.3 during the first 15 days of equilibration and continues to increase gradually over the final 15 days to end with a pH of 7.6 ± 0.2. All levels of the HA amended treatments (Figure 2.3d) show a gradual increase in pH over time, all starting around pH 5 ± 0.1 and ending 0.2 to 0.4 pH units higher than the control samples around pH 8 ± 0.1. All IP6 and TPP amended treatments (Figure 2.3e and f) also showed an increase in pH over time with the lowest amendment levels for both (0.09 g P by 100 g soil) showing a similar increase at the midway point of the experiment that the control samples showed, about 1.1 pH unit. The TPP amended sample with the highest P level (0.46 g P by 100 g soil) was the only 0.46 sample to end with a pH reading lower (7.7 ± 0.1) than the two lower P levels for TPP amended samples (8.2 ± 0.1 and 8.1 ± 0.1).

While both oxic and anoxic control treatments started off at approximately the same pH, all oxic samples ended at lower pH level than they started at while all anoxic samples ended higher than they started. IP6 and TPP amended treatments decreased pH under oxic conditions but increased pH under anoxic conditions.

Figure 2.4 shows the oxidation reduction potential (ORP) level in millivolts (mV) versus the time (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP amended [(c) and (f)] sediment samples as well as the different P_{Total} levels as outlined in Table 2.2 under oxic and anoxic conditions for 30 days of equilibration. The ORP for the oxic control samples gradually increased through the first 15 days to 806 ± 3.4 mV where it begins to decrease and ends up at a lower ORP (682 ± 13 mV) than it began at (732 ± 0.4 mV). All of the oxic HA amended (Figure 2.4a) treatments had initial (672 ± 4.4, 657 ± 2.6, and 655 ± 2.1 mV from lowest to highest amendment levels) and final ORP (636 ± 2.1, 624 ± 2.7, and 616 ± 0.6 mV from lowest to highest amendment amount) values lower than the control samples. Oxic HA amended samples showed the same trend of increasing the first 15 days and decreasing the last 15 days to end up at lower ORP than they began as the oxic control samples. Both the IP6 and TPP (Figure 2.4b and c) amended treatments, like the HA amended samples, had lower ORP (mV) results than the control samples. For both IP6 and TPP amended samples, the higher P level showed lower ORPs. Unlike HA amended samples though, all levels of IP6 and TPP amended samples ended at a higher ORP than they began at.

Unlike the oxic ORP samples, the ORP for anoxic samples was considerably lower with a majority of readings having negative values. The ORP values for the control samples slowly decreased the first 15 days (-291 ± 17 mV) and then slightly increased through the last 15 days. Control anoxic sample ORP values still ended lower at -272 ± 7.8 mV than their initial value -145 ± 7.3 mV. HA amended (Figure 2.4d) samples showed the same trend as the control samples of decreasing ORP values the first 15 days and increasing ORP slightly the last 15 days with all HA amended samples having a final ORP value 30 mV lower than the final control ORP value -300 ± 1.7 mV. All HA amended samples had lower initial and final ORP values than the control samples. The initial ORP reading at all concentrations of IP6 amended samples (Figure 2.4e) had positive mV readings (183 ± 3.9, 160 ± 23.9, and 124 ± 30.7 mV from lowest to highest IP6 amended treatment). All readings dropped down to negative mV values by the third day and followed the same trend as the HA amended and control samples. The only exception to this was the day 7 reading for the 0.28 g P per 100 g soil level that spiked back up to an almost positive mV value (-63 ± 1.6) before dropping back to the negative 300 mV range like the rest of the 0.28 IP6 amended values by day 15. The TPP amended samples (Figure 2.4f) looked very similar to the IP6 amended samples except both the two highest P concentrations (0.28 g P and 0.46 g P by 100 g soil) showed the same spike in mV at the day seven sampling period (-13 ± 1.5 and -48 ± 9.9 mV respectively) before decreasing back to the -300 mV range by the final sampling.

ORP was higher under oxic conditions with all but three anoxic samples having negative mV values. Both oxic and anoxic control samples displayed a greater disparity in redox status than all P treatments.

Figure 2.5 shows the DOC level in mg L^{-1} versus the time (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP amended [(c) and (f)] sediment samples under oxic and anoxic conditions. DOC values for control samples under oxic conditions show a general decrease over the length of the experiment from 22.6 ± 9.1 mg L^{-1} to 8 ± 1.3 mg L^{-1} with the exception of a spike at day 15 to 33.8 ± 10.3 mg L^{-1}. All levels of the HA amended treatments (Figure 2.5a) show this same decrease in DOC over time; 57.8 ± 36.1 to 6.9 ± 3.5 mg L^{-1}, 20.9 ± 6.03 to 11.7 ± 2.02 mg L^{-1}, 24.2 ± 11.7 to 15.1 ± 0.47 mg L^{-1} from lowest HA amended sample to highest. Here we can note the difference in scale between the HA amended (0 to 100 mg L^{-1}) and the IP6/TPP amended samples (0 to 900 mg L^{-1}). The lowest concentrations (0.09 g P by 100 g soil) of IP6/TPP amended samples (Figure 2.5b and c) show similar DOC concentrations and a similar decrease over time as the control samples; 53.1 ± 0.0 to 12.5 ± 1.2 mg L^{-1} for IP6 amended sample and 37.2 ± 3.3 to 35.5 ± 8.8 mg L^{-1}, for TPP amended sample. The two higher concentrations of IP6 and TPP amended samples both show an increase in DOC concentrations over time. Higher concentration IP6 amended samples increased from 134.7 ± 15.1 to 178.3 ± 18.0 and 89.4 ± 23.7 to 548.2 ± 61.3 mg L^{-1} and TPP amended samples increased from 101 ± 20.1 to 317.4 ± 30.2 and 156.2 ± 6.14 to 575 ± 13.3 mg L^{-1}.

As with the oxic DOC graph, note the difference in scale between the HA (0 to 100 mg L^{-1}) and IP6/TPP amended samples (0 to 900 mg L^{-1}) for the anoxic DOC samples. The anoxic control samples showed slight increases and decreases in DOC concentration throughout the length of the experiment. The DOC for the control sample was initially 18.1 ± 7.2 mg L^{-1} and got as high as 28.8 ± 9.6 mg L^{-1} and as low as 16.9 ± 4.5 mg L^{-1} before ending with a DOC concentration of 24.6 ± 4.5 mg L^{-1}. The three P amendments at all treatment levels showed an increased DOC levels over time, with IP6 and TPP amended samples (Figure 2.5e and f) showing a greater increase over time as compared to the HA amended samples (Figure 2.5d). The HA amended samples increased from 16.7 ± 3.6 to 47.6 ± 1.7 mg L^{-1}, 21.7 ± 10.8 to 57.7 ± 3.7 mg L^{-1}, and 26.2 ± 2.8 to 70.3 ± 5.2 mg L^{-1}) from lowest to highest amendment concentration.

Under oxic conditions, the DOC for HA amended treatments decreased over time while HA amended treatments increased DOC over time under anoxic conditions. IP6 and TPP amended treatments increased DOC throughout equilibration under both oxic and anoxic conditions. A photo of each of the batch amendment treatments is provided in Figure 2.6. Amendment with IP6 and TPP resulted in the evident dispersion of the soil clay fraction and dispersion/solubilization of organic matter, which is evident in the DOC values (Fig. 2.5). Polyphosphates are generally considered to be strong dispersing agents due to their ability to increase net negative charge on soil clays and oxides in a manner that enhances particle repulsion. In addition, both IP6 and TPP contain high levels of Na^+ and increase the soil pH, all of which enhances electrostatic charge repulsion and clay dispersion.

Figure 2.7 shows the concentration of soluble P in mg kg^{-1} of sediment versus the time (in days) for the control, HA [(a) and (d)], IP6 [(b) and (e)], and TPP amended [(c) and (f)] sediment samples under oxic and anoxic conditions. P in solution generally decreases over time under both oxic and anoxic conditions for all treatments and concentrations. The oxic control treatments show decreasing soluble P levels over most of the experiment length from 0.003 ± 0.0008 to 0.00 ± 0.00 mg kg^{-1} P of dry sediment. There is a slight increase in soluble P concentration at the final time (0.006 ± 0.0003 mg kg^{-1} of dry sediment), but this increase is only evident at the expanded scale of the HA graph (Figure 2.7a). The HA treated samples are shown on a 0.00 to 0.05 mg kg^{-1} P of dry sediment scale while the IP6 and TPP amended samples are shown on a 0.00 to 2.0 mg kg^{-1} of dry sediment scale. The oxic HA amended treatments show a similar trend as the control samples with treatments decreasing from 0.014 ± 0.002 to 0.00 ± 0.00 mg kg^{-1} of dry sediment, 0.024 ± 0.002 to 0.007 ± 0.003 mg kg^{-1} of dry sediment, and 0.027 ± 0.002 to 0.014 ± 0.003 mg kg^{-1} of dry sediment from lowest to highest amendment concentration. Both the IP6 and TPP amended treatments show a decrease in soluble P concentration over time. IP6 amended samples (Figure 2.7b) decreased from 0.15 ± 0.002 to 0.008 ± 0.0005 mg kg^{-1} of dry sediment, 0.69 ± 0.03 to 0.27 ± 0.01 mg kg^{-1} of dry sediment, and 1.24 ± 0.05 to 0.76 ± 0.01 mg kg^{-1} of dry sediment from lowest to highest amendment addition concentration. TPP amended treatments (Figure 2.7c) decreased from 0.29 ± 0.02 to 0.05 ± 0.009 mg kg^{-1} of dry sediment, 1.02 ± 0.076 to 0.74 ± 0.0005, and 1.72 ± 0.002 to 1.52 ± 0.018 mg kg^{-1} of dry sediment from lowest to highest amendment addition concentration.

The anoxic control treatments stayed steady at ≈ 0.15 ± 0.002 mg kg^{-1} of dry sediment throughout the course of the experiment. The anoxic HA amended treatments (Figure 2.7d) showed the same general decrease in soluble P over the length of the experiment except for the last sample, like the HA amended oxic treatments. HA treated amendments decreased from 0.026 ± 0.002 to 0.019 ± 0.001 mg kg^{-1} of dry sediment, 0.032 ± 0.001 to 0.019 ± 0.0002 mg kg^{-1} of dry sediment and 0.042 ± 0.0002 to 0.027 ± 0.0002 mg kg^{-1} of dry sediment from lowest to highest amendment addition. Also, similarly to the oxic treatment, the HA treated anoxic samples are shown on a 0.00 to 0.05 mg kg^{-1} of dry sediment scale while the IP6 and TPP amended samples (Figure 2.7e and f) are shown on a 0.00 to 2.0 mg kg^{-1} of dry sediment scale. Both the IP6 and TPP amended treatments also show a decrease in soluble P over time. IP6 amended samples decreased from 0.046 ± 0.001

to 0.045 ± 0.002 mg kg^{-1} of dry sediment, 0.54± 0.01 to 0.18 ± 0.03 mg kg^{-1} of dry sediment, and 1.1 ± 0.01 to 0.45 ± 0.01 mg kg^{-1} of dry sediment from lowest to highest amendment addition concentration. TPP amended treatments decreased from 0.22 ± 0.03 to 0.11 ± 0.01 mg kg^{-1} of dry sediment, 1.02 ± 0.04 to 0.55 ± 0.03, and 1.79 ± 0.05 to 1.06 ± 0.03 mg L^{-1} of dry sediment from lowest to highest amendment addition concentration.

Figure 2.8 shows the level of pore water soluble U and Ni in mg kg^{-1} for control, HA, IP6, and TPP amended sediment samples as a function of the amendment levels under unsaturated batch conditions. HA was effective at reducing U solubility at all P treatment levels compared to the control. Both IP6 and TPP increased U solubility in pore water, with TPP doing it to a much greater extent than IP6. HA, IP6, and TPP were all more effective than the control at reducing the amount of Ni extracted from pore water at all amendment levels.

2.4 Discussion

The effectiveness of different P materials at immobilizing U and Ni in contaminated sediment (see Table 2.4) was tested in batch experiments under varying conditions. Oxic control samples showed a stable pH, positive ORP values, and stable DOC levels over time. Oxic control samples also showed a low (only up to 3 mg kg^{-1}) but increasing soluble U concentration over time, a soluble Ni concentration that increased over time (up to 60 mg kg^{-1}), with minimal P in solution. Under oxic conditions, the increase in U solubility observed for the control may reflect the continued exposure and slow desorption kinetics of U-containing phases throughout equilibration. Conversely, anoxic control samples showed an increasing pH, negative ORP values, and stable DOC levels over time. Anoxic control samples also showed a low soluble U concentration (1 mg kg^{-1}), a decreasing Ni concentration, and essentially

Table 2.4: General data trends observed for the three P treatments.

