# Mineral Dissolution and Groundwater Arsenic (As) and Uranium (U) Contamination in Newfoundland

by

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# ABSTRACT

The studies presented in this thesis provide critical insights in understanding: (i) arsenic and uranium hosting minerals in natural sediments, and (ii) mechanisms that control arsenic and uranium release from natural sediments to groundwater.

Two distinct sediment samples were collected, characterized, and examined with batch leaching experiments. Scanning electronic microscopy equipped with energy dispersive spectroscopy (SEM-EDX) and sequential extraction results showed that silicate minerals are the main arsenic hosting mineral, containing 75% of the total arsenic. Carbonate, Fe-Mn oxyhydroxides and silicate minerals are the major uranium hosting mineral. Batch leaching experiments showed that, besides desorption, dissolution of Fe oxyhydroxides and silicate minerals is an important mechanism controlling arsenic release. Uranium release increased with increasing pH, Eh, citrate, bicarbonate and natural organic matter (NOM) concentrations. Uranium desorption is the dominant uranium release mechanism under most of the water chemistry conditions tested in our leaching experiments.

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# Nomenclature

As – arsenic

CREAIT - Core Research Equipment & Instrument Training Network

Dfob – siderophore trihydroxamate desferrioxamine B

DO – dissolve oxygen

DOC – dissolve organic carbon

EDX – energy dispersive X-ray spectroscopy

Eh – oxidation/reduction potential

HDPE - high density polyethylene

ICP-MS – Inductively coupled plasma mass spectrometry

kV - kilovolt

L – liter

LOD - limit of detection

M – mole

m – meter

MAC - maximum acceptable concentration

mg/L – milligrams per liter

mL – milliliter

MLA – mineral liberation analysis

mm – millimeter

mM – millimole

mV – millivolt

NOM – natural organic matter

pH – power of hydrogen; a measure of hydrogen ion activity

ppm – parts per million

SEM – scanning electron microscopy

TIC - total inorganic carbon

TOC – total organic carbon

XRD – X-ray diffraction

U - uranium

µg/L – microgram per liter

µM – micromole

# Chapter 1. Introduction and Overview

Groundwater is an important source of drinking water. Arsenic (As) and uranium (U) are common contaminants in groundwater. Arsenic and uranium in groundwater are often the result of water-rock interactions, i.e., As and U are released from their storage in rocks and sediments to groundwater via mineral dissolution and/or desorption processes. In order to predict and control As and U contamination in groundwater, we need the knowledge of occurrence of As and U in nature, their forms of existence, and the geochemical processes that control As and U release from rocks/sediments to groundwater.

## 1.1 Arsenic in nature, its chemical forms, toxicity and release mechanisms

Arsenic is widely distributed in the environment, and ranks 20th in abundance in relation to the other elements (Voigt et al., 1996; Plant et al., 2003; Nriagu et al., 2007). More than 300 minerals have arsenic as one of their constituents and arsenic is a component of some ores, especially nonferrous ores containing Cu, Pb, Zn and Au (Lorenzen et al., 1995; Rageh et al., 2007). Arsenic (As) in the environment originates from natural enrichment, and is intensified by man-made activities (Korte and Fernando, 1991; Smedley and Kinniburgh, 2002). Arsenic occurs naturally in a wide range of minerals. The most common As-containing minerals are arsenopyrite (FeAsS), realgar (AsS), and orpiment ($As_2S_3$) (Nriagu et al., 2007). Arsenic concentration in natural water varies greatly, ranging from < 0.0005 mg/L to > 5 mg/L (Smedley and Kinniburgh, 2002). Although elevated arsenic in groundwater can be found in a variety of hydrogeologic regions, it occurs most commonly in geothermal regions (Ballantyne and Moore, 1988; Welch et al., 1988; Langner et al., 2001), areas of evaporative concentration (Welch et al., 1988), alluvial and deltaic aquifer containing iron oxides (Nickson et al., 1998; Ahmed et al., 2004; Akai et al., 2004), and areas that contain arsenic-bearing sulfide deposits (Schreiber et al., 2000). In Newfoundland, Canada, As is found in igneous and sedimentary rocks. Igneous rocks such as granite have As concentrations ranging from 0.2-13.8 mg/kg while sedimentary rocks such as shale, limestone, and sandstone have higher As concentrations ranging from 0.3-500, 0.1-20, and 0.6-120 mg/kg, respectively. Sulfide minerals are the main As bearing formations in Newfoundland since they are abundant in mafic lavas and igneous rock (Allard, 1995; Rageh et al., 2007; Serpa et al., 2009).

Arsenic (As) occurs in four oxidation states (-3, 0, +3, and +5), and prevails as both inorganic and organometallic species. The forms of arsenic are dependent on pH, redox potential (Eh) (Fig. 1.1 & 1.2), and microbial activity (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). In aqueous solution, As toxicity depends on its speciation and oxidation state. Compared to As (V), As (III) is more soluble, mobile and toxic (Rageh et al., 2007). A large portion of arsenic is in the form of As (III) in aquatic sediments because As (V) is reduced to As (III) under reducing conditions (Chuang et al., 2005). Arsenites ($H_3AsO_3$ and $H_2AsO_3^-$) normally predominate in slightly reduced soils whereas arsenates ($H_2AsO_4^-$ and $HAsO_4^{2-}$) occur predominantly in well oxidized soils (Goh and Lim, 2004).

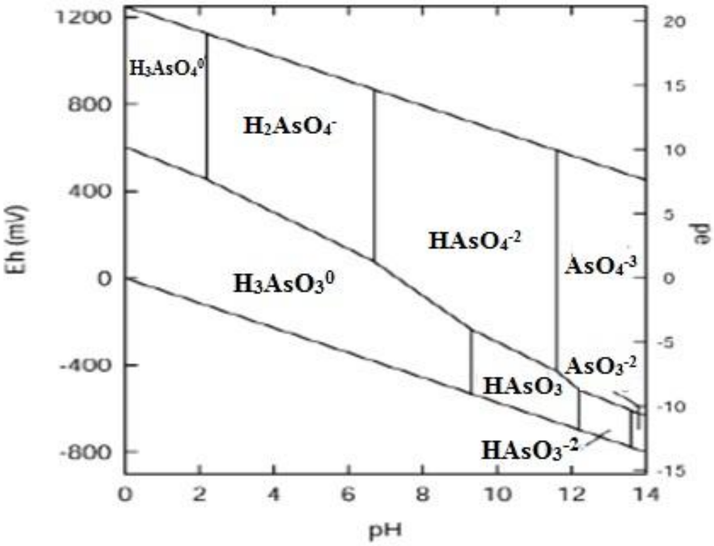

Figure 1.1: Eh-pH diagram for aqueous As species in the system As–$O_2$–$H_2O$ at 25°C and 1bar total pressure. The curvy line separates the As between the oxidation states, V and III (source: Smedley and Kinniburgh 2002).

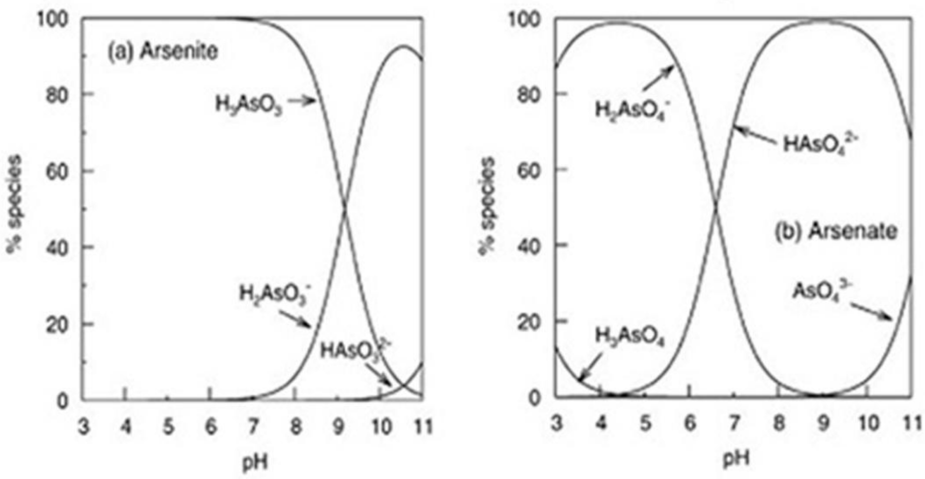

Figure 1.2: Dissociation diagram for (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M; Eh = 0.0 mV) (source: Smedley and Kinniburgh 2002).

Arsenic (As) is both toxin and carcinogen. Once As concentration in the human body reaches toxic level, every organ, including heart, blood/bone marrow, liver and skin, will be affected (Ferreccio et al., 2000; Gonzaga et al., 2006; Wasserman et al., 2011). Toxic levels of As also lead to impairment of mitochondrial function, which results in optic and peripheral neuropathy (Carelli et al., 2002; Sadun, 2002). Over the past two decades, there has been a growing concern about the health risks associated with high levels of As in the environment, especially in groundwater which are used as drinking water sources. In many cases, adverse health effects of As have been associated with the consumption of As-tainted drinking water (Smedley and Kinniburgh, 2002). The maximum acceptable concentration (MAC) for arsenic in drinking water recommended by Health Canada is 0.01 mg/L (Rageh et al., 2007).

Geogenic arsenic contamination in aquifer rocks has been reported in various parts of the world, viz. Bangladesh, India, Thailand, Vietnam, Inner Mongolia, Greece, Hungary, USA, Canada, Chile, Argentina and Mexico (Fig. 1.3) (Smedley and Kinniburgh, 2002; Visoottiviseth et al., 2002; 2005; Wang and Mulligan, 2006; Ravenscroft et al., 2009). Arsenic contamination of water and food crops through natural release of the element from aquifer rocks have recently been notably observed in Bangladesh and West Bengal, India (Hopenhayn, 2006; Halder et al., 2012). Elevated arsenic (As) concentrations in sediments in Newfoundland, Canada have been known since 1990 when extensive lake-sediment samples were collected and analyzed as a part of Canada wide Geochemical Reconnaissance Program (Davenport et al., 1993; 1994; Serpa et al., 2009). Fig. 1.4 illustrates a survey carried out by Newfoundland and

Labrador Department of Environment and Conservation, on As occurrence in sedimentary rocks and groundwater. Arsenic concentrations in some domestic water wells in Newfoundland exceed the maximum acceptable concentration (MAC) of 0.01 mg/L. In 2009, one hundred and sixteen (116) groundwater samples were collected from existing water wells drilled into bedrock of the Dunage and Gander zones by Newfoundland and Labrador Department of Natural Resources and Department of Environment and Conservation, and arsenic concentrations above the MAC of 0.01 mg/L have been found in more than 50 percent of the water samples. The concentrations of arsenic varied between "0 and 0.790" mg/L (Serpa et al., 2009). Of 52 sources including surface water and groundwater surveyed by Newfoundland and Labrador Department of Environment and Conservation, 49 had As concentrations exceeding the MAC of 0.01 mg/L (Rageh et al., 2007). Avalon Peninsula, located in the eastern part of the province where the majority of the population resides, has contaminated wells and higher concentrations of As in well water (Rageh et al., 2007). The Gander Bay area was also identified as having moderate to high concentrations of arsenic in groundwater (Rageh et al., 2007).

The knowledge of extent of As release and release mechanisms under water chemistry conditions relevant to natural soil water and groundwater is essential for predicting and controlling As contamination in subsurface environment. A number of mechanisms have been proposed to explain arsenic release from rocks and sediments to groundwater. Oxidizing dissolution of As-sulfide minerals is an important release mechanism (Nickson et al., 1998; Bose and Sharma, 2002; Harvey et al., 2002; Serfes et al., 2005; Casentini and Pettine, 2010). Arsenic-bearing sulfides are stable under reducing conditions, but are oxidized and leach solutes when exposed to atmosphere (oxygen) and water. Weathering of As-bearing sulfides may lead to the formation of acidic drainage and release of As to natural waters (Lengke et al., 2009). The oxidation rates of As-bearing sulfides are strongly dependent on pH, dissolve oxygen (DO) and the presence of $Fe^{3+}$ and bacterial activity (Langner and Inskeep, 2000; Langner et al., 2001; Lengke and Tempel, 2001).

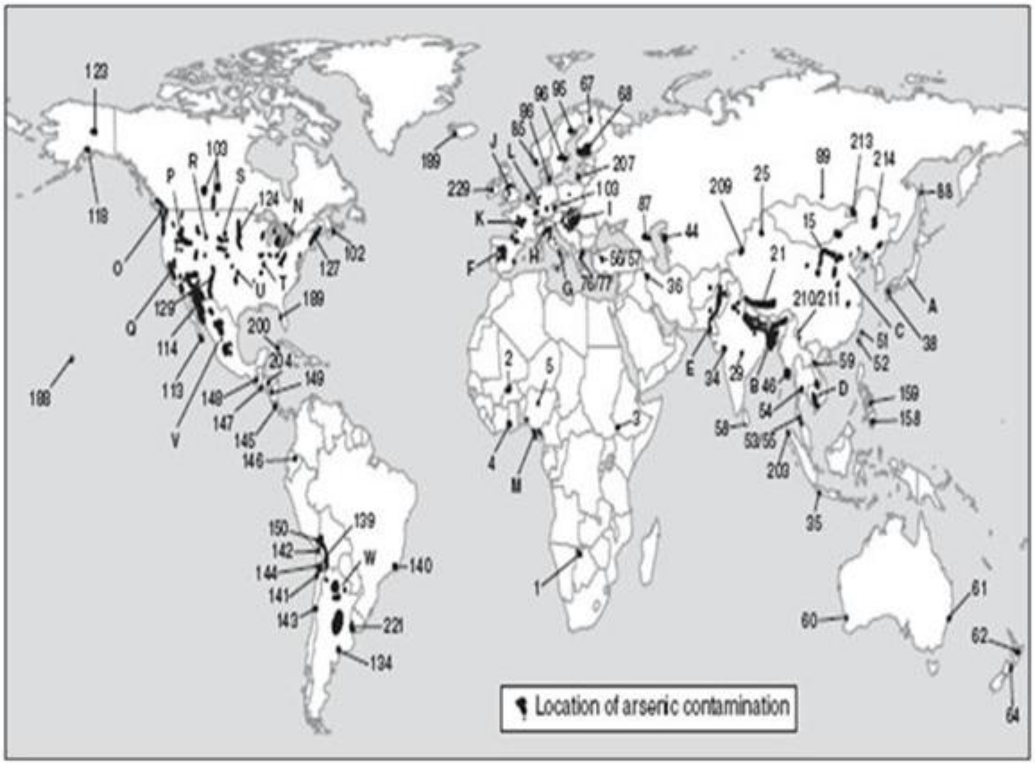

Figure 1.3: Worldwide distribution of As contamination (source: Ravenscroft et al., 2009).