Condition	**Amendment**	**pH**	**ORP**	**DOC**	**P**	**U**[mg kg^{-1}]	**Ni**[mg kg^{-1}]
Oxic	None [Control]	↔	+ values	↔	Ø	Low [3]	Up to 60
	HA	↗	↘	↗	↗	↓	↓
	IP6	↑	↘	↑	↑	↑	↓
	TPP	↑	↘	↑	↑	↑	↓
Anoxic	None [Control]	↑	Negative values	↔	Ø	Low [1]	Up to 25
	HA	↗	↘	↗	↗	↓	↓
	IP6	↑	↘	↑	↑	↑	↓
	TPP	↑	↘	↑	↑	↑	↓

↔= stable over time; ↗= slight to moderate increase; ↘= slight to moderate decrease
↑= strong increase; ↓= strong decrease; Ø = essentially zero

Note: Control values assess the variable over time while P amendment values are in relation to control values.

no P in solution over time. The main differences between oxic and anoxic control samples were the pH and ORP conditions.

A very important factor that controls U behavior in the soil environment is redox status. It has been noted that tetravalent actinides can form stronger complexes than hexavalent actinides with any given ligand (8), and the reduced oxidation state of uranium, U(IV), is orders of magnitude less soluble than the oxidized state, U(VI). A large percentage of spent nuclear fuel materials is comprised of uranite (UO_2) which tends to oxidize to the +6 oxidation states $(UO_2)^{2+}$ under oxidizing conditions (57). Control samples placed in anoxic environment had lower soluble concentrations of both U and Ni than control samples tested under oxic conditions. Under anoxic conditions, a decrease in soluble U concentration was observed, possibly indicating the more mobile U(VI) may be undergoing chemical reduction to less soluble U(IV) over the duration of the batch experiment.

This study evaluated the effect of HA and two soluble polyphosphate $(PO)_4^{3-}$ sources on U immobilization in contaminated sediments. Along with oxidation state, U speciation is highly influenced by both pH and uranyl's ability to form strong complexes with inorganic oxyanions like phosphate $[(PO)_4^{3-}]$ and carbonate CO_3^{2-} (57). The HA amendment was found be more effective than either IP6 or TPP treatment at reducing the amount of U in solution. HA amended samples show U levels lower than observed in control samples throughout the equilibration period suggesting that HA addition is effective at reducing U solubility, even in systems that may undergo seasonal and episodic changes in saturation and redox conditions. The HA amendment was found to moderately increase sample pH and slightly increase sample DOC in comparison to control samples under both oxic and anoxic conditions which agrees with observations found in the literature. Arey et al. (1999) attributed, in part, the buffering capacity of the phosphate anion to the pH increase in HA amended sediment samples (2). The HA amended samples also visually showed lower solubilization and dispersion of organic matter and clay dispersion compared to the two other phosphate amendments (Fig. 2.6). Previous studies using electron microscopy by Arey et al. (1999) and Seaman et al. (2001) found that in samples treated with HA amendment, U was generally associated with a secondary Al-rich precipitate as opposed to residual HA (2; 59). Based on the literature and our results (i.e., U not released from HA amended samples), the main mechanism of U immobilization is a co-precipitation with newly formed P mineral.

Both IP6 and TPP amendments were found to be less effective than HA amendment at reducing U concentrations in solution. IP6 and TPP amendments strongly increased sample pH, sample DOC levels, and sample soluble U concentrations over control samples. Samples amended with IP6 and TPP also showed strong visual evidence of the solubilization/dispersion of organic matter within the samples. These observations are in agreement with the literature: (*i*) Majs (2011) found that neither Na-IP6 nor TPP were effective at immobilizing U (or Ni) as both amendments triggered dispersion of organo-mineral colloids or complexes that contained significant amounts of U (and Ni) (34); (*ii*) Seaman et al. (2003) also found that the use of higher levels of Na-IP6 amendment favored metal solubilization over immobilization due to the metal to ligand ratios involved (58); (*iii*) Arey et al. (1999) observed increased DOC for sediments with higher organic matter and suggested that U(VI) complexation with soil organic acids enhanced U solubility (2); and (*iv*) Sowder et al. (2003) found metal solubility increased with the presence of organic carbon in the system and U concentrations in solution were highly correlated with DOC; the same DOC correlation was not seen for Ni (66).

The degradation of more soluble phosphate forms (such as IP6 and TPP) eventually resulting in insoluble contaminant-phosphate precipitates can be enhanced either through direct or indirect microbial processes. Tang et al. (2006) found that three classes of phytases tested could hydrolyze precipitated phosphates and release inorganic orthophosphate from calcium, magnesium, and manganese phytates (69). Beazley et al. (2011) observed uranyl phosphate precipitation and increases in soluble phosphate in solution in a column experiment resulting from acid phosphatase production by microbial populations in a U contaminated sediment (5).

At all treatment levels in both oxic and anoxic systems, HA was effective at reducing the amount of U in solution. The amount of Ni in solution increased over time for HA amended treatments. However, HA was still effective at reducing the amount of Ni in solution as compared to the control under oxic conditions; HA amendments reduced the Ni in solution from 55 to 90 % depending on amendment level as compared to the control. HA was also effective at reducing the amount of Ni in solution under anoxic conditions at all treatment levels. Under oxic conditions, HA decreased pH, ORP, and DOC at all amendment concentrations. Under anoxic conditions, HA increased pH and decreased ORP at all amendment levels. HA decreased DOC at the two lowest amendment levels but increased it at the highest amendment level under anoxic conditions, in part reflecting the changes in pH.

IP6 and TPP increased the amount of U in solution at all treatment concentrations under both oxic and anoxic conditions. Total P in solution generally decreased over time under both oxic and anoxic conditions for all IP6 and TPP treatments. IP6 and TPP treated amendments increased the amount of Ni in solution over time under both oxic and anoxic environments. Both IP6 and TPP decreased pH under oxic conditions and increased pH under anoxic conditions at all treatment levels. Under oxic conditions both IP6 and TPP increased ORP at all treatment levels. Excluding the initial readings, IP6 increased ORP at all treatment levels under anoxic conditions. TPP decreased ORP at the lowest amendment addition, but increased ORP and the two higher amendment additions under anoxic conditions. Both IP6 and TPP increased DOC at all treatment levels under oxic conditions. IP6 also increased DOC at all treatment levels under anoxic conditions. TPP decreased DOC at the lowest and highest amendment additions, but increased DOC at the middle amendment concentration under anoxic conditions.

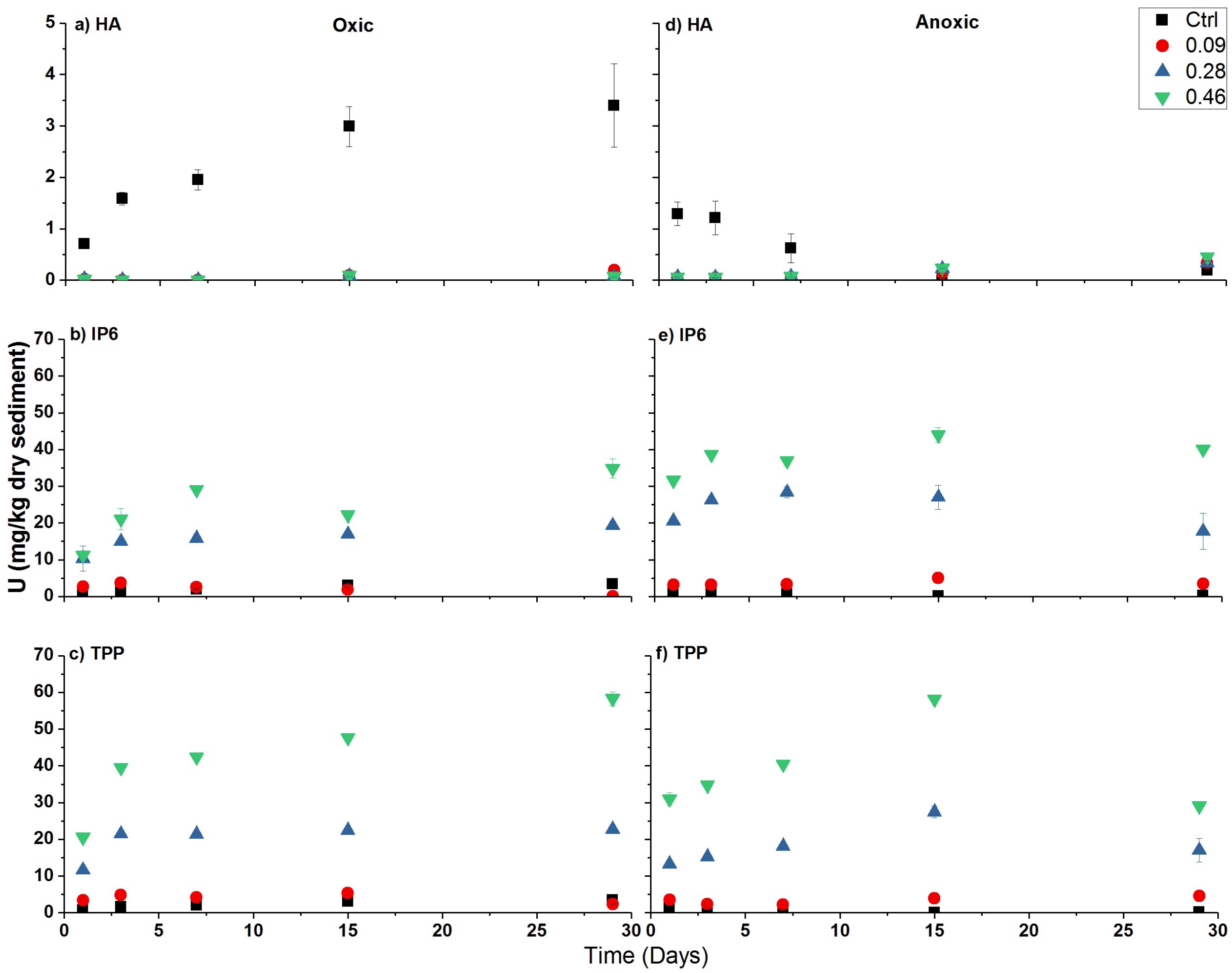

Figure 2.1: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g soil) on soluble U in contaminated Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

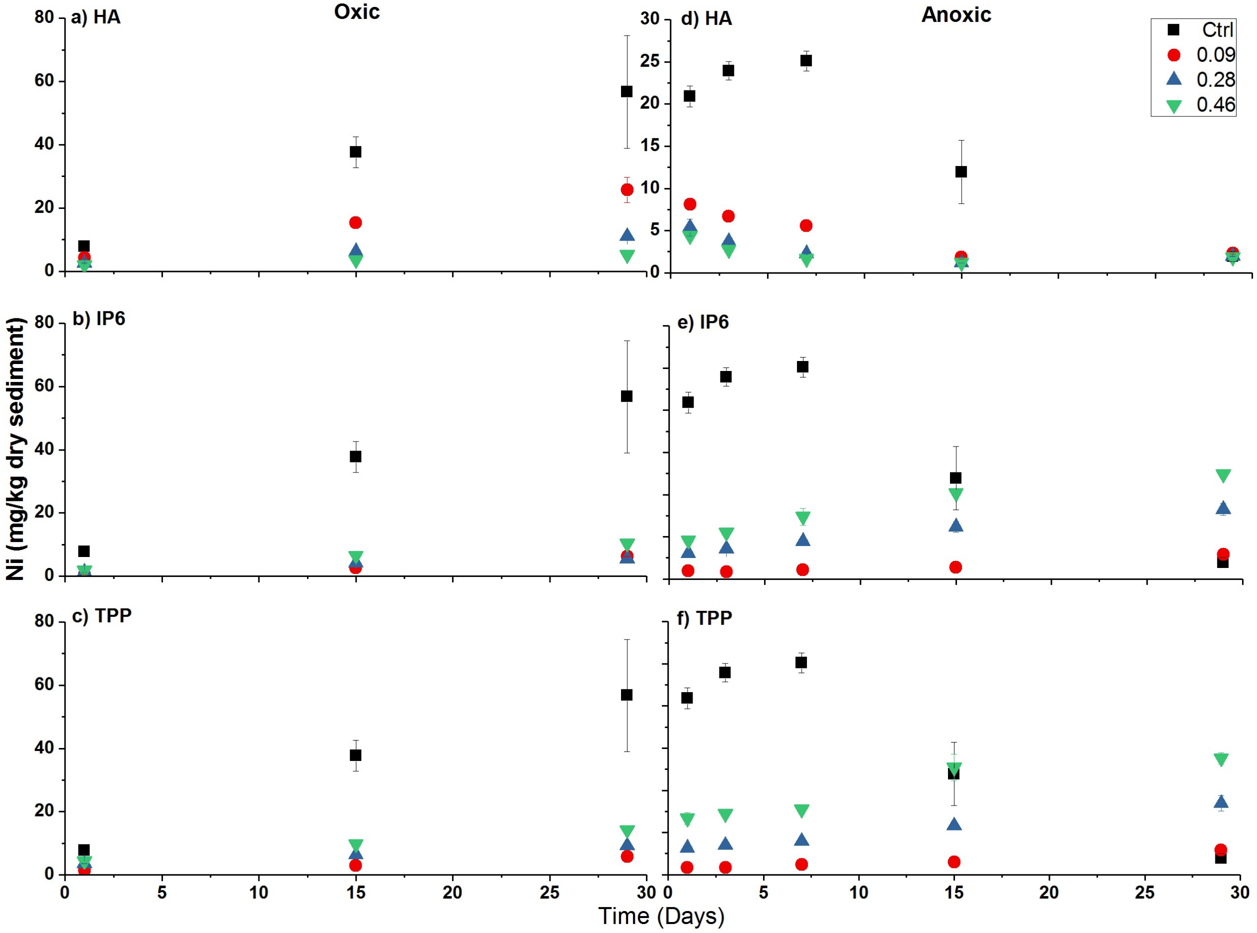

Figure 2.2: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g soil) on soluble Ni in contaminated Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

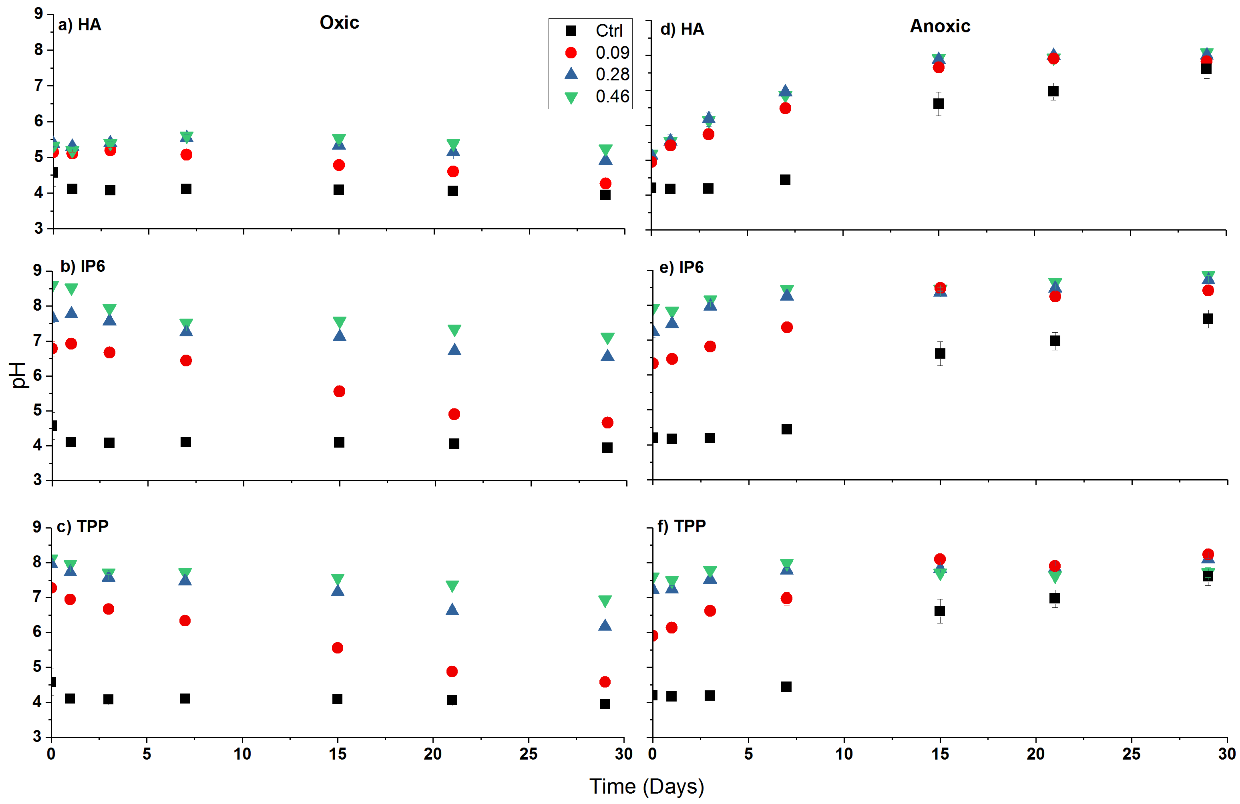

Figure 2.3: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the pH of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

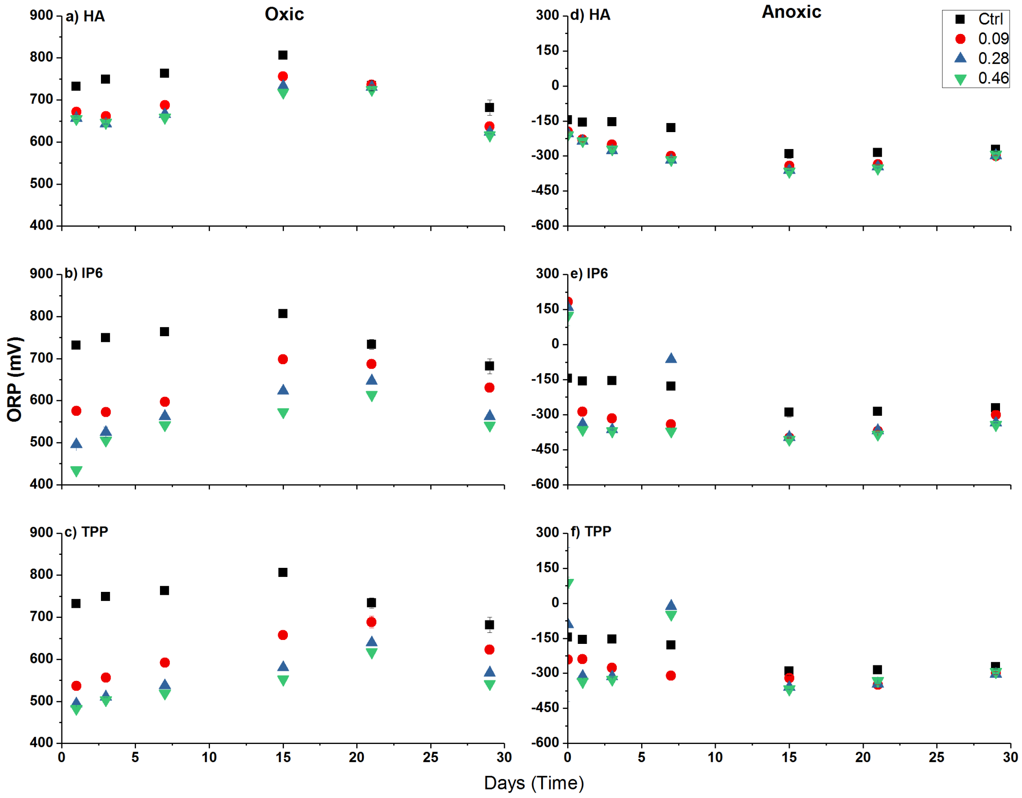

Figure 2.4: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the ORP of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

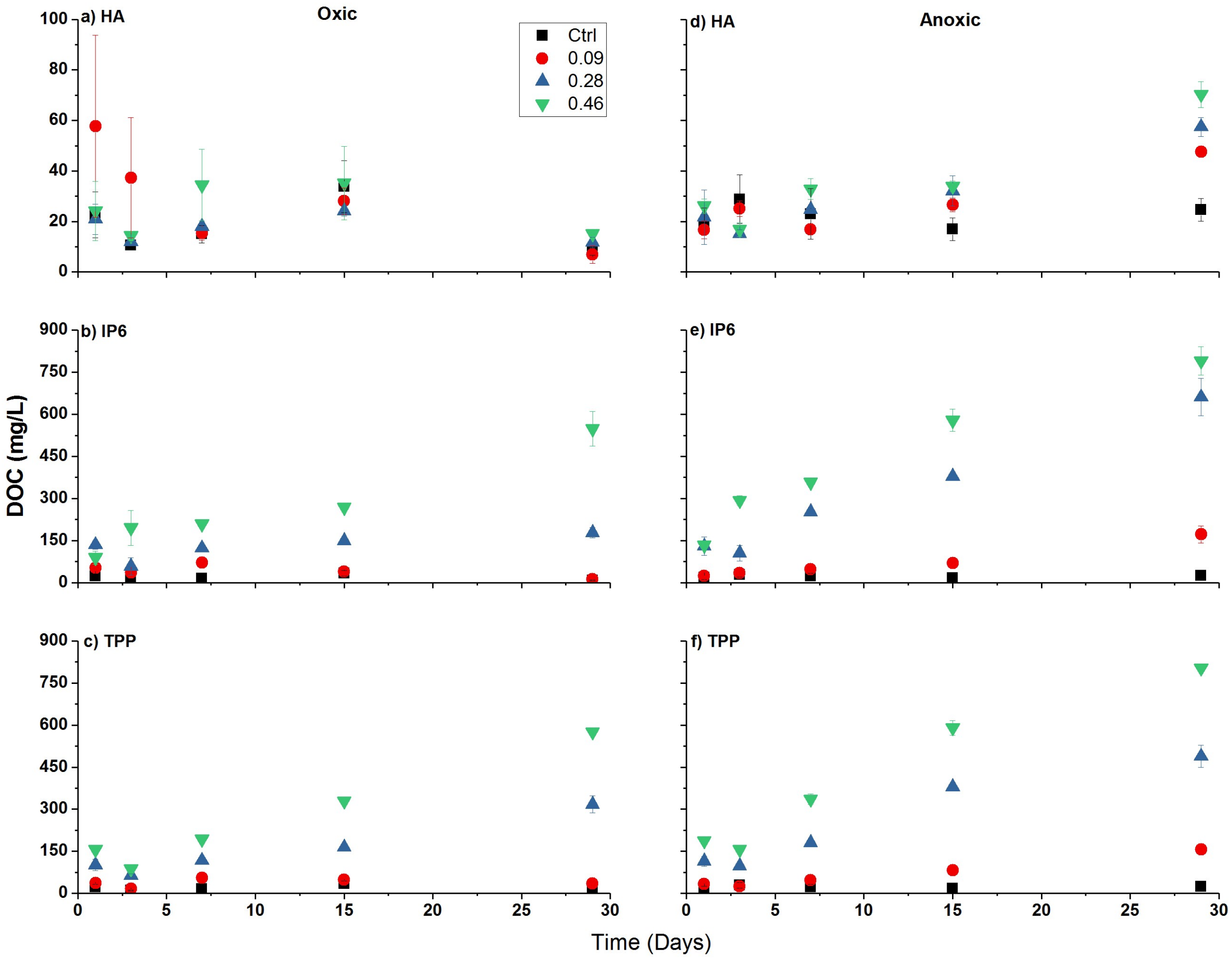

Figure 2.5: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on the DOC of Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

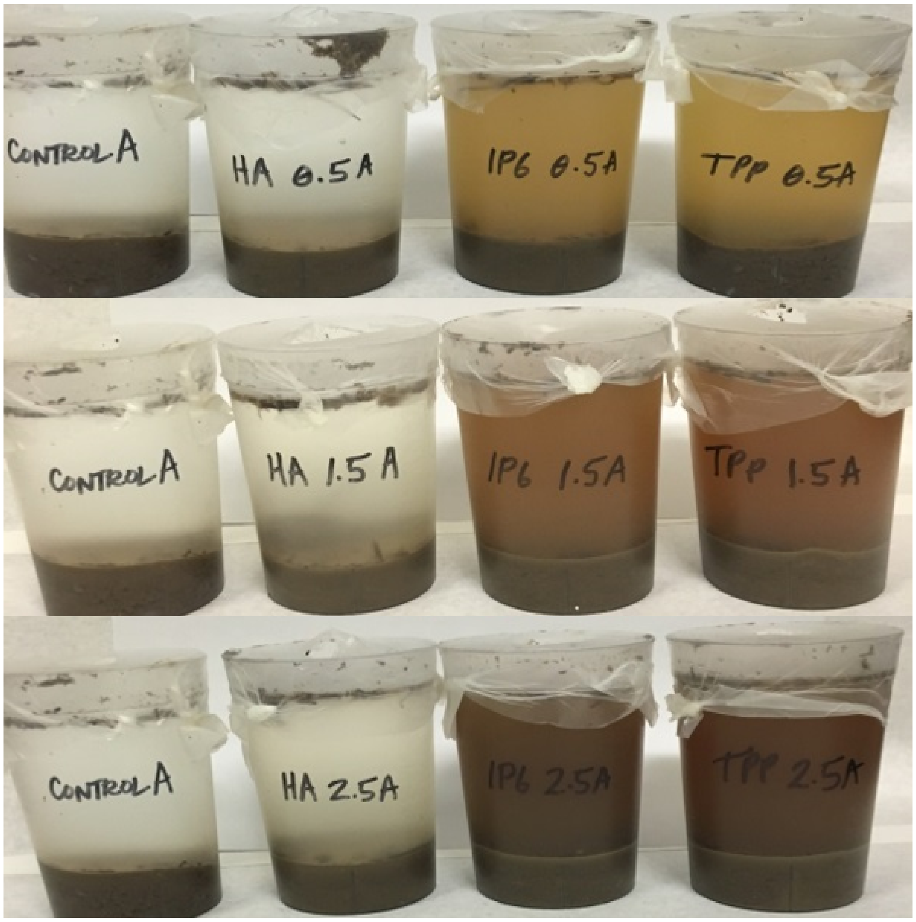

Figure 2.6: Dispersal of organic matter in contaminated Steed Pond sediment amended with HA, IP6, and TPP, and then equilibrated in ARW background solution.