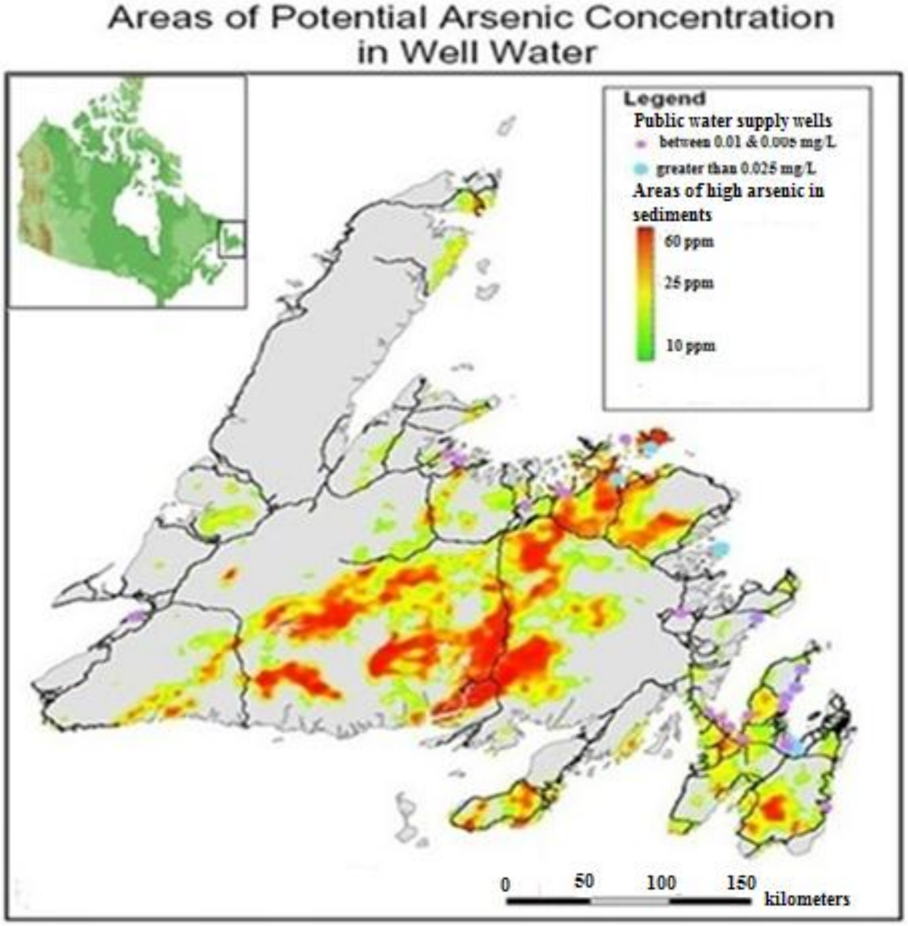

Figure 1.4: Areas of potential arsenic concentrations in sediment and well water in Newfoundland (source: www.env.gov.nl.ca/env/waterres/cycle/groundwater/well).

At high pH, dissolution is the most likely mechanism for arsenic release whereas at acidic to near-neutral pH, arsenic is very strongly adsorbed by oxides minerals as arsenate ion (Smedley and Kinniburgh, 2002; Corkhill et al., 2008). Some studies showed dissolution rates of arsenic containing iron sulfide minerals at pH 13-14 under oxidizing conditions are approximately six to eight times greater than those at pH 2.3 to 8.2 (Lengke and Tempel, 2002; Craw et al., 2003). Microbial activities play important roles in controlling sulfide mineral dissolution. Some researchers concluded the main role of iron- and sulfur-oxidizing bacteria is oxidation of $Fe^{2+}$ to $Fe^{3+}$ and elemental sulfur to sulfate (Corkhill et al., 2008; Lengke et al., 2009). Because $Fe^{3+}$ in solution can rapidly attack sulfide surface, As-bearing sulfides will be oxidized as rapidly as the bacteria can generate $Fe^{3+}$. In addition, an increase in acidity by oxidizing elemental sulfur to sulfate may increase As oxidation rates (Corkhill et al., 2008; Lengke et al., 2009).

Reductive dissolution of Fe (III) oxyhydroxides is an important arsenic release mechanism under reducing conditions. Arsenic bound to Fe (III) oxyhydroxides is released to groundwater during mineral dissolution (Bhattacharya et al., 1997; Nickson et al., 1998; Harvey et al., 2002; Ahmed et al., 2004; McArthur et al., 2004; Fendorf et al., 2010). Reductive dissolution is thought to be the main mechanism of groundwater As contamination in Bangladesh, India, Thailand, Vietnam, Inner Mongolia, some parts of USA, Argentina and Mexico (Nickson et al., 1998; Smedley and Kinniburgh, 2002; McArthur et al., 2004; Nriagu et al., 2007; Rageh et al., 2007; Hoang et al., 2010). It has been observed that the rates of reductive dissolution of iron (III) oxyhydroxides in the presence of reducing agents such as ascorbate, phenols, thiol-containing compounds, and fulvic and humic acids are high under acidic conditions ($pH < 5$). This is because the rates are proportional to the amount of the reducing agents adsorbed to the Fe oxyhydroxide surface (LaKind and Stone, 1989; Dos Santos Afonso and Stumm, 1992), and at lower pH, more reducing agents can be adsorbed (Suter et al., 1991; Deng, 1997).

Microbial degradation of organic matters in aquifers contributes to reductive dissolution of Fe and Mn oxyhydroxides and arsenic release by reducing redox potential of groundwater (McArthur et al., 2001; Harvey et al., 2002). In addition, many microbes can secrete chelating agents to promote mineral dissolution. Siderophores, small-molecular compounds (generally <1 kDa) that strongly bind Fe and facilitate mineral dissolution, are produced by many organisms (Neilands, 1995; Macrellis et al., 2001; Boukhalfa and Crumbliss, 2002; Kraemer, 2004). The presence of siderophore can increase Fe oxyhydroxides and alumino-slicates mineral dissolution by up to ten folds (Rosenberg and Maurice, 2003; Duckworth et al., 2009). Siderophore concentrations are generally low in natural system, and 0.01-2 mM aqueous siderophores in soil environments have been measured in some studies (Hersman et al., 1995). *Pseudomonas* genera bacteria, which can secrete siderophore, were found to favor Fe oxyhydroxides and clay dissolution and consequent mobilization of adsorbed As (Liermann et al., 2000; Cocozza et al., 2002; Kraemer, 2004; García-Sánchez et al., 2005).

Although Fe oxyhydroxides are usually a minor component in sediments, they are considered as the most important mineral that controls groundwater As contamination in shallow aquifers where sulfide minerals are absent (Smedley and Kinniburgh, 2002; Seddique et al., 2008; Masuda et al., 2012). Silicate minerals are usually the most abundant component in many natural sediments, they could be major arsenic-hosting minerals (Manning and Goldberg, 1997; Breit et al., 2001; Stollenwerk, 2003; Seddique et al., 2008). Arsenic in silicate minerals are usually incorporated into the structure of the minerals, rather than adsorbed onto mineral surface as in the case of Fe oxyhydroxides

(Tessier et al., 1979) and silicate minerals are usually more stable compared to Fe oxyhydroxides in terms of dissolution. Therefore, silicate minerals have been largely neglected as a potential source of As contamination in groundwater. A few recent studies argued that silicate minerals (e.g., biotite and chlorite) are the primary source of As pollution in groundwater (Seddique et al., 2008; Masuda et al., 2012). Further investigations are needed in order to understand the role of silicate minerals in groundwater As contamination.

## 1.2 Uranium in nature, its chemical forms, toxicity and release mechanisms

Uranium (U) is important not only for being one of the heaviest elements that occurs in nature and nuclear fuel but also for its chemical and radioactive implications to human health and environment (McKinley et al., 2006; Mkandawire, 2013). Uranium is ubiquitous in the earth, and occurs in nearly 200 different minerals (Burns, 1999; Herring, 2013). Naturally occurring uranium deposits are mainly comprised of a few common minerals including oxides (uraninite and pitchblende), silicates (coffinite, soddyite, uranophane, and uranothorite), phosphates (autunite), and vanadates (carnotite) (Wiedemeier et al., 1995). Uranium is prevalent in the crust with an average concentration of 2.76 mg/kg (Herring, 2013). As the most abundant actinide element, U averages 1.2 to 1.3 mg/kg in sedimentary rocks, ranges from 2.2 to 15 mg/kg in granites, and from 20 to 120 mg/kg in phosphate rocks (Langmuir, 1997). Small amounts of U are prevalent in soil and rock, and dissolved U at very low concentrations is found in most natural waters (Mkandawire, 2013). Typical groundwater concentrations of dissolved uranium are on the order of a few µg U/L (Wiedemeier et al., 1995). Most of alarming U contaminations are associated with anthropogenic activities including nuclear fuel cycle, phosphate fertilizer production process and improper disposal of U mine tailings, however groundwater uranium contamination often occurs naturally due to natural geochemical processes (Chen et al., 2005; James and Sinha, 2006). According to the Newfoundland and Labrador Department of Natural Resources, in Newfoundland, uranium is mostly found in volcanic rock and sandstone, and the concentration of uranium in bedrock varies from 4.2 to 41.5 mg/kg.

Uranium mainly occurs in +4, +5 and +6 oxidation state (i.e., U (IV), U (V) and U (VI)). Most important oxidation states in nature are uranous U(IV) and uranyl U(VI) (Welch and Lico, 1998). Under ambient oxidizing conditions, the predominant uranium oxidation state is U (VI). U (IV) may dominate where oxygen is limited. The metallic form, U (0), which is readily oxidized to U (IV) and eventually U (VI) under oxidizing conditions, does not occur naturally. Other oxidation states of uranium, i.e., U (V) and U (III), are rare and generally unstable compared to U (IV) and U (VI) under ambient conditions (Finch and Ewing, 1992; Finch and Murakami, 1999). In general, the solubility, and hence mobility, of uranium is greatest when it is in the U (VI) state (Wiedemeier et al., 1995). In aqueous solutions, the forms of uranium are dependent on pH and redox potential (Eh) (Dinh Chau et al., 2011) (Fig. 1.5).

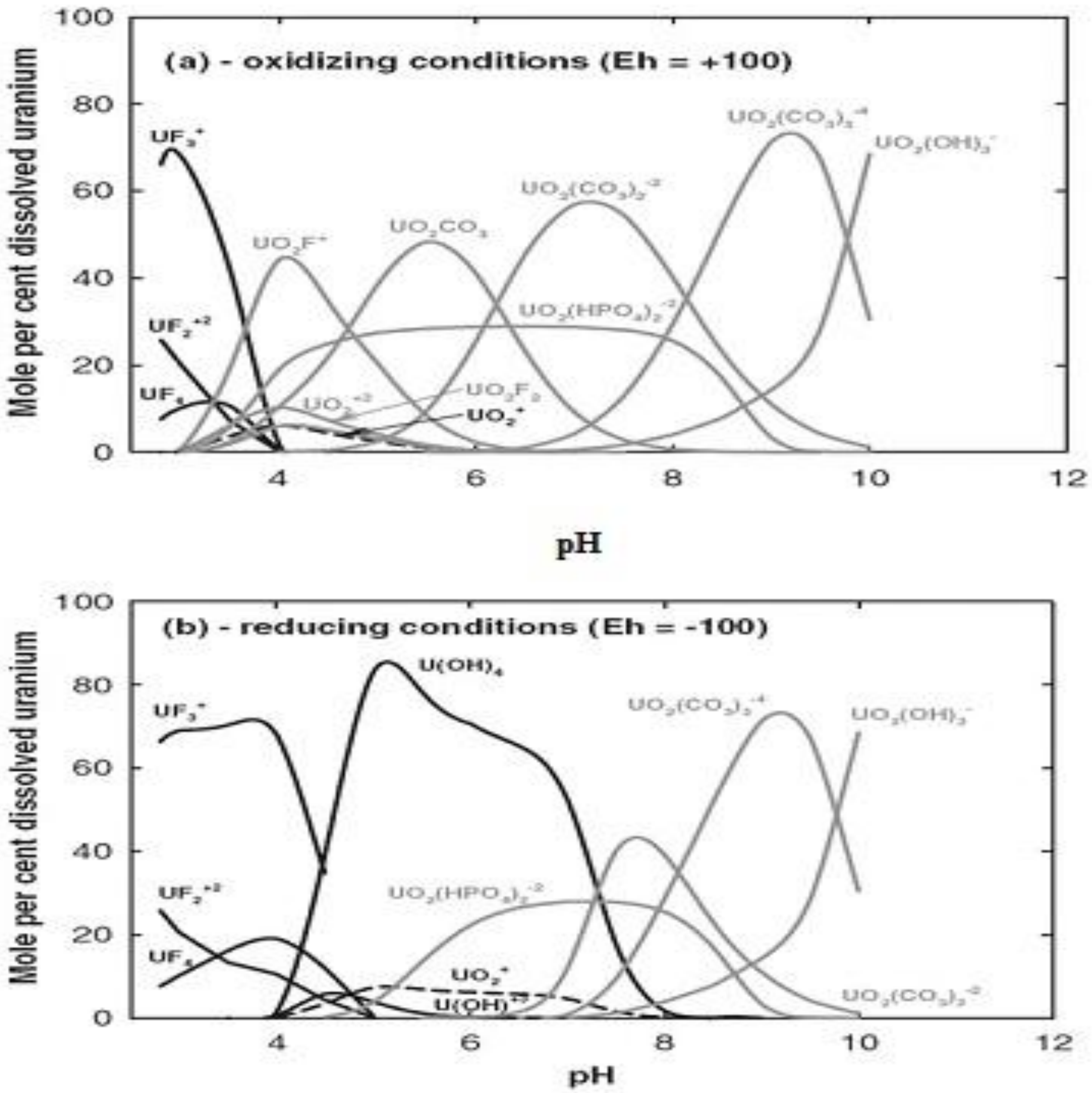

Figure 1.5: Distribution of uranium complexes in groundwater as a function of pH (T = 10°C) for (a) oxidizing and (b) reducing conditions, calculated using PHREEQC-2 code (source: Dinh Chau et al., 2011).

Uranium contamination is a major environmental threat to human health (Nordberg, 2007). The risk of U exposure is primarily due to its toxicity as a nephrotoxic heavy metal (i.e. leading to kidney diseases), rather than its radioactive character

(Zamora et al., 1998; Kurttio et al., 2006). Renal defect, diminished bone growth, and DNA damage are the primary health concerns of uranium (Craft et al., 2004). Natural uranium exposure mostly derives from ingestion of contaminated groundwater, as well as trace amounts from food (Brugge et al., 2005). The maximum acceptable concentration (MAC) for uranium in drinking water recommended by Health Canada is 0.02 mg/L (HealthCanada, 1996).

Although less prevalent compared to groundwater arsenic contamination, geogenic U contamination in aquifers represents a phenomenon of global extent (Frengstad et al., 2000; Bleise et al., 2003). According to Newfoundland and Labrador Department of Environment and Conservation, elevated U concentrations (> 0.02 mg/L) in well water were found in different parts of the province (Fig. 1.6). A large portion of central and western part of Newfoundland is at risk of potential high uranium concentration in groundwater.