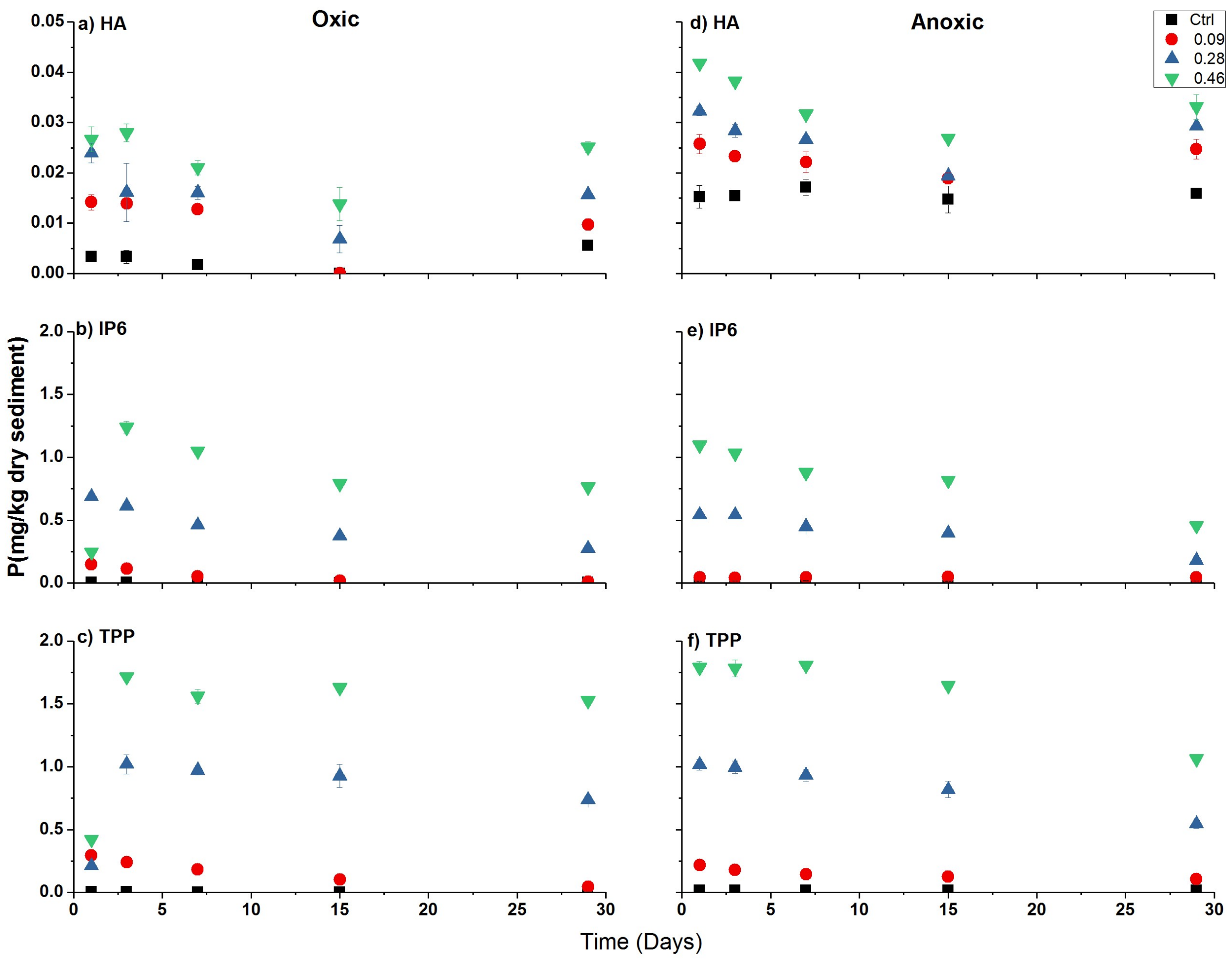

Figure 2.7: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on soluble P in Steed Pond sediment equilibrated in ARW under oxic and anoxic conditions. Error bars represent 95% confidence intervals.

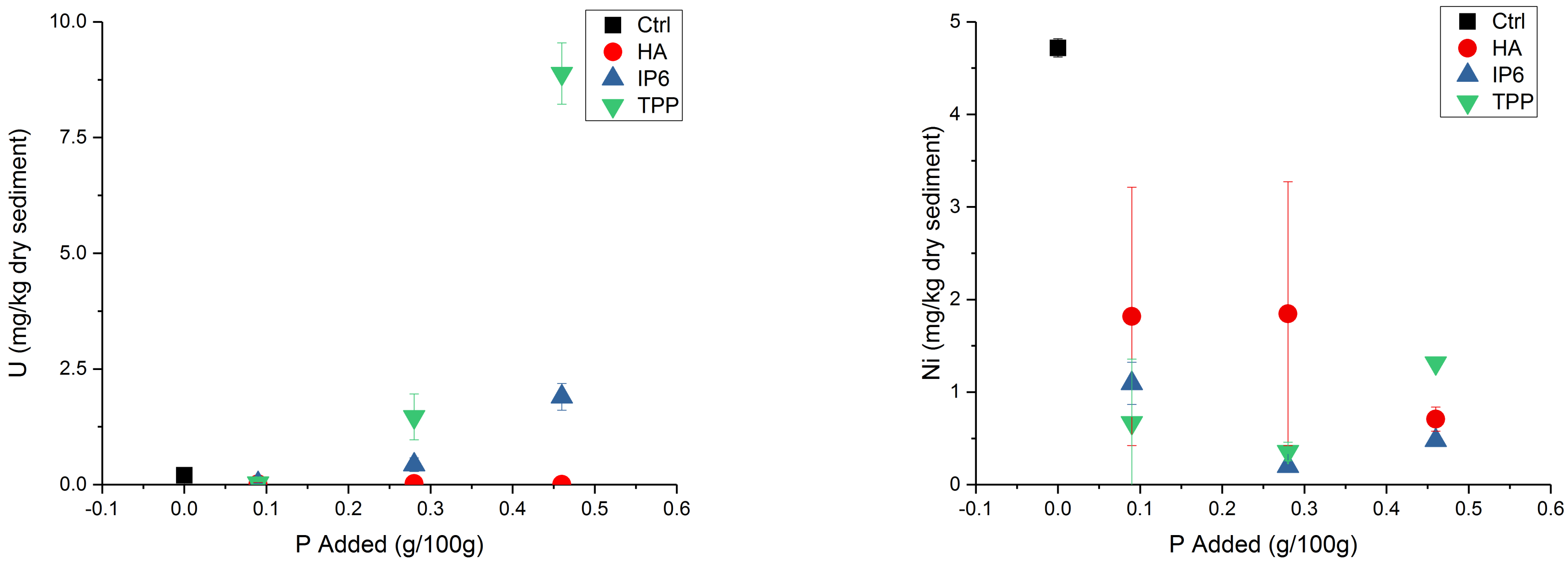

Figure 2.8: Effect of HA, IP6, and TPP amendments at varying levels (g P per 100 g sediment) on soluble U and Ni in Steed Pond sediment equilibrated in unsaturated batch conditions. Error bars represent 95% confidence intervals.

Chapter 3

Effect of Phosphate Amendments on Contaminant Partitioning in Soil

3.1 Introduction

In-situ contaminant immobilization is generally far less disruptive to contaminated ecosystems and less expensive than conventional soil removal and disposal, especially when applied to expansive areas (38). *In-situ* immobilization covers a wide range of soil remediation strategies and generally focuses on changing the chemical speciation of the target contaminant through the addition of a reactive phase such as liming materials, phosphates, zeolites, clays, Fe metal, Fe and Mn oxides, and organic matter. By adding a reactive binding agent (amendment) to the soil while leaving the soil structure and function generally intact, *in-situ* remediation aims to reduce the contaminants labile fraction (the fraction that can be easily released in solution) (32). *In-situ* amendments effectively reduce contaminant mobility by promoting the formation of insoluble precipitates or by enhancing the soil's capacity to bind the contaminant via more stable sorption mechanisms. However, the immobilized contaminant remains in place and may become a hazard again, necessitating a thorough understanding of the underlying mechanisms controlling contaminant partitioning in treated systems.

Tims Branch is a second-order stream and a tributary of Upper Three Runs Creek draining approximately 16 km^2 and eventually feeding into the Savannah River on the SRS, a DOE facility. Tims Branch received approximately 44,000 kg of depleted U from the M Area fuel and target assembly fabrication facility between 1954 to

1984, seventy percent of which was deposited in Steed Pond. Steed Pond is a former farm pond approximately 4.5 hectares in area which acted as a settling basin for contaminants (19; 66), making it an ideal candidate for *in-situ* remediation. Tims Branch-Steed Pond also received large amounts of Ni and other contaminants associated with nuclear materials production (51).

Chemical immobilization using phosphate amendments, such as mineral apatite $[Ca_5(PO_4)_3(OH,F,Cl)]$, hydroxyapatite $[Ca_5(PO_4)_3(OH)]$, and phosphate salts, has proven effective in reducing the mobility of several metal (Pb and others) and radionuclide (U and others) contaminants (3; 7; 40; 47; 58; 59; 65). This approach is generally limited to surficial areas of contamination where relatively insoluble reactants can be readily mixed with the contaminated material. Previous research has investigated a range of soluble PO_4-containing materials, including inositol hexaphosphate (IP6) and sodium tripolyphosphate (TPP), to potentially overcome such limitations (2; 58; 59; 74). Success depends on the material's compatibility with the geology and groundwater chemistry of a given site (34; 58; 56). The potential effectiveness of IP6 and TPP relies on the compound yielding orthophosphate through degradation reactions, which can then precipitate with the target contaminants.

The reduced oxidation state of uranium, U(IV), is orders of magnitude less soluble than the oxidized state, U(VI). Under oxidizing conditions and neutral pH, U(VI) species can be immobilized by adsorption to iron minerals (33). Under reducing conditions, U(VI) can be reduced to immobile U(IV) by reduced iron [Fe(II)] or sulfur species (15; 27). While the direct precipitation of uranium-phosphate solids has been noted in previous studies using more soluble PO_4-containing materials than HA (74), so has enhanced mobilization and possible migration of contaminants (34; 58; 56), increasing the need to understand the fundamental mechanisms controlling contaminant partitioning in any treated system.

In order to identify the effect of water content and redox conditions on the mechanisms and efficacy of the P-based amendments in immobilizing target contaminants, three different batch tests were conducted. The current objective was to better understand U and Ni solid-phase distribution in Steed Pond sediments and whether different phosphate treatments or batch conditions effect their distribution or mobility within the environment. Toxicity Characteristic Leaching Procedure (TCLP) and sequential extraction techniques were used to improve our understanding of the effect phosphate amendments have on U and Ni immobilization and solid-phase distribution in Steed Pond sediments. The EPA TCLP extraction is a standardized method for determining if a soil/sediment can be classified as hazardous waste (meaning they would have to be treated at a hazardous waste facility). As a commonly performed test, TCLP extraction allows for comparison with other studies that perform the same procedure. Sequential extraction schemes are designed to selectively extract contaminants associated with a specific reactive soil fraction, depending on the fraction it is associated with (organic, amorphous Fe-oxide, or crystalline Fe-oxide) or the mechanism controlling sorption (cation or anion exchange). As an operational method, it may be better to consider sequential extractions as indicative of the chemical conditions under which the contaminant of interest may become bioavailable and/or mobile.

3.2 Materials and Methods

The residual sediment from the oxic and anoxic saturated batches from the previous chapter (Chapter 2) were used, as well as a controlled unsaturated batch test. Residual soils from the oxic and anoxic saturated batches were air dried prior to extraction.

The unsaturated batch test consisted of the same soil and amendment ratios as the oxic and anoxic batches. The soil and the amendment were mixed together and ultra-pure water was added to reach 60 percent of the water retention capacity of the soil by recorded weight. The batch treatments were equilibrated for 3 weeks at room temperature and maintained at a constant water level, i.e. 60 percent of the water retention capacity. After the equilibration period, pore water was extracted using centrifugation (J6-MI, Beckman Coulter) (3,000 rpm for 30 minutes). As in the previous chapter (Chapter 2), pore solution from the unsaturated treatments were acidified (2% HNO_3) and analyzed for U and Ni by ICP-MS. Residual sediment samples were air dried, homogenized, and split into subsamples. Contaminant partitioning was evaluated on the air dried samples using the TCLP (EPA Method 1311 (73)) extraction and a commonly used sequential extraction method (39) (detailed below).