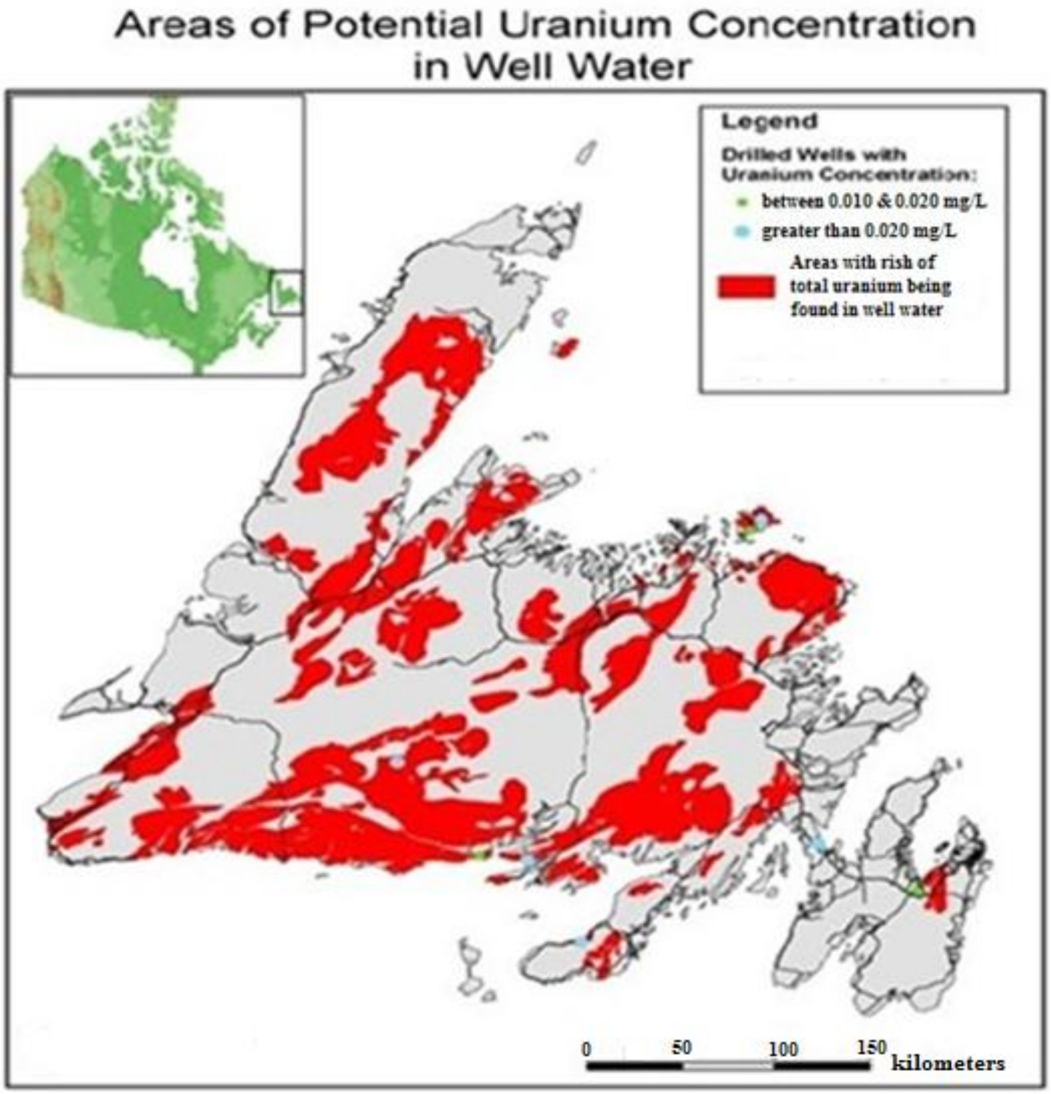

Figure 1.6: Areas of potential uranium concentrations in sediment and well water in Newfoundland (source: www.env.gov.nl.ca/env/waterres/cycle/groundwater/well).

Uranium release from sediments to groundwater is a complicated process and significantly influenced by water chemistry. Maximum solubility of uranium is observed in oxidizing, phosphate-free, carbonate-rich solutions (Kelly et al., 2003; Catalano et al., 2006; Kelly et al., 2006). In oxidized surface- and ground water, uranium is usually transported as highly soluble uranyl ion ($UO_2^{2+}$) and forms different complexes depending on pH and redox potential (Langmuir, 1997). Under oxidizing conditions and environmental pH, U (VI) species dominate in aqueous solution. These highly soluble species are generally either hydroxyl or carbonate complexes of the uranyl ion ($UO_2^{2+}$), although greater influence on U (VI) speciation may be exerted by elevated concentrations of potential inorganic or organic ligands in zones near contaminant source (Wang et al., 2005; Catalano et al., 2006). Under oxidizing condition, adsorption/desorption of U (VI) is strongly influenced by pH (Echevarria et al., 2001). Under reducing conditions, stable U (IV) solid phases are mainly uraninite ($UO_2$), or coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) if high dissolved silica pertains (Duff et al., 1999). Organic complexes of U (IV) associated with humic materials may also retain U (IV) in the solid phase (Bednar et al., 2007). The solubility of the U (IV) phases is extremely low; therefore reducing conditions effectively diminishes the movement of uranium in soils and sediments (Wiedemeier et al., 1995; Duff et al., 1999). The most common uranium ore-forming process involves reductive precipitation of U as a result of microbiological activities (Langmuir, 1997). U (IV) solid phases and U (VI) aqueous complexes could co-exist in cases where strictly reducing conditions are not achieved (Casas et al., 1998). In reducing environments, partial dissolution of U(IV) solids can occur even if there are only slight changes in the surrounding conditions, and the solid phase is chiefly in its reduced form (Gayer and Leider, 1957; Ryan and Rai, 1983; Casas et al., 1998). The partial dissolution of uraninite strongly depends on pH, redox potential and carbonate content (Casas et al., 1998).

The solubility and mobility of U(VI) in the subsurface is greatly influenced by carbonates and natural organic matter (NOM) (Echevarria et al., 2001; Bednar et al., 2007). Carbonates in water effectively decrease U(VI) adsorption to soil particles through the formation of negatively-charged carbonate complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. The formation of these carbonate complexes, which have a much lower affinity than uranyl and hydroxy-complexes for soil minerals such as hematite and clays, increases U (VI) desorption from soil (Giblin et al., 1981; Ho and Miller, 1986). Natural organic matter (NOM) has functional groups that form complexes with metals (including U), so that the physical and chemical properties of the metals are affected (Langmuir, 1997; Nierop et al., 2002; Schmitt et al., 2002). Dissolved natural organic matter competes with uranium for sorption sites on oxide and clay particles, which hinders U(VI) adsorption, but promotes U(VI) desorption (Schmitt et al., 2002; Jackson et al., 2005; Bednar et al., 2007).

Although the solubility and mobility of uranium have been extensively studied, there have been relatively fewer studies carried out on U release from heterogeneous natural sediments, and it is not clear what geochemical processes are involved in U release under natural conditions. To advance the knowledge of U release in groundwater and predict groundwater U concentration under different geochemical conditions, it is necessary to identify the minerals in heterogeneous natural sediments that host U, and determine the mechanisms and extent of U release under water chemistry conditions relevant to natural soil water and groundwater.

## 1.3 Research focus

My M.Sc thesis is intended to identify the major minerals in natural sediments that host and release As and U, and determine release mechanisms and extent of As and U release under a range of water chemistry conditions relevant to natural soil water and groundwater. The findings from this research are described in two chapters entitled:

1) Arsenic release from sediment to groundwater: mechanisms and the importance of silicate minerals (Chapter 2).

2) Uranium release from sediment to groundwater: influence of water chemistry and insights into release mechanisms (Chapter 3).

Chapter 2 outlines my investigation into the mineral phases that control As contamination in groundwater, and the role of silicate minerals on As storage and release. Sequential extraction results showed that silicate minerals, which make up the bulk of the sediment (98%), are the main As reservoir, containing 75% of the total As. Fe oxyhydroxides, a minor component in the sediment, are the second largest As reservoir and hold 16% of the total As. I discovered that both desorption and mineral dissolution contributes to groundwater As contamination, and that pH, Fe and Al chelators, and redox potential (Eh) strongly influence mineral dissolution and As release. Most importantly, I found that under conditions of high pH, extensive dissolution of Fe oxyhydroxides coating, and the presence of Fe and Al chelating agents, substantial quantities of As were released from silicate minerals to groundwater due to the significant dissolution of silicate minerals.

Chapter 3 outlines the investigation of the major minerals in a heterogeneous natural sediment that host and release U, and determined the mechanisms and extent of U release under a range of water chemistry conditions. A natural sediment was collected, characterized, and examined with batch leaching experiments to investigate U release mechanism and the effects of water chemistry on U and major element release. SEM-EDX and sequential extraction showed that carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals are the major U hosting minerals, and substantial amounts of U exit as absorbed uranyl ion. My batch leaching experiments showed that U release from natural sediments to water is a complicated process which involves a number of interactive geochemical reactions including: U desorption from mineral surface, dissolution of U-bearing minerals, formation of aqueous U complexes, and reductive precipitation of U.

Overall, the research presented in this thesis demonstrates the importance of silicate minerals both as an As storage phase and a potential source of As contamination in groundwater. This research also shows U desorption from mineral surfaces, promoted by formation of low-adsorbing aqueous U complexes, is probably the dominant U release mechanism under oxidizing conditions.

## 1.4 Co-authorship Statement

### 1.4.1 Design and Identification of the Research Proposal

The initial concept for this project was described in a grant proposal written by my supervisor (Dr. Tao Cheng) before I started my M.Sc program at Memorial University of Newfoundland. During my first semester, I completed a literature review. At the beginning of my second semester, I wrote my M.Sc thesis research proposal, and improved the proposal by incorporating suggestions from my supervisory committee member (Dr. Paul Sylvester). The details of field sampling, sample characterization and leaching experiments described in Chapter 2 and 3 were decided during discussions between me and my supervisor.

### 1.4.2 Practical Aspects of the Research and Data Analysis

I organized the practical aspects of the research. I collected the samples from the sampling sites with assistance from my supervisor and Qing Wang. Sediment samples were characterized by X-ray diffraction (XRD) and scanning electronic microscopy equipped with energy dispersive spectroscopy (SEM-EDX) with assistance from Wanda Aylward (XRD) and Michael Shaffer and David Grant (SEM-EDX). A five step sequential extraction was performed by me with assistance from Lakmali Hewa. I conducted the leaching experiments described in Chapter 2 and 3. All extracted water samples were analyzed by ICP-MS with assistance from Lakmali Hewa, and I processed all the raw data. All the analytical facilities were parts of and managed by the Core Research Equipment & Instrument Training (CREAIT) Network at Memorial University of Newfoundland. The data analysis described in the thesis was performed by myself, with guidance from my supervisor and my supervisor committee member.

### 1.4.3 Manuscript Preparation

I am the author of this document, which integrates the work described above into a single M.Sc thesis. The thesis has benefitted from the inclusion of revisions and refinements suggested by supervisor and committee member. Chapter 2 and Chapter 3 of this thesis have been submitted to peer-reviewed journals, and I am the first author on these submissions.

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# Chapter 2. Arsenic Release from Sediment to Groundwater: Mechanisms and the Importance of Silicate Minerals

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## Abstract

Mineral dissolution plays an essential role in controlling geogenic arsenic (As) contamination in groundwater. Although reductive dissolution of Fe oxyhydroxides is generally considered the key As release mechanism in many aquifers, some recent studies argue that silicate minerals, normally considered “inert” in terms of As release, are the primary source of As in groundwater. The objective of this study was to identify: (i) As-hosting minerals in a natural sediment, and (ii) mechanisms that control As release from these minerals under specific water chemistry conditions. A sediment sample was collected, characterized, and examined with batch leaching experiments. Sequential extraction results showed that silicate minerals, which make up the bulk of the sediment (97.88%), are the main As reservoir, containing 75% of the total As. Fe oxyhydroxides, a minor component in the sediment, are the second largest As reservoir and hold 16% of the total As. Batch leaching experiments showed that, besides desorption, dissolution of Fe oxyhydroxides and silicate minerals is an important mechanism controlling As release from sediment to water, and that high pH, the presence of Fe and Al chelators, and extensive dissolution of Fe oxyhydroxide coating promote silicate mineral dissolution and As release from sediment to water. The findings demonstrate the importance of silicate minerals both as an As carrier phase and as a potential source of As contamination in groundwater.

**Keywords:** Arsenic release, Sediment, Fe oxyhydroxides, Silicate minerals, Groundwater contamination

## 2.1 Introduction

Groundwater is an important drinking water source in many parts of the world. Arsenic (As) contamination in groundwater is a major environmental threat to human health. Ingestion of As through drinking water has affected more than 100 million people worldwide (Kapaj et al., 2006; Chen et al., 2013). Both anthropogenic pollution and natural geochemical processes can cause arsenic contamination in groundwater. Anthropogenic activities that release arsenic into the environment include metal mining and smelting, fossil fuel processing and combustion, wood preserving, pesticide production, and disposal and incineration of municipal and industrial wastes (Popovic et al., 2001; Wang and Mulligan, 2006). Compared to anthropogenic As contamination, geogenic groundwater As contamination is more common and has been reported all around the world (Smedley and Kinniburgh, 2002; Visoottiviseth et al., 2002; Tsai et al., 2009; Basu et al., 2013; Chen et al., 2013).

Geogenic As contamination in groundwater is governed by: (i) As concentration and mineral composition of the aquifer materials, and (ii) physicochemical properties of groundwater (Smedley and Kinniburgh, 2002; Serpa et al., 2009). Arsenic occurs naturally in the earth’s crust with average concentration of 2-5 mg/kg. Much higher As concentrations may be found in Fe deposits, sedimentary Fe ores, Mn nodules, As pyrite, aquitards, clay rich lenses in aquifers, and aquifers containing Fe and Mn oxyhydroxides (Lin and Puls, 2000; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Common arsenic-containing minerals include arsenopyrite (FeAsS), mispickel (FeAsS), realgar (AsS), and orpiment ($As_2S_3$) (Nriagu et al., 2007). Arsenic also exists as adsorbed arsenate and arsenite ions on the surface of minerals such as Fe and Mn oxyhydroxides and clays (Pierce and Moore, 1982; Lin and Puls, 2000). Oxidizing dissolution of As-bearing sulfide minerals is considered the main As release mechanism in aquifers rich in sulfide minerals (Nickson et al., 1998; Bose and Sharma, 2002; Harvey et al., 2002; Casentini and Pettine, 2010). Sulfide minerals are stable under reducing conditions, but when exposed to oxygen and water, mineral structures are destroyed and As released (Langner and Inskeep, 2000; Lengke et al., 2009). In many swallow aquifers where sulfide minerals are absent, Fe oxyhydroxides have been proposed as the key mineral that controls As contamination (Nickson et al., 1998; Smedley and Kinniburgh, 2002; McArthur et al., 2004; Nraigu et al., 2007; Rageh et al., 2007). Fe oxyhydroxides have high affinity for arsenate and arsenite, and serve as sinks for arsenic under oxidizing conditions (Lin and Puls, 2000). When groundwater changes from oxidizing to reducing conditions (e.g., during microbial degradation of organic matters in sediments), Fe(III) is reduced and Fe oxyhydroxides dissolve, and As associated with Fe oxyhydroxides is released to groundwater (Bhattacharya et al., 1997; Nickson et al., 1998; Harvey et al., 2002; Ahmed et al., 2004; McArthur et al., 2004; Fendorf et al., 2010). Dissolution of Fe oxyhydroxides is influenced by Fe chelators in pore water. Siderophores, a group of small organic compounds, are strong Fe chelators produced by bacteria, fungi and plants to facilitate Fe acquisition from water (Casentini and Pettine, 2010). Siderophores can promote dissolution of Fe minerals (Neilands, 1995; Macrellis et al., 2001; Boukhalfa and Crumbliss, 2002; Kraemer, 2004) and lead to As release to pore water (García-

Sánchez et al., 2005). Besides mineral dissolution, desorption of adsorbed As from mineral surface is another important As release mechanism (Anawar et al., 2004). Natural organic matter and competitive ions such as phosphate and carbonate have been shown to displace adsorbed As from minerals (e.g., Fe oxyhydroxides and clays) and increase As concentration in groundwater (Xu et al., 1991; Nickson et al., 2000; Appelo et al., 2002; Grafe et al., 2002; Goh and Lim, 2004; McArthur et al., 2011; Sahu et al., 2012; Wang and Mulligan, 2013).