TCLP

TCLP extraction was performed for all treatments with 30 mL of the extracting solution added to 1.5 grams of sediments in centrifuge tubes. The TCLP extraction solution consists of 0.1 M glacial acetic acid and 0.0643 M sodium hydroxide to achieve a final pH of 4.93. Samples were placed on a reciprocating shaker for 18 hours, centrifuged, and then the supernatant was filtered through 0.2 μm pore-size filters. Filtered samples were acidified with trace-metal grade HNO_3 to $pH < 2$ and analyzed for U and Ni by ICP-MS.

Sequential Extraction

In the current study, a sequential extraction protocol based on the modified Miller et al. (1986) method was used (39). The same method has been previously applied in other studies involving U immobilization, i.e. Arey et al. (1999) and Seaman et al. (2001) (Table 3.1) (2; 59). Each extraction was performed in triplicate for each of the sediment treatments. Approximately 0.75 g of air-dried sediment (from the batch experiments) was contacted with each reagent in sequence from least to most chemically aggressive. Procedural order and [target extract phase] as listed: 1) deionized water [water soluble]; 2) 0.5 M $Ca(NO_3)_2$ [exchangeable]; 3) 0.44 M glacial acetic acid + 0.1 M $Ca(NO_3)_2$ [acid soluble]; 4) 0.01 M $NH_2OH * HCl$ + 0.1 M HNO_3 [Mn occluded]; 5) 0.1 M $Na_4P_2O_7 * 10H_2O$ [organically bound]; 6) 0.175 M $(NH_4)_2 - C_2O_2 * H_2O$, 1 M $H_2C_2O_4$ [amorphous Fe oxides]; 7) reduction with 0.5 g Na dithionite in sodium citrate buffer 0.15 M $Na_3H_5C_6O_7$ + 0.05 M $H_8C_6O_7$ [crystalline Fe oxides] (Table 3.1). U and Ni in sequential extractions were analyzed using ICP-MS.

3.3 Results

3.3.1 Toxicity Characteristic Leaching Procedure Results

Figure 3.1 shows the level of TCLP-extractable U in mg kg^{-1} for control, HA, IP6, and TPP amended sediment samples as a function of the amendment levels under oxic (3.1a), anoxic (3.1b), and unsaturated conditions (3.1c). TCLP extraction results were corrected for initial contaminant removal during the 30-day batch equilibrations to avoid biasing treatments for which a large portion of the most labile U fraction was already removed during initial treatment equilibration (see Chapter 2). The corrected TCLP extraction results are provided in 3.1d, e, and f.

Under all three test conditions, TCLP-extractable U was highest for the corrected control samples (i.e., 128 ± 15 mg kg^{-1} oxic, 120 ± 39 mg kg^{-1} anoxic, and 102 ± 28 mg kg^{-1} unsaturated). It is interesting to note that the TCLP-extractable U levels for the corrected oxic and anoxic controls were quite similar given that the two treatments were equilibrated under different atmospheres. However, the lower level of TCLP-extractable U observed for the unsaturated controls may reflect the much

Table 3.1: Sequential extraction procedure for trace element partitioning assessment. (Modified Miller et al. 1986 method)

Step	Target Fraction	Reagent	Time (h)	Notes
1	Water soluble	deionized water	16	
2	Exchangeable (outer-sphere complexes)	0.5 *M* calcium nitrate	16	
3	Acid soluble (inner-sphere complexes)	0.44 *M* acetic acid 0.5 *M* calcium nitrate	8	
4	Manganese oxides	0.01 *M* acidified hydroxylamine hydrochloride	0.5	
5	Organically bound	0.1 *M* sodium pyrophosphate	24	
6	Amorphous Fe oxides	0.175 *M* ammonium oxalate 0.1 *M* oxalic acid	4	darkness or red light
7	Crystalline Fe oxides	0.15 *M* sodium citrate 0.05 *M* citric acid 0.75 g sodium dithionite	0.5	50°C

lower degree of agitation, mixing, and disturbance the unsaturated samples experienced when compared to the more conventional oxic and anoxic batch equilibrations. When not corrected for U extracted during the initial batch experiments, each of the three P amendments followed the same trend of decreasing TCLP-extractable U with increased treatment levels for oxic, anoxic, and unsaturated conditions, with IP6 and TPP appearing to be clearly more effective than HA. However, the trends are less obvious after correcting for U extracted during initial batch equilibrations. The oxic samples amended with the highest levels of TPP were the only samples that did not follow the trend of decreasing TCLP-extractable U with increasing amendment addition. At lower amendment levels, the HA amended samples showed higher TCLP-extracted U concentrations than either IP6 or TPP amended samples under both oxic and anoxic conditions. At the lowest HA amendment level, TCLP-extracted U concentrations were 98 ± 2 mg kg^{-1} and 109 ± 44 mg kg^{-1} under oxic and anoxic conditions, respectively. At the highest HA amendment level, TCLP-extracted U concentrations decreased to 64 ± 7 mg kg^{-1} (oxic) and 45 ± 13 mg kg^{-1} (anoxic). IP6 and TPP showed similar TCLP-extractable U concentrations for the different amendment levels under both oxic and anoxic conditions. At the lowest IP6 and TPP amendment levels, TCLP-extractable U concentrations were 75 ± 7 and 82 ± 6 mg kg^{-1}, respectively, under oxic conditions and 90 ± 22 and 71 ± 18 mg kg^{-1} (IP6 and TPP) under anoxic conditions. At the highest amendment levels, extractable U concentrations were 28 ± 8 and 31 ± 6 mg kg^{-1} (IP6 and TPP) under oxic conditions and 20 ± 9 and 26 ± 4 mg kg^{-1} (IP6 and TPP) under anoxic conditions.

While the same U concentration decrease with increased amendment addition was seen under unsaturated conditions, HA and IP6 showed more similar TCLP-extractable U concentrations for the various amendment levels and a slightly higher TCLP-extractability than TPP-amended samples. For the unsaturated treatments, U and Ni concentrations in water extractable fraction were not corrected as less than 1 mL of pore water was extracted from 20 g of soil. The correction was considered insignificant because of the very low solution to soil mass ratio inherent to the unsaturated test conditions. Samples treated at the lowest level of all three amendments showed similar U extraction concentrations: 85 ± 15 mg kg^{-1} for HA, 82 ± 12 mg kg^{-1} for IP6, and 77 ± 4 mg kg^{-1} for TPP. At the next highest amendment level, HA and IP6 amended samples had TCLP-extracted U concentrations of 74 ± 7 mg kg^{-1} and 73 ± 3 mg kg^{-1}, respectively, while TPP amended samples had a TCLP-extracted U concentration of 54 ± 6 mg kg^{-1}. At the highest amendment level, samples treated with HA and IP6 had U concentrations at 61 ± 16 mg kg^{-1} (HA) and 60 ± 9 mg kg^{-1} (IP6) while TPP treated samples at this amendment level had U concentration of 30 ± 4 mg kg^{-1}. Higher levels of IP6 and TPP amendment made pore water extremely difficult to extract through centrifugation due to the amount of clay dispersion those amendments caused.

Extractability of U decreased with increasing treatment level for all treatments under all conditions tested with the exception of the samples amended at the highest level of TPP under oxic conditions. Even then, these samples still showed less U extractability than control samples.

Figure 3.2 shows the level of TCLP-leachable Ni in mg kg^{-1} for control, HA, IP6, and TPP amended sediment samples as function of the amendment levels under oxic (3.2a), anoxic (3.2b), and unsaturated conditions (3.2c). The corrected TCLP extraction results are provided in 3.2d, e, and f. Correcting for the Ni extracted during initial equilibration was especially important because of the high amounts of Ni extracted in the controls before correction. Also, note the difference in scales used for Ni extracted samples in the corrected oxic figure versus every other Ni figure. There was a three times increase in the Ni concentration between the control sample under saturated oxic conditions and the unsaturated control once corrected for Ni fraction removed during initial treatment equilibration. It also appeared that uncorrected, the samples treated with P amendments under oxic conditions were not as effective as the control sample (18 ± 2 mg kg^{-1}) at decreasing Ni TCLP leachability except at the highest treatment level. Also, HA amended oxic samples increased TCLP Ni extractability with increasing amendment addition (20 ± 2 mg $^{-1}$ at lowest treatment level and 22 ± 7 mg kg^{-1} and highest amendment levels) when not corrected.

Once corrected, all HA amended samples had TCLP-extractable Ni concentrations lower than the control (75 ± 2 mg kg^{-1}) under oxic conditions, and all P amended samples had decreased TCLP-leached Ni concentrations with increasing amendment level under oxic conditions. IP6 and TPP amended samples were slightly more effective at controlling Ni TCLP-leachability than HA amended samples under oxic conditions. HA amended samples decreased TCLP-leachable Ni concentrations from 46 ± 2 mg kg^{-1} at the lowest HA amendment level to 27 ± 7 mg kg^{-1} at the highest HA amendment level under oxic conditions. IP6 and TPP amended treatments had similar amounts of Ni leached at the different amendment levels and decreased from 29 ± 2 (IP6) and 28 ±3 (TPP) mg kg^{-1} at the lowest amendment levels to 24 ± 1 (IP6) and 27 ± 1 (TPP) mg kg^{-1} at the highest amendment levels under oxic conditions.

Under anoxic conditions, Ni was most TCLP-extractable for the control (30 ± 7 mg kg^{-1}) and lowest HA (32 ± 7 mg kg^{-1}) amended samples. The HA sample with the lowest amendment addition was the least effective anoxic sample at immobilizing Ni (32 ± 7 mg kg^{-1} Ni), and was not as effective as the anoxic control. The two other HA treated samples were more effective than both the control and lowest HA amendment with TCLP-extracted Ni concentrations of 26 ± 4 mg kg^{-1} and 25 ± 4 mg kg^{-1} respectively. IP6 and TPP amended samples were all more effective than the control at lowering TCLP Ni extractability under anoxic conditions with both IP6 and TPP amendments being generally more effective at higher amendment levels; the exception was the highest TPP amended sample. Anoxic IP6 amended samples at the lowest amendment level had Ni TCLP-extractable concentrations similar to the control at 28 ± 7 mg kg^{-1} but the middle amendment level dropped to 24 ± 3 mg kg^{-1} Ni and the highest IP6 level had a Ni TCLP-extracted concentration of 24 ± 1 mg kg^{-1}. Anoxic TPP amended samples result in similar Ni concentrations as IP6 amended samples. The lowest TPP amendment level result in a Ni concentration of 25 ± 4 mg kg^{-1}, the middle amendment level had 23 ± 1 mg kg^{-1} Ni, and the highest amendment level had 28 ± 2 mg $^{-1}$.

For the unsaturated samples, the control had a Ni TCLP-extractable concentration of 23±3 mg kg^{-1}. HA amended samples were similarly effective at controlling TCLP Ni extractability at all amendment levels at 23 ± 1 mg kg^{-1} Ni (lowest amendment level) and 24 ± 3 mg kg^{-1} Ni (middle amendment level) and the highest amendment level (22 ± 2 mg kg^{-1}). IP6 and TPP treated unsaturated samples showed decreasing Ni TCLP-extractability with increasing amendment levels. At the lowest amendment levels, IP6 amended samples had TCLP-extracted Ni concentrations of 23 ± 3 mg kg^{-1} and TPP amended samples had 25 ± 2 mg kg^{-1} at the lowest amendment level in unsaturated conditions. At the middle amendment levels in unsaturated conditions both IP6 and TPP amended samples dropped to similar TCLP-extracted Ni concentrations (21 ± 1 and 19 ± 1 mg kg^{-1} for IP6 and TPP). The highest amendment levels we again similarly effective at immobilizing Ni in unsaturated conditions with IP6 at 17 ± 1 mg kg^{-1} and TPP at 15 ± 1 mg kg^{-1} Ni.

3.3.2 Sequential Extraction

Sequential extractions for U were conducted on Steed Pond sediment amended with either HA, IP6, or TPP at three different treatment levels for each amendment under oxic, anoxic, and unsaturated conditions (see Methods and Materials from Chapter 2). Regardless of the batch conditions (oxic, anoxic, or unsaturated), U fractionation was dominated by the Mn-oxide occluded and organically bound fractions (ranging from 21-46 % each depending on amendment and redox condition), consistent with observations from Arey et al. (1999) for similar sediments (2).