Although it is well accepted that Fe oxyhydroxides are the most important minerals in controlling groundwater As contamination in shallow aquifers where sulfide minerals are absent, Fe oxyhydroxides are usually a minor component in sediments and exists as coatings on other mineral grains (Smedley and Kinniburgh, 2002; Seddique et al., 2008; Masuda et al., 2012). Silicate minerals are usually the most abundant component in many natural sediments, and they could be a major As-hosting phase (Manning and Goldberg 1997; Breit et al., 2001; Stollenwerk, 2003; Seddique et al., 2008). Silicate minerals are usually more stable compared to Fe oxyhydroxides in terms of dissolution, and As in silicate minerals are usually incorporated into the structure of the minerals, rather than adsorbed onto mineral surface (as in the case of Fe oxyhydroxides) (Tessier et al., 1979). As such, arsenic associated with silicate minerals are not normally considered “bioavailable”, and largely neglected as a potential source of As contamination in groundwater. A few recent studies, however, argued that silicate minerals (e.g., biotite, chlorite) are the primary source of As pollution in groundwater

(Seddique et al., 2008; Masuda et al., 2012). The role of silicate minerals in groundwater As contamination is still a matter of debate.

The main objective of this study is to identify the mineral phases that control As contamination in groundwater, and to determine As release mechanisms under specific water chemistry conditions. A natural sediment sample was collected and the major As-hosting minerals were identified. Our results showed that As concentration is the highest in Fe oxyhydroxides. However, silicate minerals host the majority of As mass. We also found that both desorption and mineral dissolution contributes to groundwater As contamination. pH, Fe and Al chelators, and redox potential (Eh) strongly influence mineral dissolution and As release, and that under conditions of high pH, extensive dissolution of Fe oxyhydroxides coating, presence of Fe and Al chelating agents, dissolution of silicate minerals could be significant, and substantial quantities of As could release from silicate minerals to water. This study demonstrates the importance of silicate minerals as a host phase for As, and as a source of groundwater As contamination.

## 2.2 Materials and methods

### 2.2.1 Sample collection and characterization

A glacial till sample (Fig. 2.1) was collected on 9th December 2011 from a site (latitude: N 47.42093398 and longitude: W 53.19789456) near Avondale, Newfoundland, Canada (Fig. 2.2), a town located in Avalon Peninsula in Eastern Newfoundland, where arsenic concentrations are high in sediments and some water wells according to

Geological Survey and Natural Resources of Newfoundland (Rageh et al., 2007; Serpa et al., 2009). The till sample was collected from a depth of 0.6 to 1 m below land surface, air dried and sieved through 0.053 mm sieve, well mixed, and stored in plastic buckets for use in all subsequent experiments. The cutoff size of 0.053 mm is recommended by the Till Protocol Working Group Canada for geochemical analysis because ore minerals are easily broken down to this size range over short distances and it contains phyllosilicates that will scavenge cations released during weathering (Nevalainen, 1989; Shilts, 1993; Lett, 1995; Tarvainen, 1995; Levson, 2001). Mineral composition of the sediment sample was determined using X-ray diffraction (XRD) and scanning electronic microscopy equipped with energy dispersive spectroscopy (SEM-EDX). XRD analyses were performed using Rigaku Ultima IV diffractometer with Cu K α radiation and operating at 40 kV and 44 mA. The samples were scanned from $2\theta = 5°$ to $90°$ at a scan rate of degree per 1s. The results obtained were processed using the MDI Jade computer program and data bases from International Centre for Diffraction Database (ICDD) and the Inorganic Crystal Structure Database (ICSD), and Jade uses Whole Pattern Fitting (i.e. Rietveld) to calculate relative concentrations (Pecharsky and Zavalij, 2008). SEM-EDX analyses were performed using FEI MLA 650 F scanning electronic microscope equipped with a Bruker EDX system with dual Xflash 5030 SDD x-ray detectors (Sylvester, 2012). The energy limit for the EDX display is limited in software at 20 kV, 4096 channels, and 5eV/channel. The acceleration voltage 25 kV is typically used for mineral liberation analysis (MLA), and the beam current (spot size) is adjusted for 10 nanoAmps (nA).

The pH, organic carbon, and metal concentrations of the sample were determined using wet chemistry methods. Sediment pH was determined by mixing 5 mM $CaCl_2$ with dry sediment sample at a solution to solid ratio of 2:1 (mL/g), and measuring the pH of the supernatant (Williams et al., 2003). Organic carbon content in the sediment sample was determined following the procedure described by Gregorich and Ellert (1993), i.e., a solution of 5 mM $CaCl_2$ was used to extract organic carbon from the sediment, and the extracted dissolved organic carbon (DOC) in the $CaCl_2$ solution was measured by a Shimadzu TOC-V analyzer. A five step sequential extraction procedure (detail procedure is described in Appendix 2A) (Tessier et al., 1979) was performed on the sediment sample to determine the elements (i.e., Fe, Mn, Al, Si, Mg, Ca, and As) contained in each of the following five phases: exchangeable phase, carbonate minerals, Fe and Mn oxyhydroxides, organic phases and residual phases, with the extracted solutions measured by ICP-MS using synthetic calibration solutions. Clays, Fe and Mn oxyhydroxides and humic acids could adsorb considerable amount of trace metals which are readily exchangeable (Gardiner, 1974; Takematsu, 1979; Moalla et al., 1997). Significant trace metal concentrations can be associated with carbonate minerals (Chester and Hughes, 1967). Fe and Mn oxyhydroxides exist as nodules, concretion, cement between particles; these oxyhydroxides could be excellent scavengers for trace metals (Baker Robert, 1968). Trace metals could be bound to various forms of oragnic matter including living oragnisms, detritus, coating on mineral particles etc (Tessier et al., 1979). Residual phase contains mostly silicate minerals where trace metals are within crystal structures, and these trace metals are not expected to release into solution under normal natural conditions (Tessier et al., 1979).

Figure 2.1: Glacial till sample.

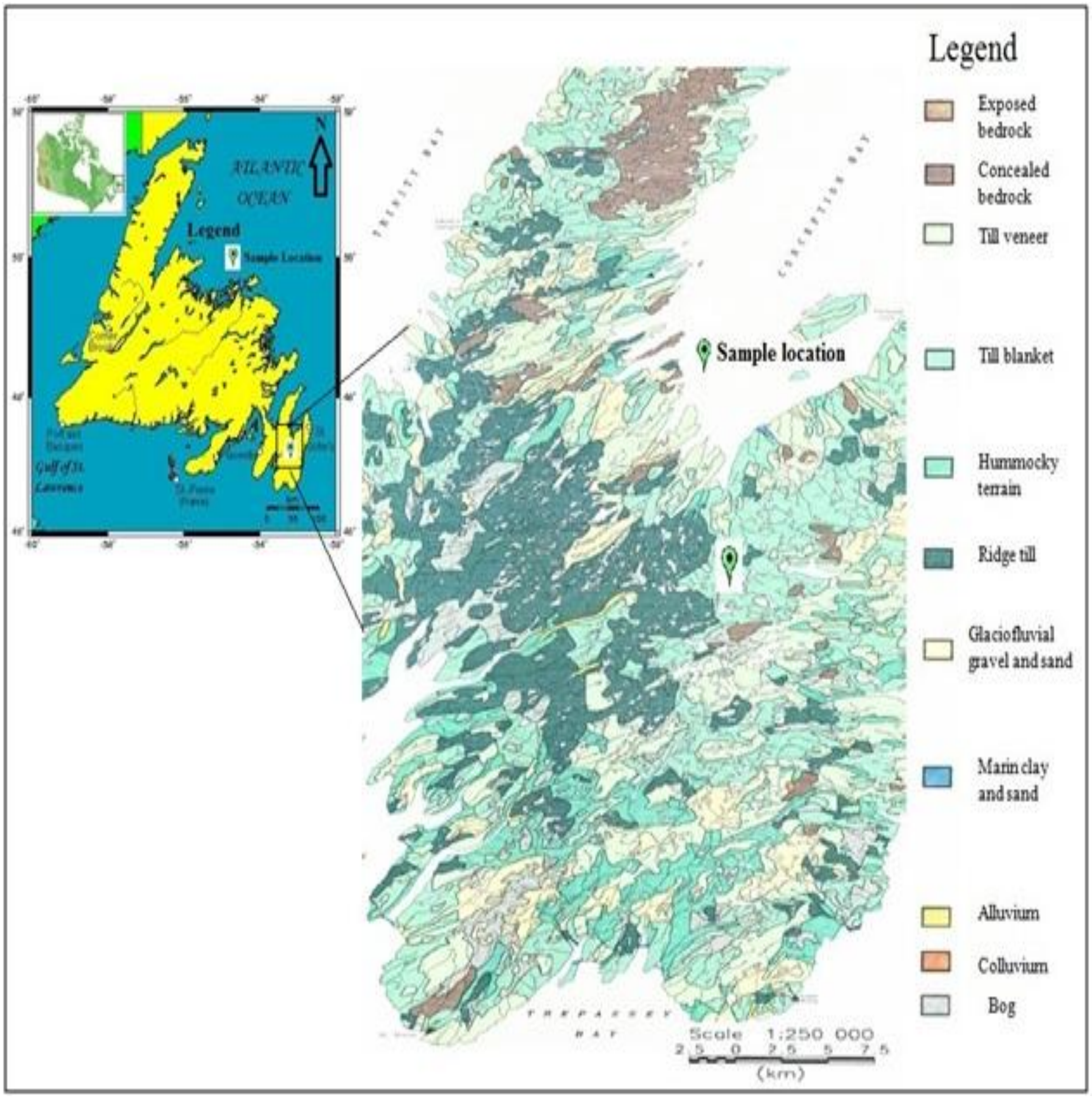


Figure 2.2: Sampling location shown on alluvial geology map (source: www.nr.gov.nl.ca/nr/mines/maps/surfnl/surfnl).

### 2.2.2 Batch leaching experiments

Hydrochloric acid (HCl), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium citrate dihydrate ($C_6H_9Na_3O_9.2H_2O$), and sodium ascorbate ($C_6H_7NaO_6$) were all analytical grade and purchased from VWR Canada. Analytical grade siderophore trihydroxamate desferrioxamine B (Dfob) [($C_{25}H_{46}N_5O_8NH_3^+$ ($CH_3SO_3)^-$] was purchased from Novartis (Switzerland). Dfob is a widely studied siderophore, consisting of a C-N backbone with to amino group (Martell et al., 2004). All the solutions used in our experiments were prepared by dissolving the chemicals in de-ionized water.

To evaluate the effects of pH, Fe and Al chelators, and Eh on mineral dissolution and arsenic release from sediment to groundwater, three types of batch leaching experiments were conducted: (i) pH experiments; (ii) siderophore experiments; and (iii) Eh experiments. We carried out four pH experiments (pH = 3.0, 5.0, 8.0 and 10), four siderophore experiments (siderophore concentration = 100 µM, pH = 5; siderophore concentration = 100 µM, pH = 8; siderophore concentration = 500 µM, pH = 5; siderophore concentration = 500 µM, pH = 8), and four Eh experiments (Eh = +350 to +200 mV; Eh = +150 to +100 mV; Eh = +50 to -50 mV; Eh = +50 to -150 mV). To prepare a sample for leaching experiments, one gram (1.000 g) air-dried, sieved sediment sample was mixed with 40 ml background solution in a 50 ml HDPE centrifuge tube. The background solution used was 0.01M NaCl solution for pH experiments, 100 or 500 µM siderophore in 0.01 M NaCl solution for siderophore experiments, and citrate and/or ascorbate in 0.01M NaCl solution for Eh experiments. In Eh experiments, four different background solutions were prepared to obtain 4 ranges of Eh values (Table 2.1). pH of the samples were adjusted and maintained by adding 1 M NaOH and/or 1M HCl to the suspensions.

Table 2.1: pH and Eh conditions of Eh experiments with various reducing agents.

| Reagents | Concentrations (M) | pH | Eh (mV) |
|---|---|---|---|
| Sodium citrate | 0.03 | 8.5-9.0 | +200 to +350 |
| Sodium ascorbate | 0.01 | 8.0-8.5 | +100 to +150 |
| Sodium ascorbate | 0.05 | 8.0-8.5 | -50 to +50 |
| Sodium citrate + sodium ascorbate | 0.03 + 0.06 | 8.0-8.5 | -150 to +50 |

The total volume of the NaOH/HCl solution used was very small (< 0.5 mL), so that the final volume of the solution was close to 40 mL. Twelve identical samples were prepared for each experiment. The centrifuge tubes holding the samples were capped and placed on a reciprocating shaker table. At pre-determined mixing time of 0, 1, 2, 4, 8, 16 days, two replicate (duplicate) sample tubes were sacrificed for each experiment. The tubes were taken off from the shaker, and the pH and Eh were immediately measured using Thermo Orion Kit Star A211 Ph Bt with pH electrode (8102 ROSS; Thermo Orion) and ORP electrode (Orion Sure-Flow Comb Redox Ele). Supernatant was withdrawn from each tube, promptly filtered through 0.45 µm nylon filters, and analyzed by ICP-MS for As, Fe, Mn, Al, Si, Mg, and Ca concentrations using synthetic calibration solutions. The limit of detection (LOD) for As, Fe, Mn, Al, Si, Mg and Ca was 0.2 µgL$^{-1}$, 115 µgL$^{-1}$, 0.17 µgL$^{-1}$, 5.3 µgL$^{-1}$, 250 µgL$^{-1}$, 1.2 µgL$^{-1}$, 0.2 µgL$^{-1}$, respectively.

## 2.3 Results and discussion

### 2.3.1 Mineral composition

X-ray diffraction (XRD) analysis showed that albite, quartz, and biotite present in the sediment sample (Fig. 2.3) indicated by many small peaks in the XRD chart. However, due to their low concentration, these minerals could not be identified by our XRD analysis because for uniformly sized, randomly oriented fine powders (approximately 1-2 µm), a detection limit of 1-5% of the total mass is expected. This is strongly dependent on sample crystallinity and other physical properties of the mineral being X-rayed (Pecharsky and Zavalij, 2008). SEM-EDX analysis confirmed the presence of albite, quartz, and biotite, and showed that major minerals (weight > 1%) in the sediment include albite (38.42 wt.%), quartz (28.71 wt.%), clays (15.86 wt.%), potassium feldspar (9.24 wt.%), chlorite (2.38 wt.%), and titanite (1.49 wt.%) (Table 2.2). SEM-EDX showed the presence of Fe oxyhydroxides (0.91 wt.%) (Table 2.2 and Fig. 2.4A). A few iron oxyhydroxides coated biotite grains, and a few pyrites ($FeS_2$) grains were also found (Fig. 2.4B). No arsenic was detected in the pyrite grains or in any of the minerals because the detection of SEM-EDX limit is ~ 0.01%. This result suggests that arsenic (if any) in the sediment sample exists in dispersed forms (i.e., impurities in mineral structures and/or adsorbed species on mineral surface).

### 2.3.2 pH, organic carbon, and phase distribution of arsenic and major elements

The sediment has a pH value of 5.30, and soluble organic carbon content of 1.24%. Sequential extraction results confirmed the presence of As in our sediment sample. Total As concentration was measured at 19.26 mg/kg by summing each fraction from sequential extraction steps (Appendix 2B). Distribution of As in different phases is shown in Fig. 2.5. The largest pool of As is the residual phase (silicate minerals), accounting for 75% of the total As. This result shows silicate minerals is the most important As-hosting phase in this sediment. The residual phase As presumably exist as impurities in the structure of silicate minerals, which are resistant to dissolution in the first 4 steps of extraction (Tessier et al., 1979). Labile phase As account for the remaining 25% of the total As. These labile As either adsorb to the surface of minerals (i.e., exchangeable As) or are associated with minerals that are easily soluble under certain conditions.

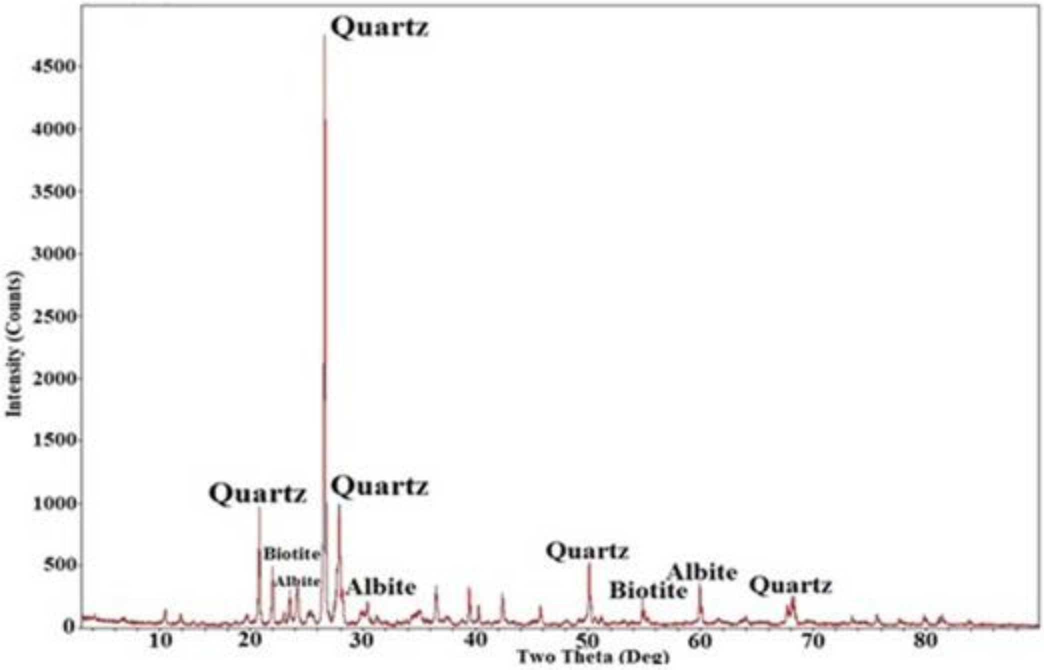


Figure 2.3: XRD profile of sediments.

Arsenic bound to Fe and Mn oxyhydroxides was the largest pool of labile As, accounting for 16% of the total As. Although the mass of Fe-Mn bound As was lower than the mass of As in residual phases, arsenic concentration in Fe oxyhydroxides was $20^+$ times higher than arsenic concentration in silicate minerals (330 mg As/kg Fe oxyhydroxides vs. 15 mg As/kg silicate minerals, calculated based on the As mass in Fe oxyhydroxides and As mass in residual phase and the ratio of weight percentages of silicate minerals and Fe oxyhydroxides minerals in our sample where silicate minerals are 107.65 higher than Fe oxyhydroxides minerals, determined by sequential extraction, and mass of Fe oxyhydroxides and silicate minerals determined by SEM-EDX) (Table 2.2 & appendix 2B).

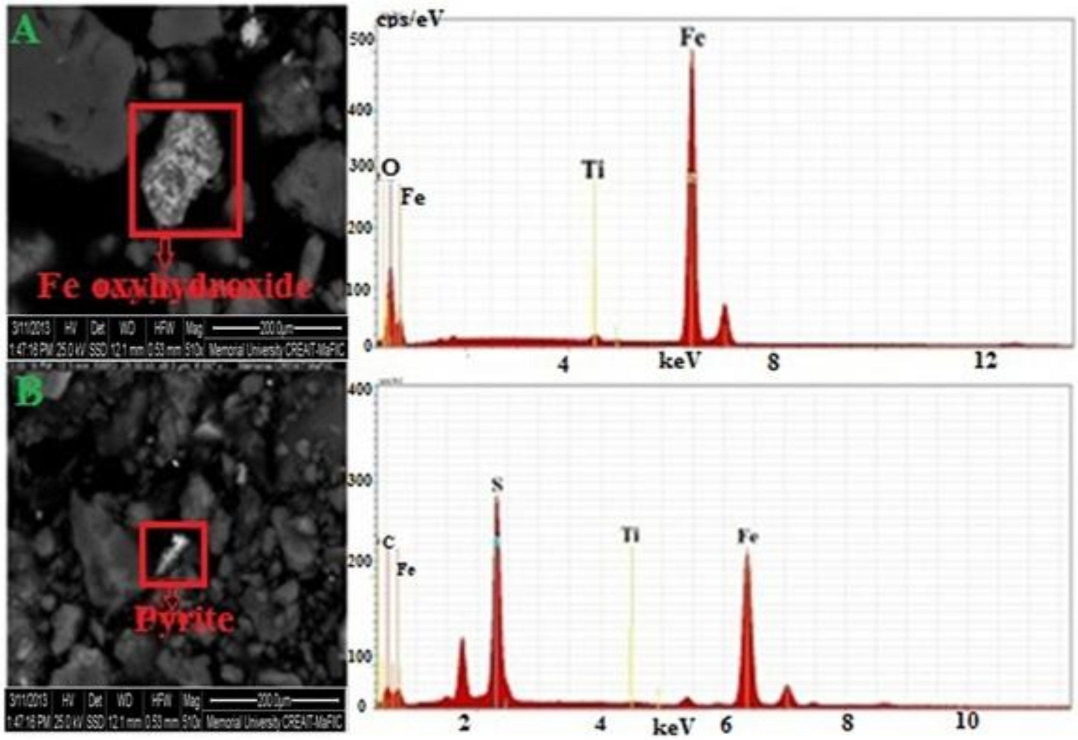


Figure 2.4: SEM images and respective EDX spectra showing (A) iron oxyhydroxide; (B) pyrite.

The high As concentration in Fe oxyhydroxides indicates this mineral could play a key role in controlling As release from sediment to groundwater. Other labile As include As in exchangeable phase, As bound to carbonate minerals, and As bound to organics, each of which accounted for 2.4%, 1.6%, 5.4% of the total As (Fig. 2.5). The labile As are expected to release to groundwater when minerals are dissolved (e.g., carbonate minerals at low pH, Fe oxyhydroxides under reducing conditions, and organics under oxidzing conditions) or when changing water chemistry conditions promote As desorption (e.g., pH increase, intrusion of $CO_2$).

Table 2.2: Modal mineralogy of sediments identified in SEM-EDX analysis.

| Minerals | Weight (%) | Grains |
|---|---|---|
| Albite ($NaAlSi_3O_8$) | 38.4 | 560 |
| Quartz ($SiO_2$) | 28.71 | 391 |
| Fe-poor Clays | 15.8 | 327 |
| Potassium Feldspar ($KAlSi_3O_8$) | 9.24 | 183 |
| Chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.(Mg,Fe)_3(OH)_6$) | 2.38 | 726 |
| Titanite ($CaTiSiO_5$) | 1.48 | 364 |
| Fe oxyhydroxides | 0.91 | 330 |
| Fe-rich Clays | 0.86 | 252 |
| Titano-Fe-oxide | 0.63 | 91 |
| Fine-grain-silicate | 0.51 | 378 |
| Zircon ($ZrSiO_4$) (these grains are very large) | 0.27 | 7 |
| Almandine ($Fe_3Al_2Si_3O_{12}$) | 0.19 | 252 |
| Plagioclase Feldspar excluding albite ($NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) | 0.15 | 81 |
| Rutile ($TiO_2$) | 0.14 | 38 |
| Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) | 0.09 | 31 |
| Biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) | 0.05 | 27 |
| Kaersutite ($NaCa_2(Mg_4Ti)Si_6Al_2O_{23}(OH)_2$) | 0.03 | 14 |
| Ilmenite ($FeTiO_3$) | 0.02 | 1 |
| Nickel (Ni) | 0.00 | 7 |
| Copper (Cu) | 0.00 | 2 |
| Cr-Spinel ($Mg(Al,Cr)_2O_4$) | 0.00 | 4 |
| Pyrite ($FeS_2$) | 0.00 | 6 |
| Unknown (could be void space and unidentified because of very small grains) | 0.00 | 552 |

The concentration of Fe, Mn, Al, Mg and Ca in the sediment sample was measured as 24.56, 0.58, 38.65, 7.97 and 5.48 g/kg, respectively by summing each fraction from sequential extraction steps (Appendix 2B). The distribution of Fe, Mn, Al, Mg, and Ca in the 5 phases is shown in Fig. 2.5. For all these elements, the weight% in the exchangeable phase (weakly adsorbed) is very low. The largest pool of Fe and Mn is in the residual phase (silicate minerals), accounting for 94% and 60% of the total Fe and Mn, respectively (Fig 2.5).

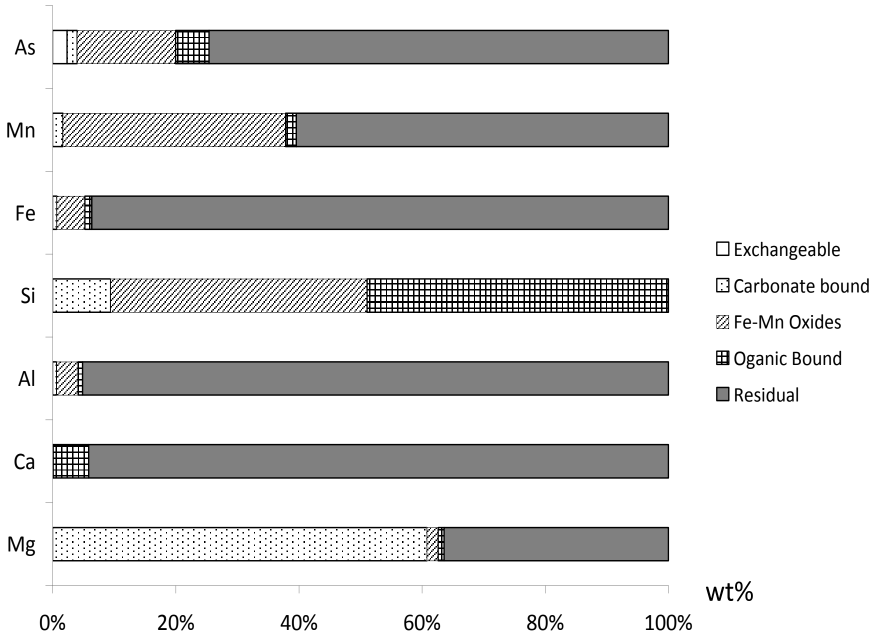


Figure 2.5: Weight percentage of different phases of As, Mn, Fe, Al, Ca and Mg.

Our SEM-EDX results showed Fe is present in a number of silicate minerals including clays, chlorite, almandine, and biotite (Table 2.2). The second largest pool of Fe and Mn is the Fe and Mn oxyhydroxides phase, accounting for 4.5% and 36.2% of the total Fe and Mn, respectively. Small amounts of Fe and Mn were found in carbonate and organic phases. No manganese minerals were identified by SEM-EDX analysis, probably because Mn quantity was below the detection limit of SEM-EDX analysis. About 95% of Al is found in the residual phase, indicating the majority of Al is in silicate minerals, consistent with our SEM-EDX results. The second largest pool of Al (3.5%) is found in the 3rd extraction step, i.e., when Fe and Mn oxyhydroxides were dissolved. This Al presumably exists in Al oxyhydroxides. Mg and Ca concentration in the sediment sample were similar (7.97 and 5.48 g/kg). However, there is a striking difference in phase distribution. The majority of Ca is in the residual phase (94%) and no Ca was detected in carbonate phase, while only 36% of Mg is in the residual phase (presumably in chlorite, biotite, and kaersuitite) and the majority (61%) is in carbonate phase. Although the presence of Al oxyhydroxides, Mn oxyhydroxides, and Mg carbonates is suggested by our sequential extraction results, these minerals were not detected by our SEM-EDX analysis, probably due to their low weight%. Residual phase Si (therefore total Si and phase distribution of Si) could not be determined due to the use of HF and formation of volatile SiF4 gas when extracting the residual phase, we nonetheless conclude, based on our SEM-EDX results, that the majority of Si in the sediment sample exist in silicate minerals (e.g., albite, clays, feldspar, chlorite, quartz).

### 2.3.3 Batch leaching experiments

#### 2.3.3.1 Effects of pH

pH exhibited a significant influence on As release from the sediment tested (Fig. 2.6). In the pH range of 3~8, arsenic release was very low. Maximum water arsenic concentration (occurred after 2~4 days of leaching) was 2.3, 1.3, and 4.6 µg/L respectively at pH 3, 5, and 8. At pH 10, arsenic release was much higher. Water arsenic concentration reached 45 µg/L after 1 day of leaching and continued to increase until the end of the experiment (t = 16 days) to 75.5 µg/L.

Arsenic release from sediments to water can be attributed to desorption from mineral surface and/or dissolution of As-bearing minerals (Chakraborty et al., 2007). For all the pH tested, arsenic release to water was rapid at the beginning, as indicated by the initial sharp increase in water As concentration (Fig. 2.6). This sharp increase suggests As release was due to desorption or fast dissolution of As-bearing minerals. At pH 3~8, after water As concentration reached maximum, it gradually decreased and leveled off, implying re-adsorption of released As to mineral surface (e.g., Fe oxyhydroxides, silicate minerals) (Lin and Puls, 2000). Both Fe oxyhydroxides and silicate minerals have high affinity for As at low to near neutral pH (Manning and Goldberg, 1997; Evangelou, 1998; Lin and Puls, 2000). At pH 10, after the initial rapid increase in water As concentration, water As concentration gradually increased until the end of the experiment (Fig. 2.6). This gradual increase indicates As release was controlled by mineral dissolution.