Under all conditions at all treatment levels for samples amended with HA the water soluble and exchangeable fractions contributed only a minor percent of the

U extracted. Typically less than 1 % of total U extracted from the water soluble, exchangeable, and crystalline Fe-oxide fractions and 2-3 % of extracted U from the amorphous Fe-oxide fraction. The acid soluble fraction represented 7-16 % of the U extracted under all conditions for samples amended with HA, with the percent of U extracted decreasing with increased amendment addition. Under oxic conditions HA amended samples had from 34-38 % U extracted from the Mn-oxide occluded fraction and 33-39 % U extracted from the organically bound fraction. Those percentages were similar under anoxic conditions at 31-40 % U extracted from Mn-oxide occluded fraction and 33-40 % U extracted from the organically bound fraction. The percentages increased slightly under unsaturated conditions with 38-45 % U extracted from the Mn-oxide occluded fraction and 38-46 % extracted from the organically bound fraction.

IP6 and TPP amended samples varied from the HA amended samples by a few percent in different fractions, but showed the same general trend with respect to U partitioning as the HA amended samples. There was still a relatively minor contribution to the percent U extracted from the water soluble, exchangeable, amorphous Fe-oxide, and crystalline Fe-oxide fractions for both IP6 and TPP amended samples under all conditions. The exchangeable and crystalline Fe-oxide fractions represented 1 % or less of the U extracted. The amorphous Fe-oxide fraction of IP6 and TPP amended samples represented 2-3 % of U partitioning under all conditions. The water soluble fraction of IP6 and TPP amended samples represented 1-5 % of U extracted under oxic conditions and 1-3 % of U extracted under anoxic and unsaturated conditions. IP6 and TPP amended samples bound 7-16 % of U in the acid soluble fraction and this percentage decreased with increased amendment addition under all conditions. Under oxic conditions, IP6 and TPP amended samples had 30-37 % of U bound to the Mn-oxide occluded fraction and 30-38 % by the organically bound fraction. Under anoxic conditions, those percentages dropped to 23-32 % in the Mn-oxide occluded fraction, while U bound to the organically bound fraction represented 34-44 % for IP6 and TPP amended samples. Mn-occluded fractions of unsaturated account for 27-39 % U and the organically bound fractions for 35-46 %.

The dominant extraction phase for Ni fractionation was the amorphous Fe-oxide extraction. This was especially true under oxic and unsaturated conditions where Ni was extracted in the amorphous Fe-oxide phase between 30-37 % under oxic conditions and between 30-48 % under unsaturated conditions. Under anoxic conditions, Ni extracted in the amorphous Fe-oxide phase represented between 17-27 %. Ni tended to be better distributed amongst all the sequential extraction fractions than U.

For HA-amended samples, under oxic and anoxic conditions, the percentage of water soluble Ni decreased with the amount of HA added. In oxic conditions it decreased from 10 % in the control sample to 1 % at the highest level of HA addition. Under anoxic conditions, the water soluble Ni fraction in HA-amended samples represented less than 1 % of the total Ni fraction. In unsaturated conditions, increased HA addition increased the percentage of Ni extraction in the water soluble fraction, but all samples represented less than 1 % of the total Ni. IP6 and TPP amended samples increased Ni concentration with increased amendment addition in the water soluble fraction under all conditions. The water soluble fraction of Ni for samples amended with IP6 and TPP represented 1-2 % under oxic and anoxic conditions and 1-7 % in unsaturated conditions.

The exchangeable fraction for samples amended with all three P treatments represented 6-8 % for Ni, which was higher than the 3 % of Ni bound in the control samples under oxic conditions. The control sample for the exchangeable fraction under anoxic conditions had a higher Ni percentage (7 %), but all three P treatment had similar Ni extraction in the exchangeable fraction as the oxic samples (6-7 %).

All samples amended with P treatments in unsaturated conditions had higher Ni percentages (6-10 %) than the control sample (3 %).

The control samples for the acid soluble fraction had 4 to 5 % of the total Ni regardless of equilibration environment. Similarly, all P treatments had 4-7 %t Ni in the acid soluble fraction no matter the amendment level, P treatment, or treatment level.

Ni fractionation was highest for the Mn-oxide occluded extraction under oxic conditions at 7-14 % for samples amended with P (the control was 7 %). Ni percentages were slightly lower under anoxic and unsaturated conditions conditions for the Mn-oxide extraction at 4-9 % for anoxic (control at 4%) and 6-9 percent in unsaturated conditions (control at 6%).

The organically bound extraction typically produced the second highest Ni fractionation next to the amorphous Fe-oxide fraction with control samples either at 14-15 % of Ni. P treated sample under oxic and anoxic conditions had Ni percentages between 13 and 17 % in the organically bound fraction. The Ni percentage range for the organically bound fraction in unsaturated conditions was slightly larger at between 12-21 % for samples amended with P.

Crystalline Fe-oxide Ni percentages ranged between 6-8 % of Ni under oxic and unsaturated conditions for all samples amended with P (control Ni fractionation was 9% oxic and 8% unsaturated). Anoxic crystalline Fe-oxide samples ranged from 7-11 % of Ni for samples amended with P (Ni was 9 % for control sample).

3.4 Discussion

Chemical extraction methods, like the TCLP and sequential extraction, can be useful for looking at contaminant distribution and making inferences about the chemical mobility and potential availability of metals and/or contaminants in sediment and soils as conditions change.

TCLP

Contaminant extractability generally decreased for both U and Ni with increased treatment addition for all amendments tested. These results generally confirm previous studies using similar sediments and HA at similar treatment levels by Arey et al. (1999), Seaman et al. (2001), and Majs (2011) under oxic conditions, but differ for samples amended with sodium phytate (2; 34; 59). HA amended soil contaminated with U and Ni show a significant decrease in TCLP-extractability. Seaman et al. (2003) and Majs (2011) found that U and Ni TCLP-extractability increased with increasing Na-IP6 addition (34; 58). Both the Seaman et al. (2003) and Majs (2011) studies involved batch equilibrations in a solution of 0.001 M $CaCl_2$ for 5 and 7 days respectively on a reciprocating shaker while this study used an AGW background solution that is closer to natural conditions and a much longer equilibration time, i.e., 30 days on an orbital shaker. This study also observed higher overall TCLP-extractable U and Ni than previous studies by Seaman et al. (2001 and 2003) and Majs (2011) using the same amendments and similar Steed Pond sediments which may be explained in part by the longer contact time and more aggressive solution.

Sequential Extraction

Sowder et al (2003) performed two versions of the Miller sequential extraction method on Steed Pond sediments: one that followed the regular protocol, and the second test that omitted the Mn-oxide extraction step (66). They found that when this extraction step was excluded that the U extracted by this extraction was redistributed to the next extraction step which targeted the organically bound fraction. The redistribution of Ni was among three different fractions, but the Ni from the Mn-oxide fraction only accounted for 8 percent of Ni as opposed to the 49 percent that was represented by the Mn-oxide fraction for U. The highest Ni percentage represented for any treatments was in the Mn-oxide fraction of this current study was 12 percent. Seaman et al. (2001) and Majs (2011) noted that with the minor amount of Mn-oxides present in these sediments, the large U fractionation in this step is most likely an operational artifact caused by the low pH (≈1.26) of the Mn-oxide fraction extractant (34; 59). The full extraction sequence was used in this experiment to allow for better comparison of other studies utilizing the same sequential extraction procedure.

Sowder et al. (2003) listed the sequential extraction steps from 1-7 from very labile (steps 1 and 2) to mildly labile (steps 3-5) to less labile (steps 6 and 7) (66). Their study, like this study, also found that Ni fractionation tended to be dominated by the amorphous Fe-oxide fraction and postulated that Ni fractionation may have been highest in typically less labile target fractions due to representation of primary or secondary phases of source term Ni deposited in Steeds Pond.

Conclusions

Even though higher U and Ni concentrations were extracted than previous studies, the use of P amendments proved effective at decreasing the extractability of both U and Ni under oxic, anoxic, and unsaturated conditions when compared to the no amendment control. Under all conditions and irregardless of P amendment or concentration, U is primarily sequestered in the moderately labile Mn-oxide and organically bound fractions. Ni was highly partitioned to the less labile amorphous

Fe-oxide fraction under oxic and unsaturated conditions, while anoxic conditions sequestered Ni primarily to the residual fraction.

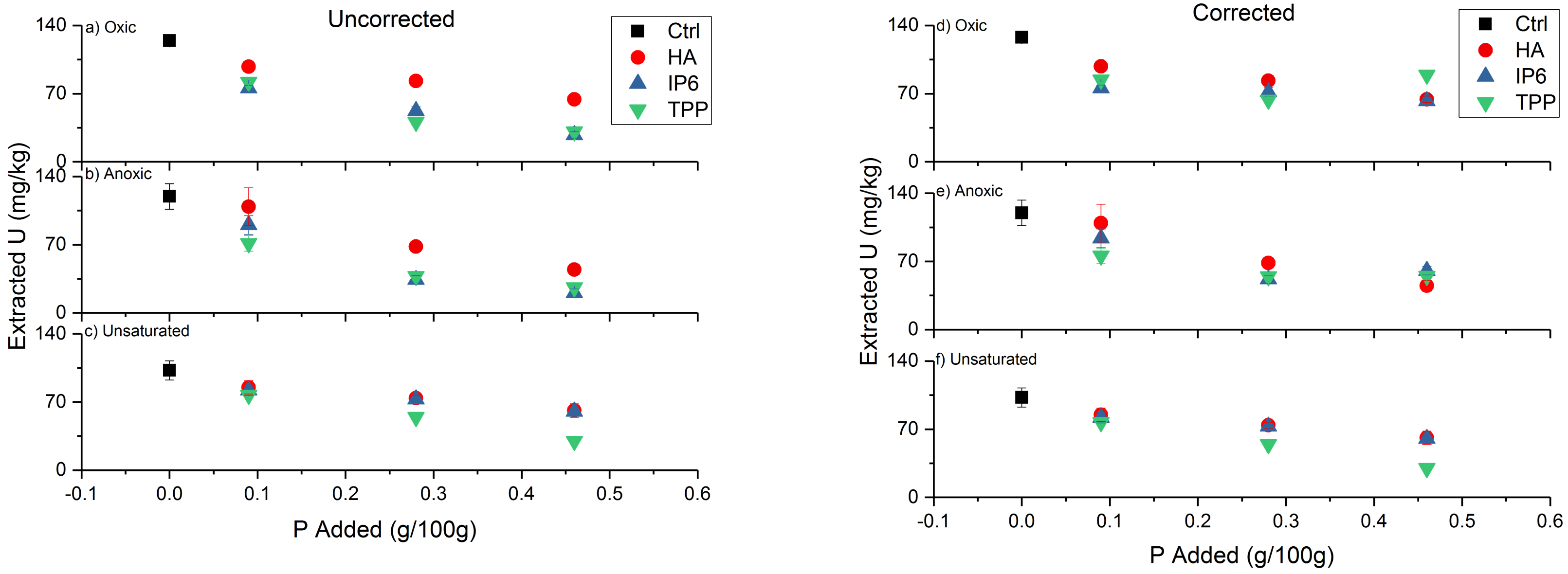

Figure 3.1: Toxicity Characteristic Leaching Procedure (TCLP)-extractability of U from contaminated Steed Pond sediment amended with HA, IP6, and TPP and then equilibrated under oxic (a), anoxic (b), and unsaturated (c) conditions. For graphs d, e, and f, the TCLP-extractable U values were corrected for U removal during initial equilibration and reported on a mass basis. Error bars represent 95% confidence intervals.