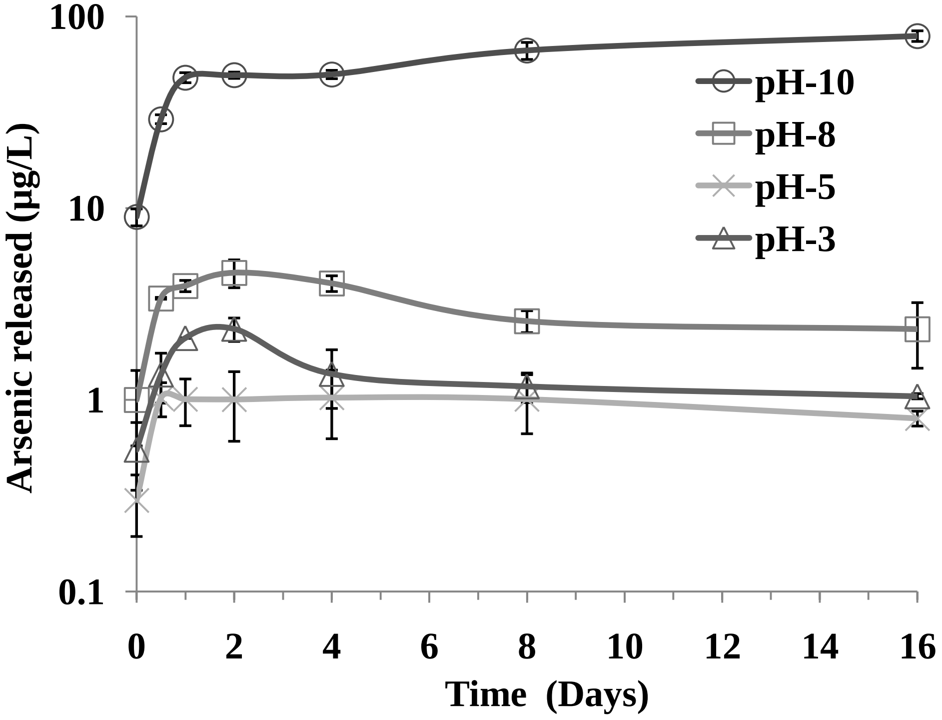


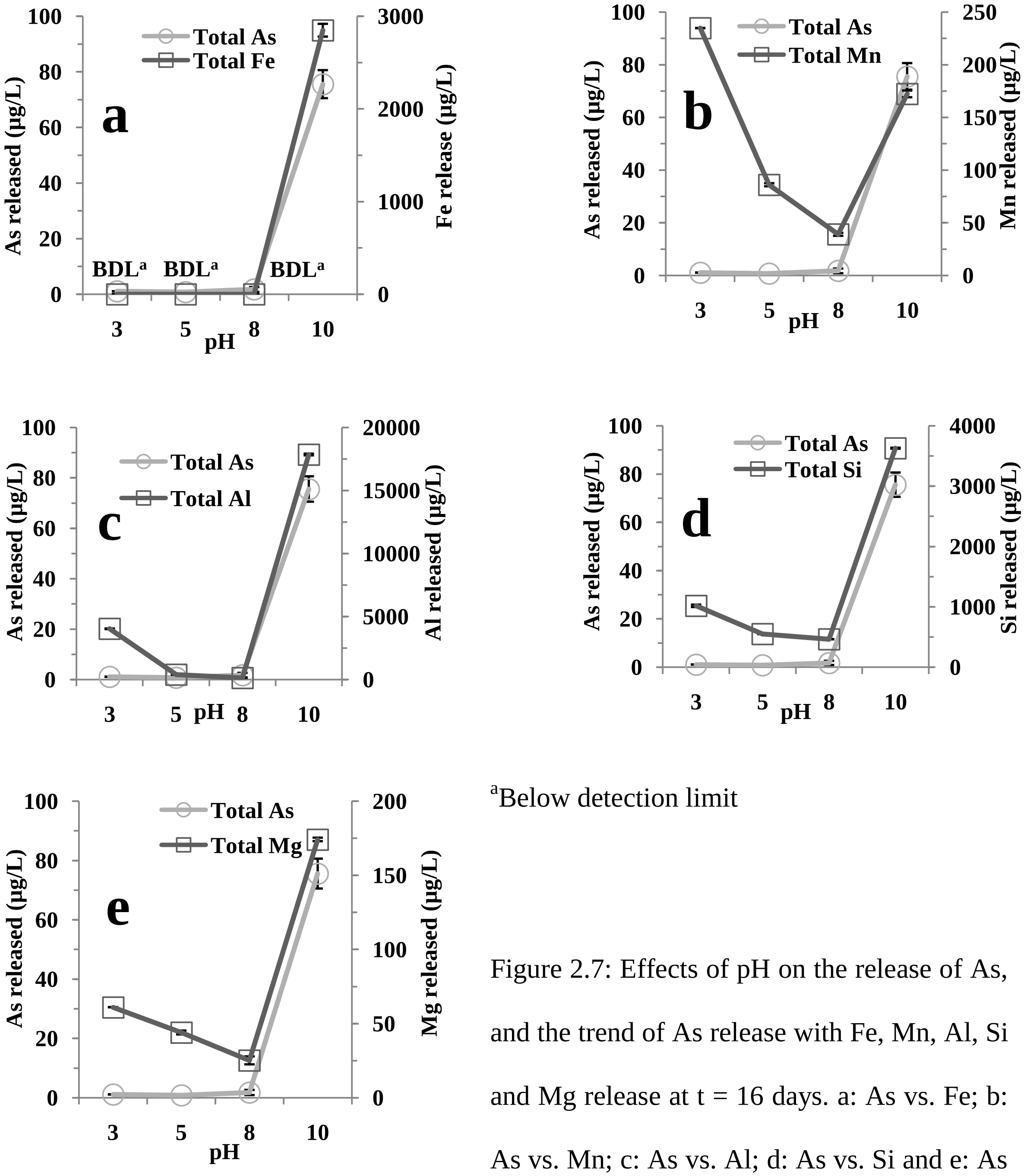
Figure 2.6: Effects of pH on As release.

pH influences mineral dissolution, as indicated by the difference in Fe, Mn, Al, Si and Mg release at different pH (Fig. 2.7a to 2.7e). In the pH range of 3~8, Fe concentrations in water were low and below detection limit (~115 µg/L), indicating both Fe oxyhydroxides and Fe-bearing silicate minerals were stable. At pH 10, high concentrations of Fe were released to water (Fig. 2.7a). Although both Fe oxyhydroxides and silicate minerals could contribute to Fe release, considering the stability and Fe concentration of Fe oxyhydroxides and silicate minerals, the Fe released to water was more likely from Fe oxyhydroxides.

Our measured Al and Si concentrations in water were highest at pH 10, moderate at low pH (3~5), lowest at pH 8 (Fig. 2.7c - 2.7d). These results reflected the influence of pH on the dissolution of silicate minerals and Al- oxyhydroxides. In addition to Fe/Al/Si, Mg and Mn were released during leaching (Fig. 2.7e and 2.7b). At low pH, water Mg was presumably from dissolution of carbonate minerals. In the pH range of 3~8, Mg concentration decreased with increasing pH, which is attributed to increased stability of Mg-carbonate minerals as pH increases. The high Mg concentration at pH 10 was caused by dissolution of Mg-bearing silicate minerals (e.g., biotite and chlorite). Unlike Fe/Al/Si/Mg, Mn concentration was the highest at low pH, decreased when pH increased from 3 to 8, but increased again as pH increased from 8 to 10. Mn released to water was presumably from Mn oxyhydroxides and/or Mn carbonates. The trend of As release, as influenced by pH, is similar to that of Fe/Mn/Al/Si/Mg in high pH range (Fig. 2.7a to 2.7e), i.e., when pH increased from 8 to 10, both arsenic release and Fe/Mn/Al/Si/Mg release increased significantly. However, the trend of arsenic release did not follow the trend of Fe/Mn/Al/Si/Mg release in the low pH range, i.e., when pH increased from 3 to 8, there was no noticeable change in Fe release and the release of Mn/Al/Si/Mg decreased, yet arsenic release increased slightly. These results imply As release is related to mineral dissolution at high pH, but not at low pH.

In the pH range 3~8, the pattern of As release as a function of leaching time was different from that of major elements (Mn/Al/Si/Mg) (Appendix 2C (Fig. 2C.1, 2C.2 and 2C.3)). Moreover, there was no strong correlation between water arsenic concentrations and water concentrations of Mn/Al/Si/Mg during leaching, as shown by the low $r^2$ value of linear regression (Appendix 2C (Fig. 2C.1, 2C.2 and 2C.3)). These results indicate at pH 3~8, arsenic release was not controlled by mineral dissolution. In our leaching experiments, one gram of sediment sample was mixed with 40 mL water. If desorption of exchangeable-phase As was the only mechanism that contributed to As release, and if 100% of the exchangeable-phase As was released to water, arsenic concentration in water would be 11 µg/L (calculated based on sequential extraction results). The maximum water As concentration measured in our experiments was 1.3 to 4.6 µg/L in the pH range 3~8, less than half of the expected As concentration if all the exchangeable-phase As was desorbed (11 µg/L). This result indicates in our experiments at pH 3~8, As release could be due to desorption of exchangeable-phase As only.

At pH 10, maximum water As concentration was 75.5 µg/L, far exceeding the expected As concentration if all the exchangeable-phase As were desorbed (11 µg/L). This suggests both desorption and mineral dissolution contributed to As release. At pH 10, Fe release was substantial (as high as 30,000 µg/L). The profile of As and Fe release during leaching were very similar, and water As and Fe concentrations were highly correlated ($r^2 = 0.97$) (Appendix 2C (Fig. 2C.4)), indicating Fe oxyhydroxides dissolution controlled As release. These results are in line with previous studies arguing that dissolution of Fe oxyhydroxides is the main process that control As release to groundwater (Ahmed et al., 2004; Akai et al., 2004; Fendorf et al., 2010).



[a] Below detection limit

Figure 2.7: Effects of pH on the release of As, and the trend of As release with Fe, Mn, Al, Si and Mg release at t = 16 days. a: As vs. Fe; b: As vs. Mn; c: As vs. Al; d: As vs. Si and e: As vs. Mg.

In our experiments water As concentrations were also correlated to water Mn concentrations, however, Mn concentrations at pH 10 were low and comparable to Mn concentrations at pH 3~8, but we have more As release at pH 10 than at pH 3~8 (Appendix 2C (Fig. 2C.1 to 2C.4)). Therefore dissolution of Mn-bearing minerals is unlikely to be a major arsenic release mechanism. At pH 10, Al/Si/Mg release was high, presumably due to high dissolution of silicate minerals. There was strong correlation between water arsenic concentrations and water concentrations of Al/Si/Mg, as shown by the high $r^2$ value of regression (Appendix 2C (Fig. 2C.4)). The strong correlation indicates a significant portion of released As was from silicate minerals. Although silicate minerals can store large quantities of As, their importance in controlling As release to groundwater has largely been neglected, due to the “inert” nature of silicate minerals. A few recent studies showed that silicate minerals could be the major source of As contamination in groundwater (Pal et al, 2002; Chakraborty et al., 2007; Seddique et al., 2008; Masuda et al., 2012). Our current study confirmed that dissolution of silicate minerals could be substantial and contribute to As release at high pH.

In summary, our pH experiments demonstrate that at relatively low pH (e.g., 3~8), mineral dissolution was limited and the main As release mechanism was desorption. At high pH (e.g., 10), mineral dissolution substantially increased, and the main As release mechanism was mineral dissolution. Both Fe oxyhydroxides and silicate minerals could contribute to As release at high pH, and As release can be significant. This partially explains why in many regions where As contamination in groundwater are reported (e.g., Bangladesh, India, Vietnam, Mongolia, Argentina, United states and few other parts in the world), groundwater is usually under alkaline conditions, and that water As concentration is positively correlated with pH (Smedley and Kinniburgh, 2002).

### 2.3.3.2 Effects of siderophore

At a fixed pH, arsenic release increased with siderophore concentrations (Fig. 2.8). At pH 5, after 16 days of leaching, water arsenic concentration was 1.3, 7.5, and 21.5 µg/L, respectively for the non-siderophore experiment (i.e., pH experiment at pH 5), 100 µM-siderophore experiment, and 500 µM-siderophore experiment. At pH 8, water As concentration after 16 days of leaching for the non-siderophore experiment (i.e., pH experiment at pH 8), 100 µM-siderophore experiment, and 500 µM-siderophore experiment was 4.6, 6.4, and 16.5 µg/L, respectively.

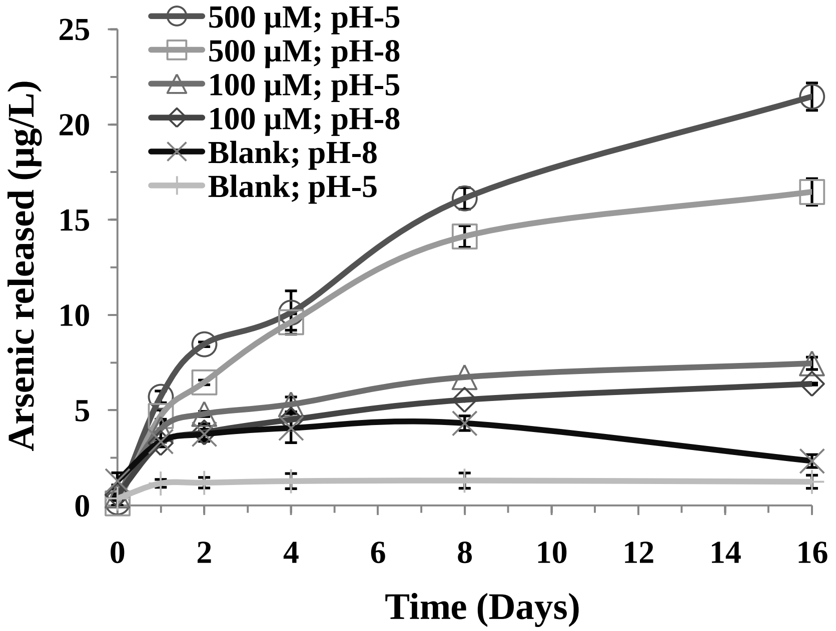
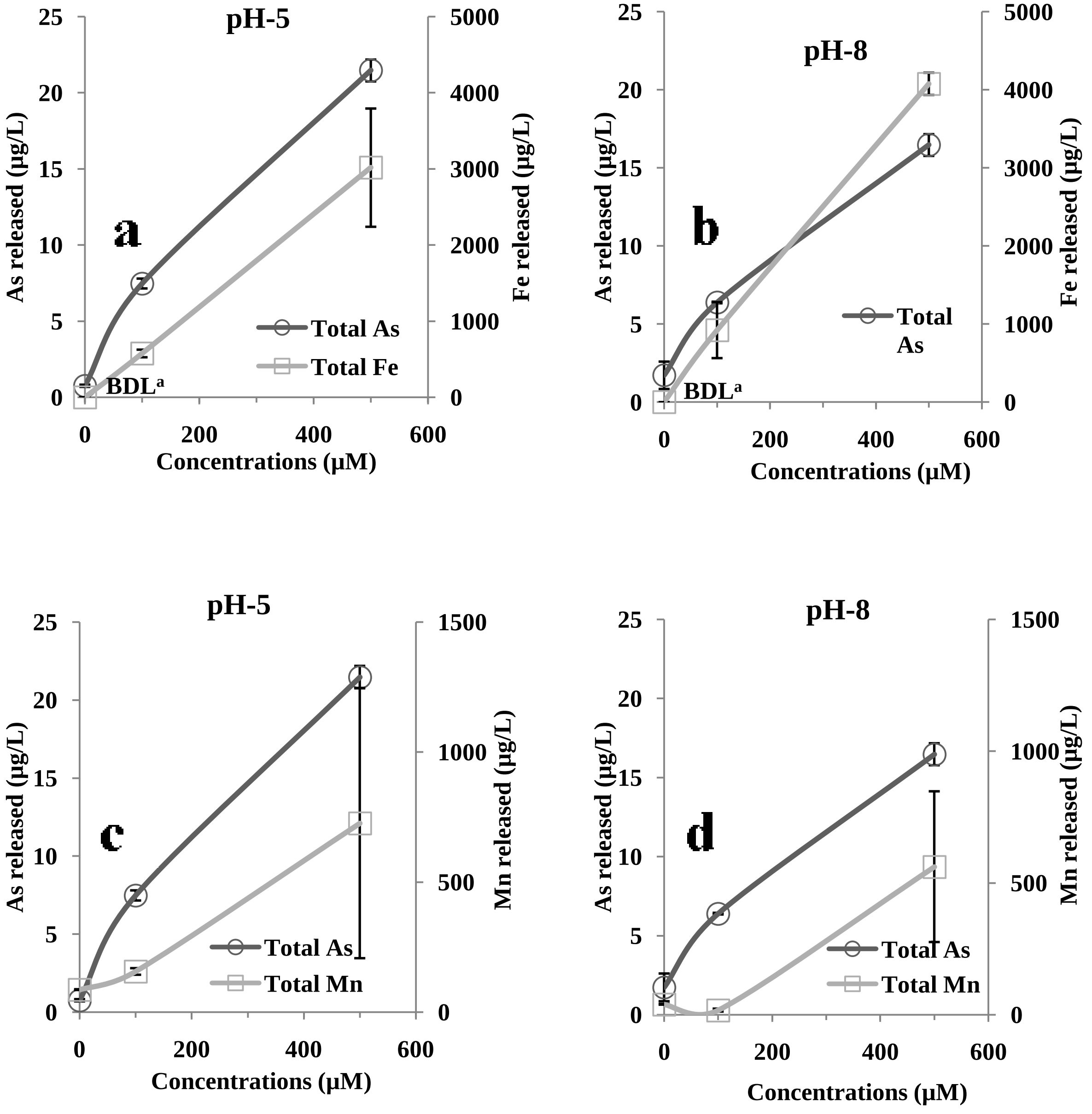


Figure 2.8: Effects of siderophore on As release.

The increase in As release in the presence of siderophore can be attributed to siderophore-enhanced mineral dissolution and/or desorption of As from mineral surface due to siderophore competition. Siderophores are small organic molecules produced by bacteria, fungi, and grasses to facilitate Fe acquisition from water by increasing the solubility of Fe-bearing minerals. Siderophores increase the dissolution of Fe-bearing and Al-bearing minerals by forming aqueous Fe(III)-siderophore and Al(III)-siderophore complexes (Holmén et al., 1997; Kraemer et al., 1999; Liermann et al., 2000; Cocozza et al., 2002). Our measurements showed that Fe/Mn/Al/Si concentrations in water increased with siderophore concentration (except for Si at pH 8), and that water As concentration increased concomitantly with Fe/Mn/Al/Si concentrations (Fig. 2.9a - 2.9h). Release of Mg was below detection limit of 3.35 μg $L^{-1}$. These results confirmed siderophore promoted dissolution of Fe and Mn oxyhydroxides and Al-bearing silicate minerals, and induced As release.

In our non-siderophore treatments, arsenic release was higher at pH 8 than at pH 5 (Fig. 2.8). In the 100 μM-siderophore and 500 μM-siderophore treatments, however, the trend was reversed: arsenic release was higher at pH 5 than at pH 8 (Fig. 2.8). This can be explained by competition between siderophore and As for surface sites. Two steps are involved in the siderophore-enhanced dissolution: (i) siderophore absorbs to mineral surface and serves as a reactant in a ligand-controlled dissolution, and (ii) siderophore forms aqueous complexes with Fe(III) or Al(III) in water, leading to increased solubility (Cheah et al., 2003). In the pH range of 5~8, siderophore is an anion and its adsorption to mineral surface is higher at lower pH 5 than at pH 8. Therefore, more As desorbed from mineral surface at pH 5, resulting in higher water As concentration (Cheah et al., 2003; Casentini and Pettine, 2010).



[a]Below Detection Limit

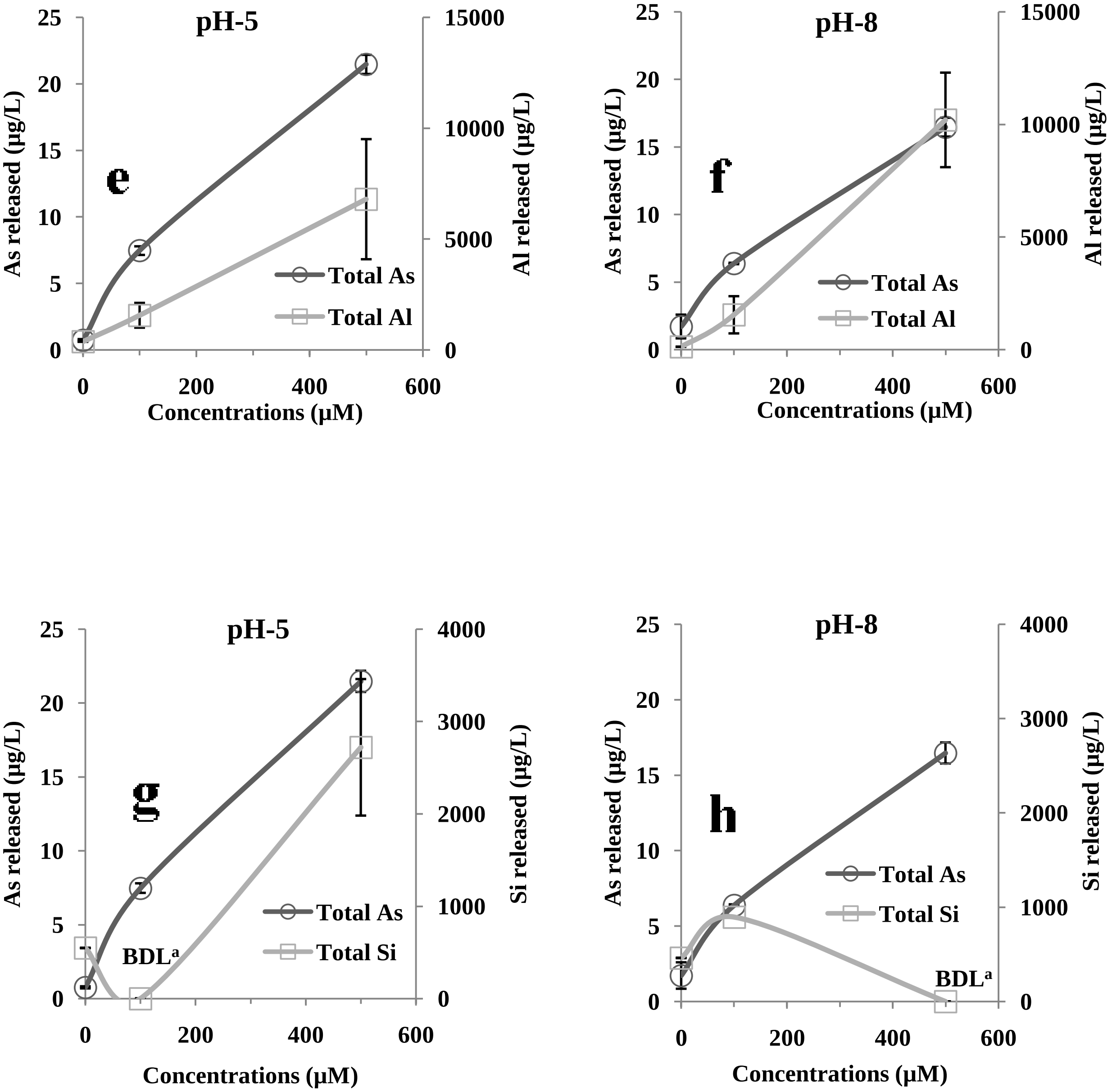


Figure 2.9: Effects of siderophore concentrations on the release of As, and the trend of As release with Fe, Mn, Al and Si release at t = 16 days for pH 5 and 8. a: As vs. Fe at pH 5; b: As vs. Fe at pH 8; c: As vs. Mn at pH 5; d: As vs. Mn at pH 8; e: As vs. Al at pH 5; f. As vs. Al at pH 8; g. As vs. Si at pH 5 and h. As vs. Si at pH 8.

In our 100 µM siderophore treatment, maximum water As concentration (occurred at t = 16 days) was 7.5 µg/L (pH 5) and 6.4 µg/L (pH 8), respectively, lower than the expected As concentration (11 µg/L) if all the exchangeable-phase As are dissolved. This suggest As release could be caused by desorption only. However, this does not exclude the possibility that mineral dissolution also contributed to As release. As a matter of fact, there was a good correlation between water As concentrations and water Fe concentrations during leaching for both pH, as shown by the high $r^2$ value of regression (Appendix 2D (Fig. 2D.1 and 2D.2)). Yet, there is no strong correlation between water arsenic concentration and water Al concentration (Appendix 2D (Fig. 2D.1 and 2D.2)). These results suggest dissolution of Fe oxyhydroxides is the major As release mechanism in the presence of 100 µM siderophore. Although dissolution of Al-bearing silicate minerals was obvious, it does not seem to contribute to As release (as indicated by low $r^2$ value), probably due to the lower As concentration in silicate minerals (compared to As concentration in Fe oxyhydroxides).

At siderophore concentration of 500 µM, the maximum water As concentration was 21.5 µg/L (pH 5) and 16.5 µg/L (pH 8), respectively, higher than the exchangeable-phase As in the sediment, indicating contribution from mineral dissolution. There was a good correlation between water arsenic concentrations and water concentrations of Fe and Mn, as well as Al and Si, as shown by the high $r^2$ value of regression (Appendix 2D (Fig. 2D.3 and 2D.4)), indicating dissolution of both Fe oxyhydroxides and Al-bearing minerals contributed to As release. Overall, our siderophore experiments showed that As release is sensitive to Fe oxyhydroxides dissolution, due to high As concentration in Fe oxyhydroxides. Conversely, arsenic release is influenced by silicate minerals dissolution only under conditions when large quantities of silicate minerals are dissolved. Contribution from silicate minerals to As release in natural subsurface environments could be substantial, since silicate minerals are usually the most abundant components in many sediments, and large amount of As are associated with these minerals.

### 2.3.3.3 Effects of Eh

Arsenic release from sediment to water was much higher under reducing conditions than under oxidizing conditions (Fig. 2.10): under oxidizing conditions, 43.5 µg/L (Eh = +350 to +200 mV) and 70 µg/L (Eh = +150 to +100 mV) As were released, respectively, after 16 days of leaching, while under reducing conditions, 227 µg/L (Eh = +50 to -50 mV) and 224 µg/L (Eh = +50 to -150 mV) As were released, respectively. In all of our Eh experiments, water As concentration after 16 days leaching was higher than the expected As concentration if all the exchangeable-phase As is released (11 µg/L), indicating contribution from mineral dissolution. Under reducing conditions, water As concentration (t = 16 days) was ~220 µg/L, twice as high as the expected As concentration if all the labile As in the sediment were released to water (120 µg/L). This result suggests As in the residual phases (i.e., As bound to silicate minerals) released under these conditions.

Redox potential significantly influenced the dissolution of Fe and Mn oxyhydroxides (Fig. 2.11a and 2.11b): when Eh changed from oxidizing to reducing conditions, Fe concentration in water (at t = 16 days) increased 5 folds from 8,829 to

48,965 µg/L, and Mn concentration in water (at t = 16 days) increased almost 10 folds from 385 to 5,165 µg/L. Under reducing conditions, significant amount of Fe was release to water, and As release was closely related to Fe release, as indicated by the similar pattern of As and Fe release and the high $r^2$ value of regression (Appendix 2E (Fig. 2E.1 and 2E.2)). These results confirmed reductive dissolution of Fe oxyhydroxides was a major mechanism for As release in these experiments. Under reducing conditions, reductive dissolution of Mn oxyhydroxides may also contribute to As release. In our experiments, Mn release was significant but much lower than that of Fe (Fig. 2.11a and 2.11b), and there was discrepancy in the pattern of As and Mn release (Fig. 2.11b). The $r^2$ value of regression between water As and Mn concentrations were lower than those for As and Fe (Appendix 2E (Fig. 2E.1 and 2E.2)). These results suggest dissolution of Mn may contribute to As release, but to a less extent compared with Fe.

Unlike Fe and Mn oxyhydroxides, dissolution of silicate minerals is not expected to be sensitive to redox potential (Masscheleyn et al., 1991). Nonetheless, we found release of Al/Si/Mg (presumably from silicate minerals) was influenced by redox potential, but to a less extent compared to Fe and Mn. When Eh changed from highly oxidizing to highly reducing conditions, Al concentration in water (at t = 16 days) increased 1.6 folds from 18,214 to 27,480 µg/L, Si 2.3 folds from 5,753 to 13,606 µg/L, and Mg 2.6 folds from 273 to 671 µg/L (Fig. 2.11c - 2.11e).

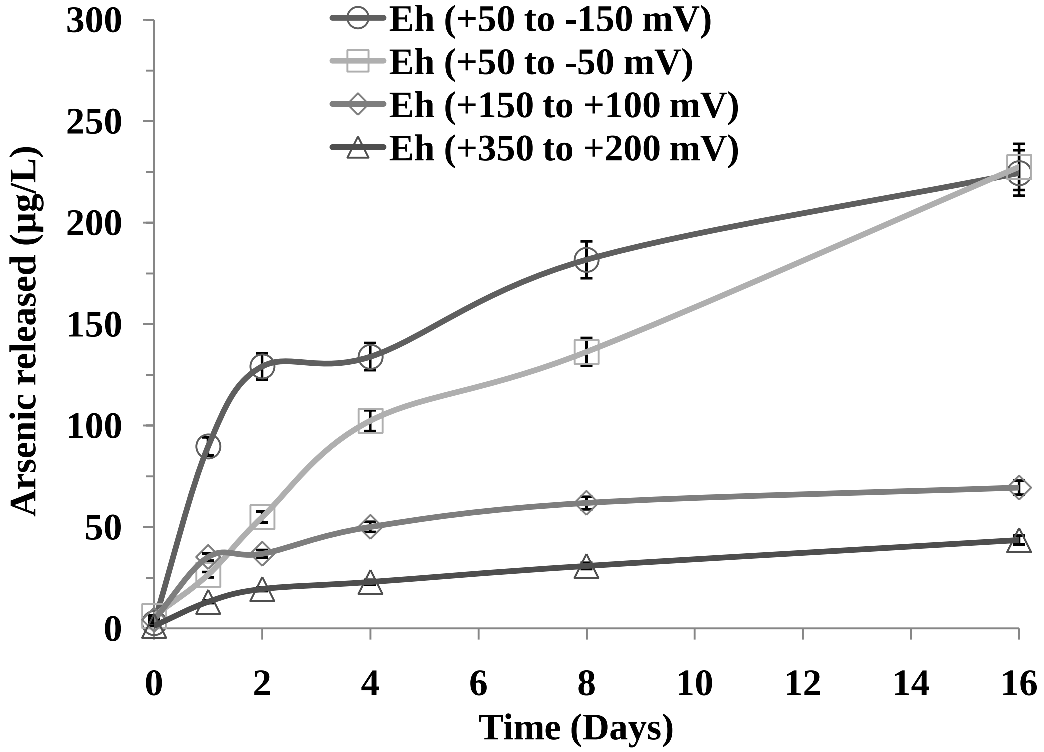


Figure 2.10: Effects of Eh on As release.