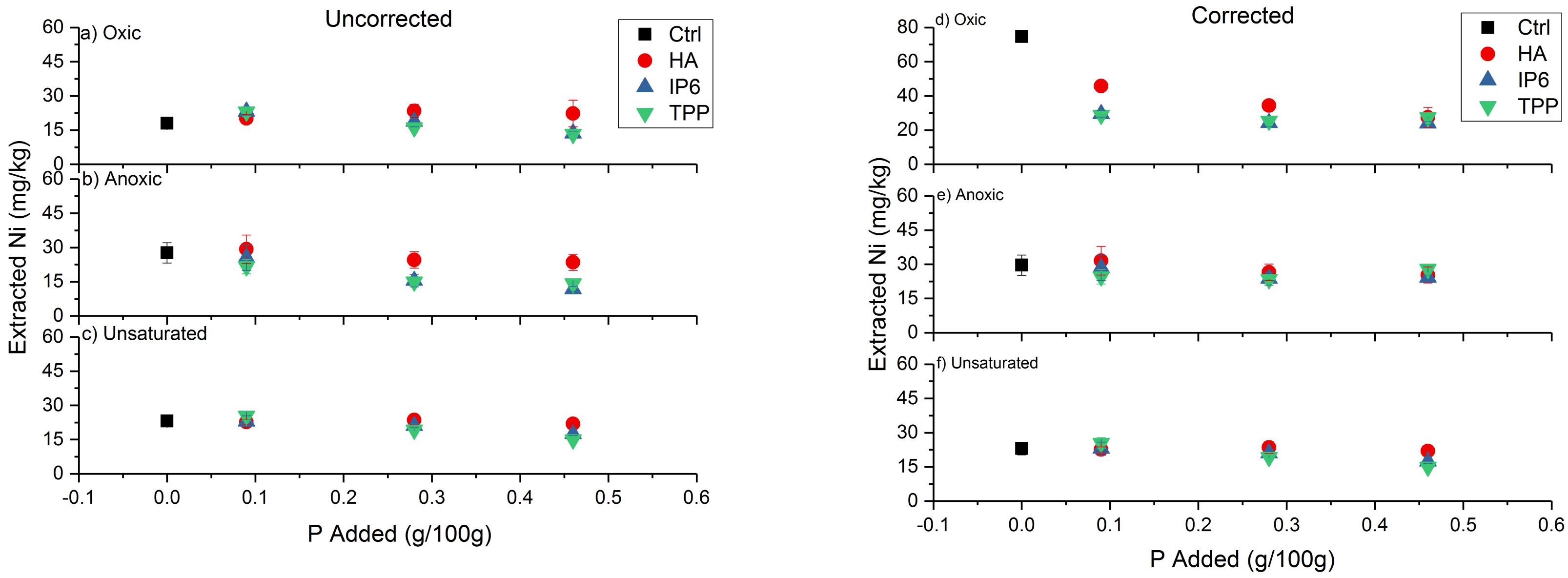

Figure 3.2: Toxicity Characteristic Leaching Procedure (TCLP)-extractability of Ni from contaminated Steed Pond sediment amended with HA, IP6, and TPP and then equilibrated under oxic (a), anoxic (b), and unsaturated (c) conditions. For graphs d, e, and f, the TCLP-extractable Ni values were corrected for Ni removal during initial equilibration and reported on a mass basis. Error bars represent 95% confidence intervals.

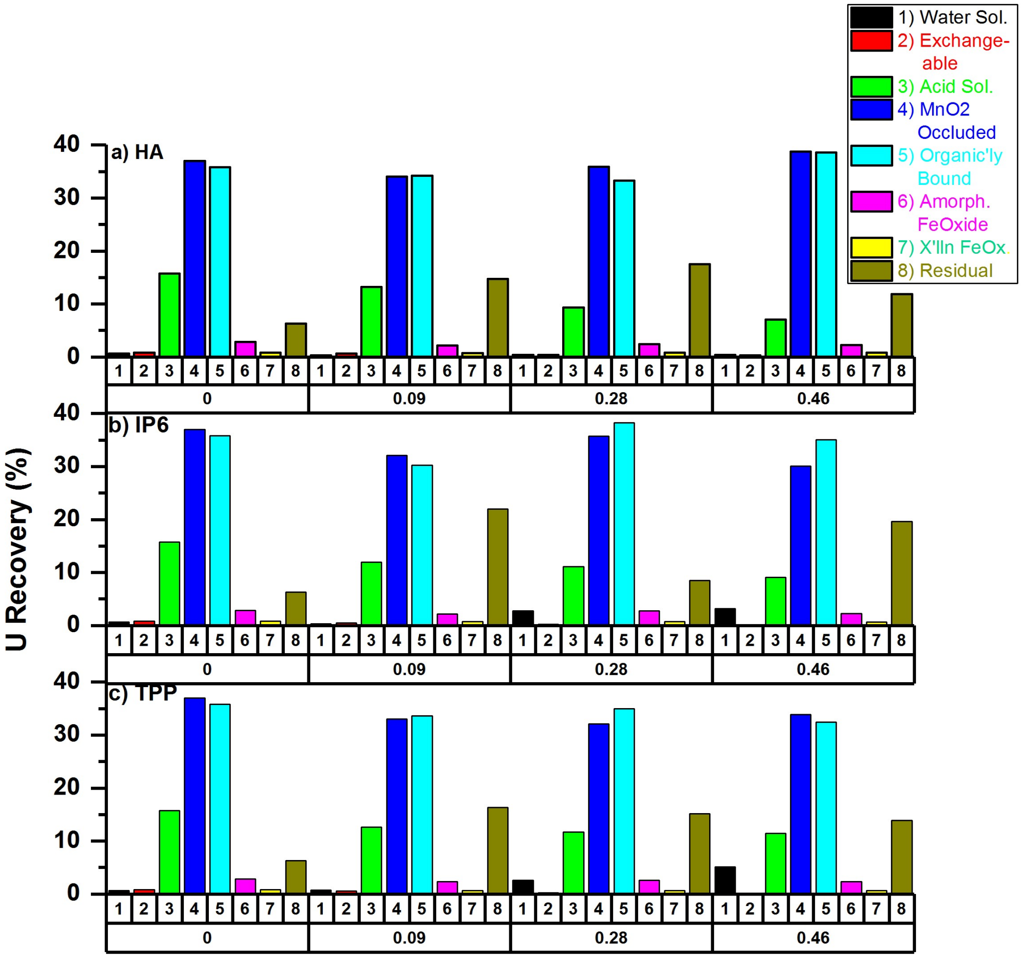

Figure 3.3: Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under oxic conditions.

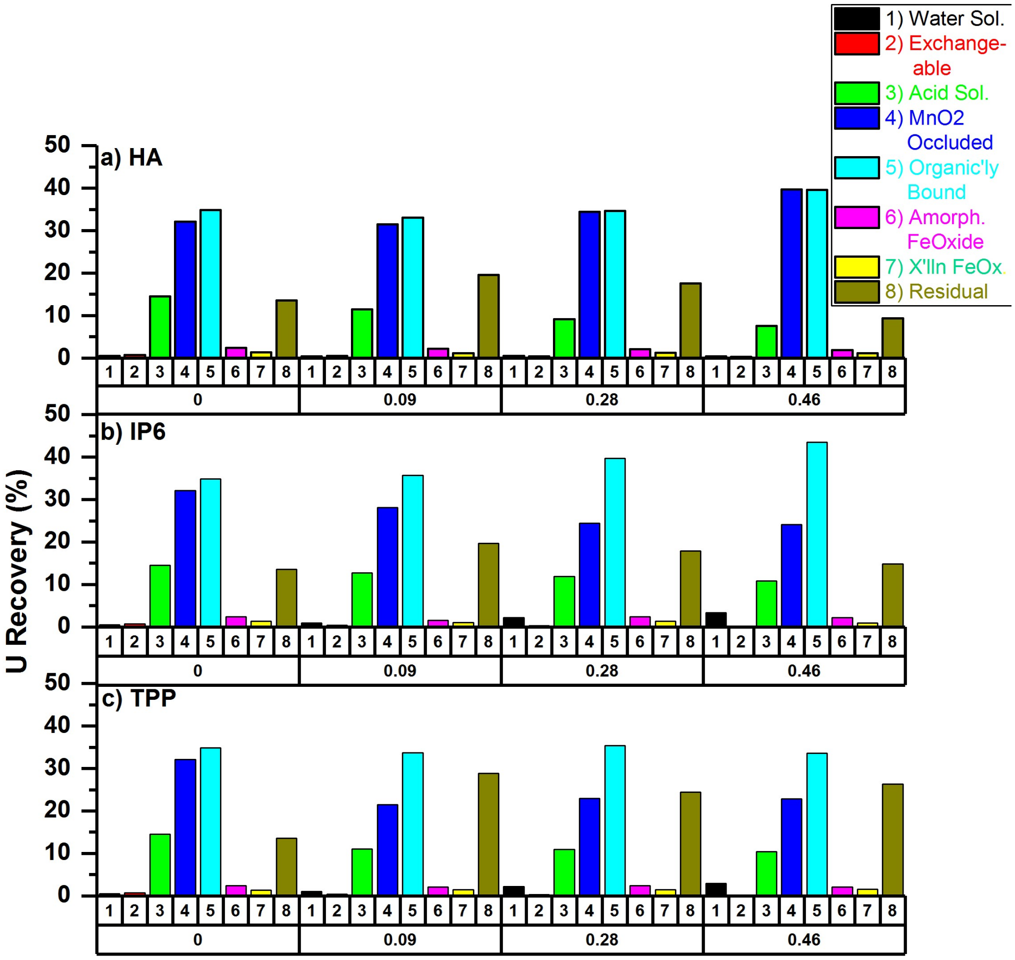

Figure 3.4: Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under anoxic conditions.

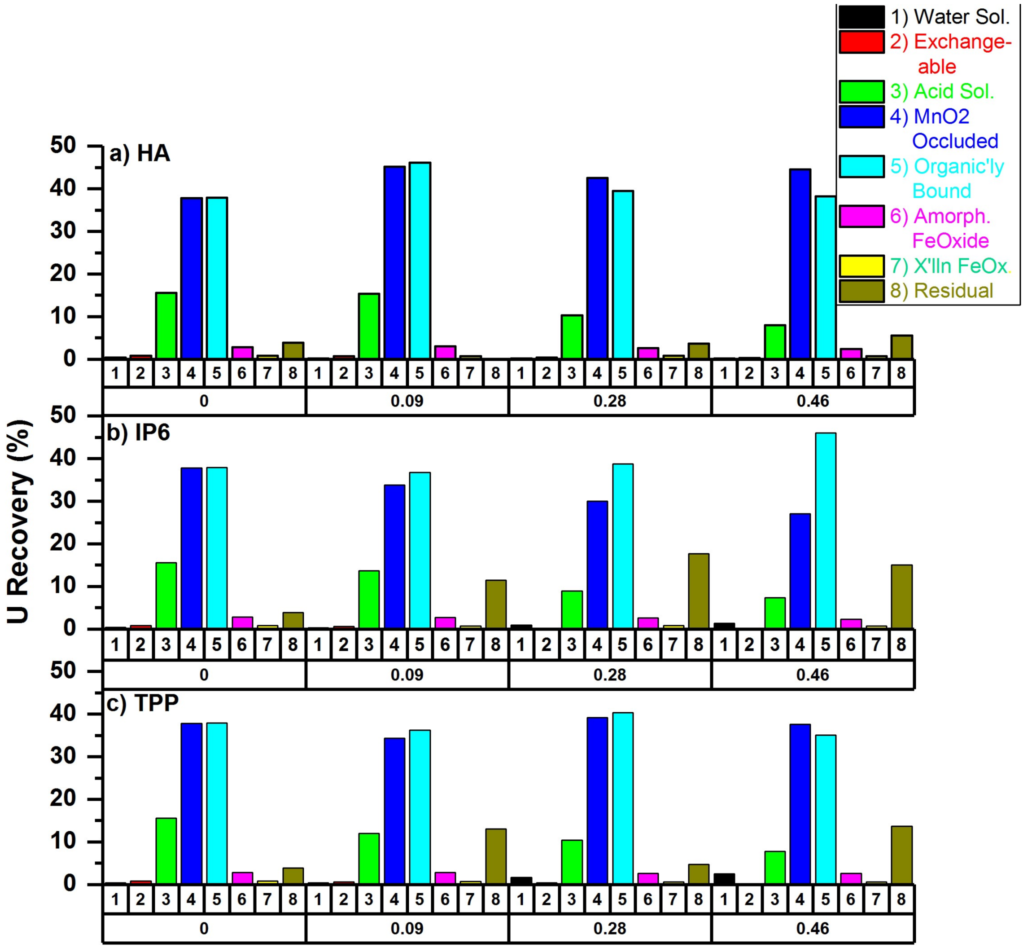

Figure 3.5: Sequential extraction results for U in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP in unsaturated conditions.

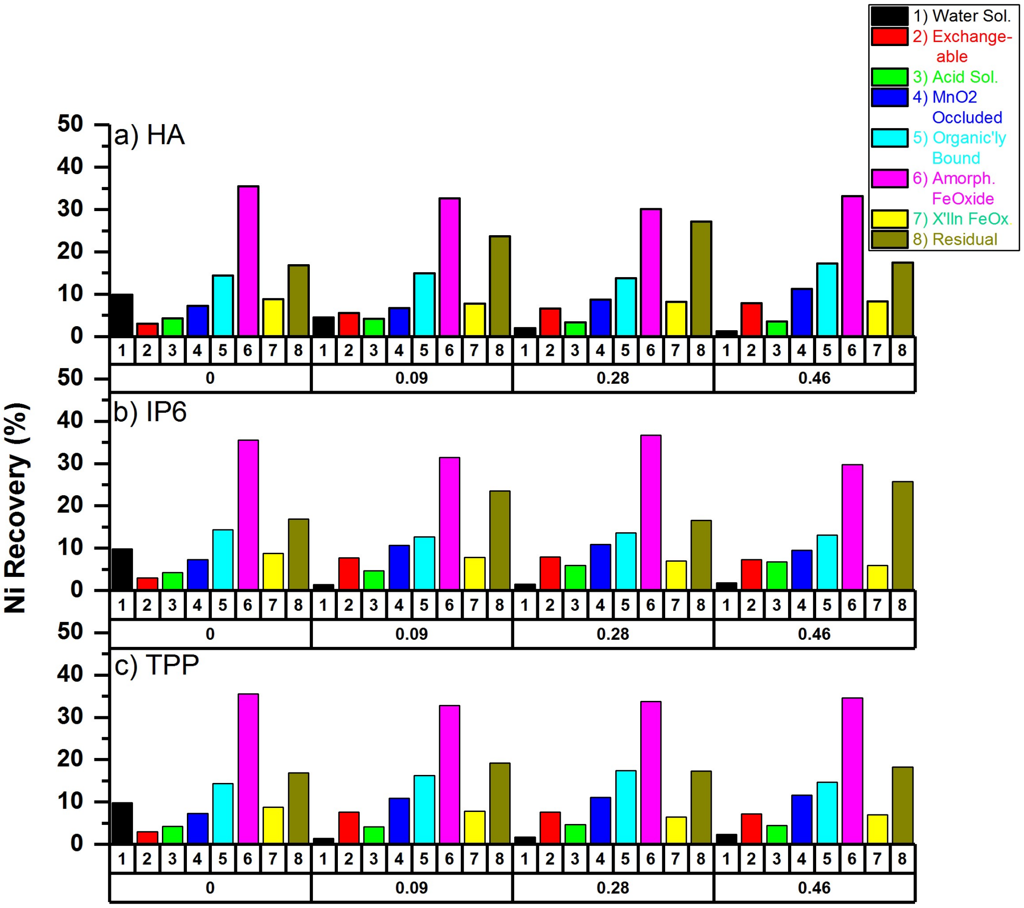

Figure 3.6: Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under oxic conditions.

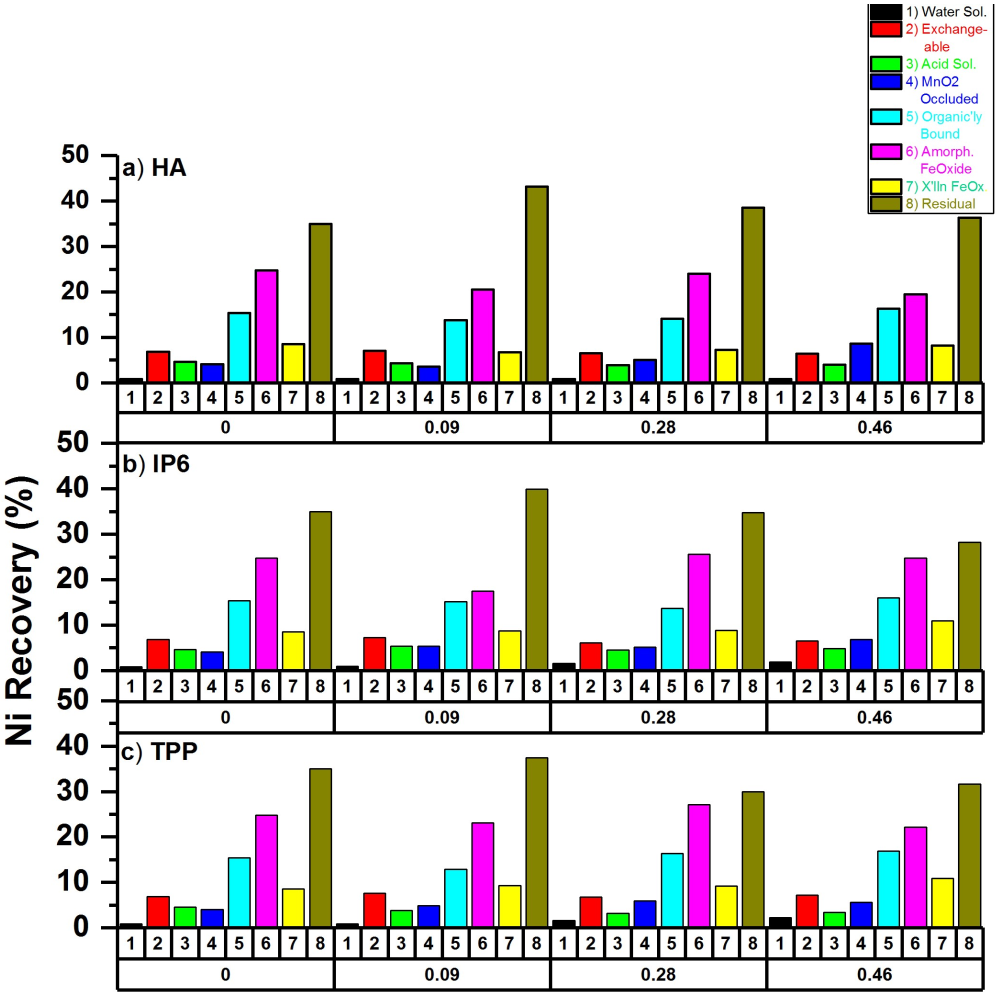

Figure 3.7: Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP under anoxic conditions.

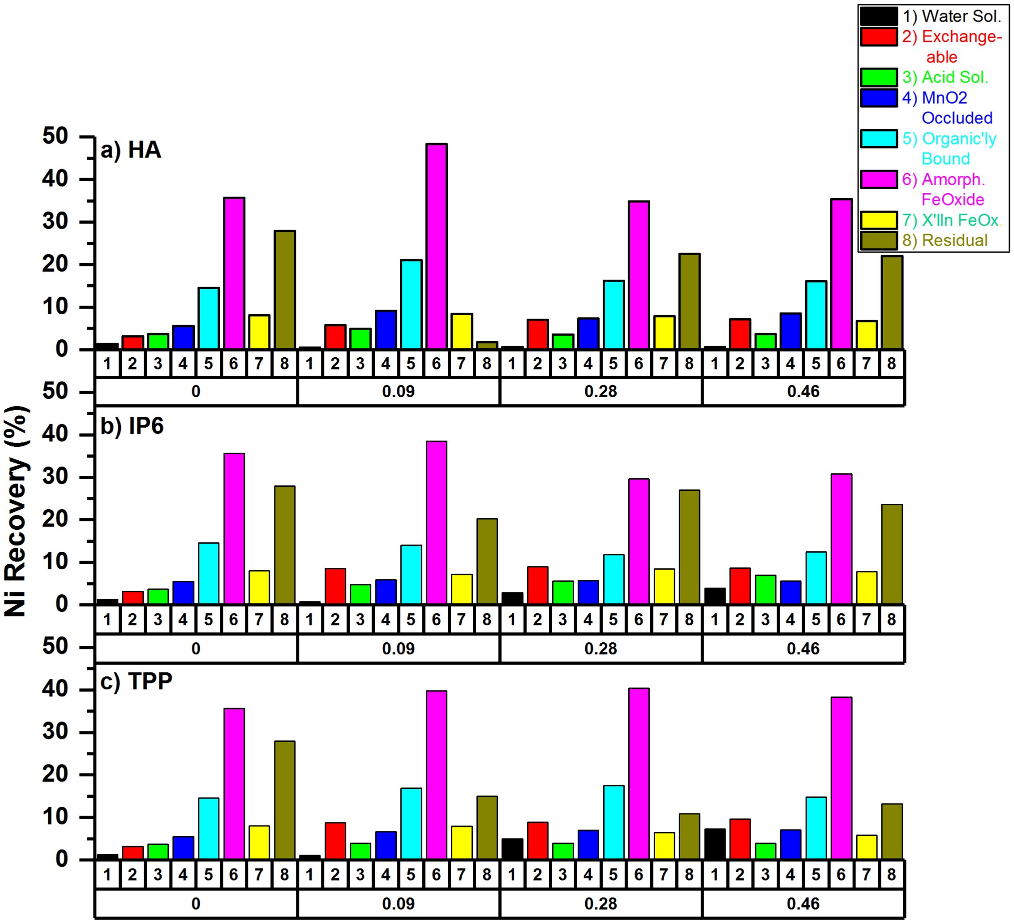

Figure 3.8: Sequential extraction results for Ni in contaminated Steed Pond sediment equilibrated in ARW and amended with varying levels of HA, IP6, and TPP in unsaturated conditions.

Chapter 4

Summary and Conclusions

For many years on the Savannah River Site, Steed Pond received large depositions of U, Ni, and other contaminants associated with nuclear materials production (19; 51; 66). Past studies have shown that apatite and other phosphate materials can be effective for the remediation of soil contaminants (45; 59; 74). Uranium has a complex chemistry and having a better understanding of how it may react under specific chemical conditions is important for use of remediation techniques like *in-situ* immobilization. This study used batch experiments to look at the effectiveness of different P materials (HA, IP6, and TPP) at immobilizing U and Ni in contaminated sediment under varying atmospheric conditions (i.e., oxic and anoxic), as well as evaluated changes in solid-phase speciation of U and Ni in amended sediments using multiple extraction techniques (i.e., TCLP and Miller et al. (1986) sequential extraction methods).

Non-amended samples under oxic conditions showed a stable pH, positive ORP values, and stable DOC levels over time, but non-amended samples under anoxic conditions had an increasing pH, negative ORP values, and stable DOC levels over time. The HA amendment moderately increased sample pH and slightly increased sample DOC in comparison to control samples under both oxic and anoxic conditions, while IP6 and TPP amendments strongly increased sample pH, sample DOC levels, and soluble U concentrations over control samples. While HA was effective at reducing the amount of U in solution at all treatment levels in both oxic and anoxic systems, both IP6 and TPP actually increased the amount of U in solution at all treatment concentrations under both oxic and anoxic conditions. This is likely the result of direct chelation or the solubilization of soil organics that enhance solubility. Our results suggest that HA addition is effective at reducing U solubility, even in systems that may undergo seasonal and episodic changes in saturation and redox conditions. The HA amended samples also visually showed lower solubilization and dispersion of organic matter and clay dispersion compared to the two other phosphate amendments. Control samples equilibrated under anoxic conditions had lower soluble concentrations of both U and Ni than under oxic conditions. The decrease in soluble U concentration observed under anoxic conditions over the duration of the batch experiment possibly indicates chemical reduction to less soluble U(IV). HA was also effective at reducing the amount of Ni in solution under oxic and anoxic conditions at all treatment levels, as compared to the control samples. IP6 and TPP decreased the amount of Ni in solution under both oxic and anoxic environments when compared to the control.

Batches equilibrated in unsaturated conditions indicate that HA was effective at reducing U solubility at all P treatment levels compared to the control. Both IP6 and TPP increased U solubility in pore water, with TPP doing it to a much greater extent than IP6. HA, IP6, and TPP were all more effective than the control at reducing the amount of Ni extracted from pore water at all amendment levels.

Using a standard sequential extraction protocol, the extracts targeting the MnO_2 occluded and Organically bound U were the dominant fractions regardless of P amendment or redox condition. Even though higher U and Ni concentrations were extracted than previous studies, the use of P amendments proved effective at decreasing the extractability of both U and Ni under oxic, anoxic, and unsaturated conditions when compared to the non-amended control. Under all conditions and regardless of P amendment or concentration, U is primarily sequestered in the moderately labile Mn-oxide and organically bound fractions. Water soluble and Exchangeable U were minor fractions for the non-amended control. HA addition decreased acid soluble U (an acetic acid based extraction) for oxic, anoxic, and unsaturated batch treatments, consistent with the TCLP results. Similar trends are observed for the TPP and IP6 treatments under oxic conditions. The increased U solubility observed in oxic, anoxic and unsaturated batch treatments for IP6 and TPP amended samples are also evident in the sequential extraction data, with a clear increase in water soluble U with increased amendment. Additionally, there does appear to be more U in the Organically bound fraction for TPP and IP6 amendments that were equilibrated under anoxic conditions. While Ni was distributed to the less labile amorphous Fe-oxide fraction under oxic and unsaturated conditions, anoxic conditions sequestered Ni primarily to the residual fraction. There was a decrease in water soluble Ni for all treatments compared to the control equilibrated under oxic conditions which was not evident under anoxic conditions. In fact, under anoxic conditions, the soluble Ni seems to increase with increasing TPP and IP6 levels, and this trend is even more evident for the unsaturated batch samples.

As a conclusion, it was identified under the conditions tested, that HA is facilitating a more irreversible immobilization of U. U in HA amended samples was lowered in solution under oxic and anoic conditions while transferring from more soluble Exchangeable and Acid soluble fractions to less soluble MnO_2 and Organically Bound fractions under oxic, anoxic, and unsaturated conditions. U from IP6 and TPP amended samples, while still dominated by MnO_2 and Organically Bound fractions, showed more Water Soluble U fractionation especially at higher amendment levels under oxic, anoxic, and unsaturated conditions, which correlates with the increased U concentrations found in solution for both under oxic and anoxic conditions.

Future research goals include evaluating the enhanced degradation of IP6 and TPP either through direct or indirect microbial processes and eventually resulting in insoluble contaminant-phosphate precipitates. Phytases have been used to hydrolyze precipitated phosphates and release inorganic orthophosphate from various phytates (69), and acid phosphatase production by microbial populations in a U contaminated sediment produced both increases in soluble phosphate in solution and uranyl phosphate precipitation (5).

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