Silicate minerals dissolution itself is not influenced by redox potential. However, significant dissolution of Fe oxyhydroxides (presumably exists as coatings on silicate minerals) at low Eh could expose silicate minerals surface to water and therefore promoted Al/Si/Mg release. Moreover, at the lowest Eh range (Eh = +50 to -150 mV), the presence of 0.03 M citrate, which serves as a chelating agent for Al (Arshad et al., 1972; Reyes and Torrent, 1997), can facilitate dissolution of Al-bearing silicate minerals. The pattern of Al/Si/Mg release was similar to As release, and there was a strong correlation between water As concentrations and water concentrations of Al/Si/Mg (Appendix 2E (Fig. 2E.1 and 2E.2)). These results showed that under reducing conditions, significant dissolution of silicate minerals could occur and result in As release. In natural aquifers, groundwater Eh could be much lower than the lowest Eh used in our experiments. Under these conditions, mineral dissolution could be substantial, and large amount of As in silicate minerals can be released.

In our Eh experiments, even under highly oxidizing conditions (+350 to +200 mV), Fe release was higher than those in our pH experiments and siderophore experiments at similar pH (Fig. 2.12). This Eh (+350 to +200 mV) was higher than the Eh in our pH experiments (average ~170 mV) and sidrophore experiments (average ~162 mV). However, Fe release in the Eh experiments (8,829 µg/L) was much higher than that in our pH experiment (< 115 µg/L) and siderophore experiment (4,000 µg/L). This result seems inconsistent with reductive dissolution of Fe oxyhydroxides. The high Fe release in our Eh experiments can be explained by the presence of citrate. High concentration of citrate (0.03 M) was added to water in our Eh experiments to control Eh. Citrate is a chelating agent for Fe, which significantly increased Fe- oxyhydroxides dissolution and therefore Fe release (Reyes and Torrent, 1997).

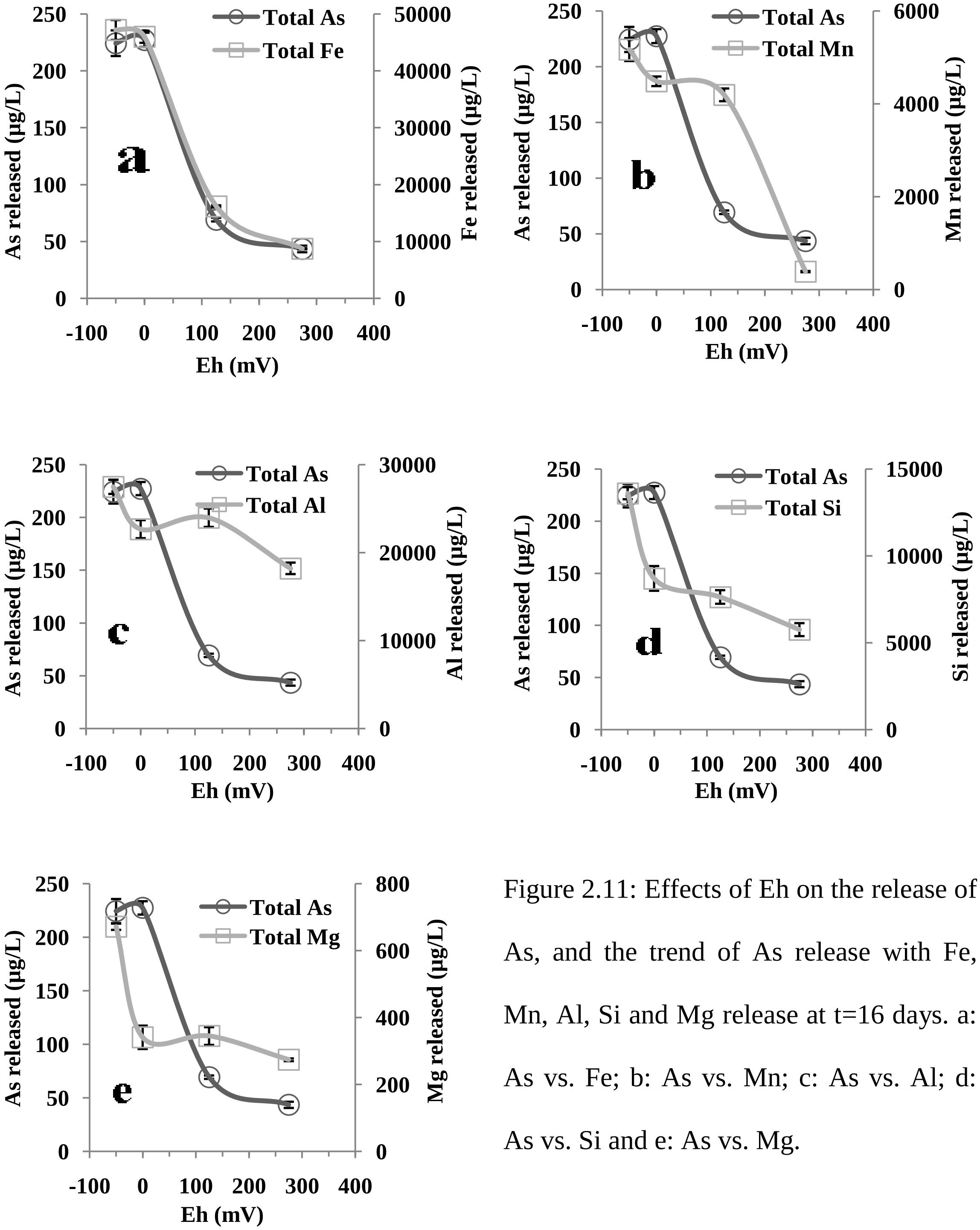


Figure 2.11: Effects of Eh on the release of As, and the trend of As release with Fe, Mn, Al, Si and Mg release at t=16 days. a: As vs. Fe; b: As vs. Mn; c: As vs. Al; d: As vs. Si and e: As vs. Mg.

In the Eh experiment, Al/Si/Mg release was also higher than those in our pH experiments and siderophore experiments at similar pH (Fig. 2.12), indicating higher dissolution of silicate minerals. Two mechanisms account for this higher dissolution: (i) citrate, which is a chelating agent for Al, could enhance the dissolution of Al-bearing silicate minerals; (ii) dissolution of Fe- oxyhydroxides coating exposed silicate minerals surface to water, leading to increased dissolution of silicate minerals (Arshad et al., 1972; Reyes and Torent, 1997). Under highly oxidizing conditions, the pattern of As release was similar to that of Fe/Mn/Al/Si/Mg, and there was strong correlation between water As concentrations and water concentrations of Fe/Mn/Al/Si/Mg (Appendix 2E (Fig. 2E.3)). These results showed that in the presence of Fe/Al chelators, significant dissolution of Fe/Mn oxyhydroxides and silicate minerals could occur and result in As release.

Under moderately oxidizing conditions (+150 to +100 mV), Fe/Mn/Al/Si/Mg and As release in our Eh experiments was higher than that under highly oxidizing conditions (+350 to +200 mV) (Fig. 2.11a to 2.11e). No citrate was added to water under moderately oxidizing conditions. Only ascrobate, which is not a chelating agent, was used to control Eh. The higher Fe release under moderately oxidizing conditions is presumably due to the lower Eh, i.e., Fe oxyhydroxides became less stable as Eh decreased. Silicate minerals dissolution was also higher under moderately oxidizing conditions, as indicated by the higher Al/Si/Mg release (Fig. 2.11c to 2.11e).

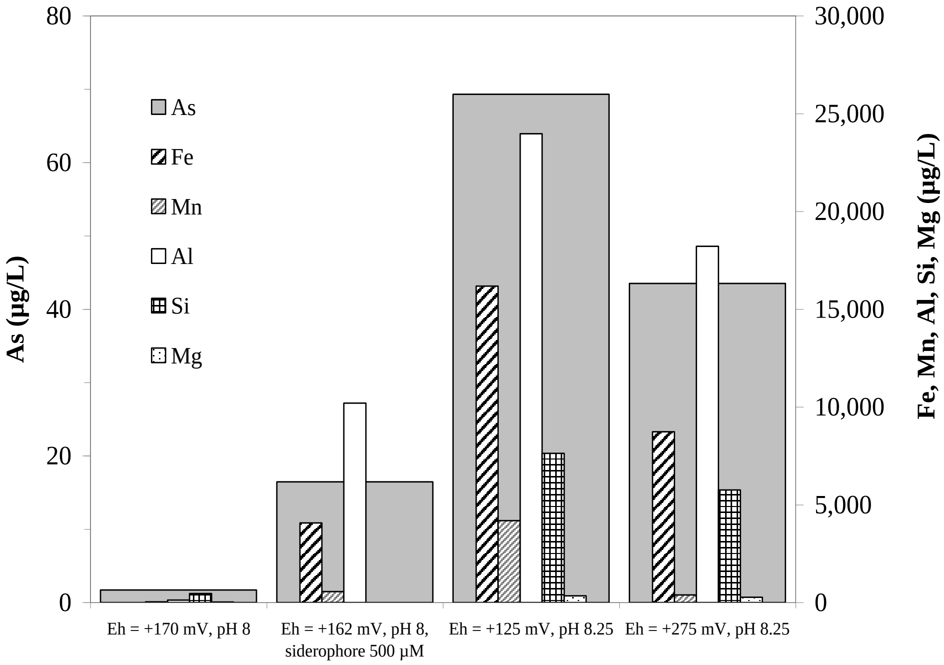


Figure 2.12: Correlation of As with Fe, Mn, Al, Si and Mg comparing different experimental conditions (pH, Eh and siderophore concentrations) at t = 16 days.

Although silicate minerals dissolution is not influenced by changes in Eh, dissolution of Fe oxyhydroxides coating exposed silicate minerals surface to water for dissolution. Under moderately oxidizing conditions, the pattern of As release was similar to Fe and Al release, and there was strong correlation between water As concentrations and water concentrations of Fe and Al (Appendix 2E (Fig. 2E.4)). These results showed that lower Eh could promote dissolution of Fe oxyhydroxides coating and silicate minerals, and that both Fe oxyhydroxides and silicate minerals may contribute to As release.

## 2.4 Conclusions

Silicate minerals and Fe oxyhydroxides are the major As-hosting phases in our natural sediment sample. Arsenic exists in dispersed forms in the sediment, i.e., they are either adsorbed onto mineral surface or incorporated into mineral structure as impurities. Arsenic is released from sediment to water as a result of mineral dissolution and/or desorption, depending on water chemistry conditions. Although Fe oxyhydroxides are a minor component in our sediment sample, they concentrate substantial quantities of As, and dissolution of Fe oxyhydroxides could be the major As release mechanism when dissolution of silicate minerals is low. Silicate minerals are the most abundant component in our sediment sample, and serves as the primary As host. Dissolution of silicate minerals could be extensive under conditions such as high pH, low Eh, and the presence of Fe and Al chelators. Substantial quantities of As could release from silicate minerals to water under these conditions. Silicate minerals are potentially an important source of As contamination in groundwater.

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# Chapter 3. Uranium Release from Sediment to Groundwater: Influence of Water Chemistry and Insights into Release Mechanisms

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## Abstract

Uranium (U) contamination in groundwater often results from natural geochemical processes such as mineral dissolution and desorption of adsorbed U from mineral surfaces. Although U mineral dissolution and U adsorption have been extensively studied, there have been relatively fewer studies on U release from heterogeneous natural sediments, and it is not clear what geochemical processes are involved in U release under natural conditions. The objective of this study is to identify the minerals in a heterogeneous natural sediment that host U, and to determine the mechanisms and extent of U release under water chemistry conditions relevant to natural soil water and groundwater. A sediment sample was collected, characterized, and examined using laboratory leaching experiments. Our results show that carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals are major U hosting minerals, and that U release is controlled by a number of interactive processes including U desorption from mineral surface, dissolution of U-bearing minerals, formation of aqueous U complexes, and reductive precipitation of U. Results from this study shed light on the important geochemical reactions that need to be considered for developing a conceptual model that predicts U contamination in subsurface environment.

**Keywords**: Uranium release, Sediment, Mineral dissolution, Desorption, Groundwater contamination

## 3.1 Introduction

Uranium (U) is a contaminant commonly found in groundwater that could pose a serious threat to human health. Dissolved U at very low concentrations is found in most natural waters (Mkandawire, 2013), and typical groundwater concentration of dissolved uranium is on the order of a few µg U/L (Herring, 2013; Wiedemeier et al., 1995). Although groundwater U contamination in some cases is caused by anthropogenic pollution such as uranium mining, processing of uranium ores, and production and disposal of radioactive materials, U in groundwater is more often introduced by natural geochemical processes: i.e., U is released to groundwater from its hosting rocks and sediments via mineral dissolution and/or U desorption from mineral surface (Chen et al., 2005; James and Sinha, 2006). Uranium is ubiquitous in the crust with an average concentration of 2.76 mg/kg (Herring, 2013). Common naturally-occurring U minerals include: oxides (uraninite and pitchblende), silicates (coffinite, soddyite, uranophane, and uranothorite), phosphates (autunite), and vanadates (carnotite). Besides discrete U minerals, a significant fraction of solid-phase U exists in the form of uranyl ion $(UO2)^{2+}$ adsorbed to mineral surfaces under oxidizing conditions (Welch and Lico, 1998; Wiedemeier et al., 1995).

The extent of U release from minerals and hence U concentration in water is controlled by U hosting mineral, oxidation state of U, and water chemistry (Fanghanel and Neck, 2002). Under reducing conditions, the oxidation state of U is +4, and the stable U (IV) phases are mainly uraninite and coffinite (Duff et al., 1999). Organic complexes of U (IV) associated with humic material may also retain U (IV) in the solid phase (Bednar et al., 2007). The solubility of U (IV) minerals is extremely low, and reducing conditions effectively diminishes the movement of uranium in soils and groundwater (Duff et al., 1999; Wiedemeier et al., 1995). Reductive precipitation of U(VI) is an effective method to immobilize U (Abdelouas et al., 1998; Finneran et al., 2002; Fredrickson et al., 2000; Lovley and Phillips, 1992), while oxidative dissolution of U(IV) minerals is a major mechanism of U mobilization (Finch and Murakami, 1999; Finch and Ewing, 1992; Wiedemeier et al., 1995). Under oxidizing conditions, the predominant oxidation state of U is +6, and U(VI) mainly exists in the form of uranyl ion. The adsorption/desorption of uranyl ion to/from the mineral surface is a major process that controls U mobility under oxidizing conditions. Important U(VI) adsorbing minerals include iron oxyhydroxides, clay minerals, and organic matters (Bowman, 1997; Catalano et al., 2006; Kelly et al., 2003; Kelly et al., 2006; Wang et al., 2005; Wiedemeier et al., 1995). Water chemistry parameters that control U adsorption include: pH, redox potential (Eh), carbonate, phosphate, and natural organic matter (Bednar et al., 2007; Cheng et al., 2004; Echevarria et al., 2001; Sanding and Bruno, 1992). Water chemistry influences U adsorption/desorption by changing surface charge and solubility of minerals, U oxidation state and speciation, as well as the speciation of aqueous and surface complexes (Bachmaf et al., 2008; Casas et al., 1998; Echevarria et al., 2001; Katsoyiannis, 2007; Wazne et al., 2003).

Although U(VI) adsorption and U(IV) mineral dissolution have been extensively studied (Giammar and Hering, 2004; Sharp et al., 2011; Ulrich et al., 2008; Wang et al., 2013), there have been relatively fewer studies on U release from solid materials, especially from heterogeneous natural sediments. It has been observed that high U concentration in water is often associated with oxidizing, carbonate-rich, and phosphate-free conditions (Catalano et al., 2006; Kelly et al., 2003; Kelly et al., 2006). However, a number of questions, which are essential in understanding U release and predicting U contamination in soil water and groundwater, are unanswered. These questions include: (i) What are the major U hosting minerals in heterogeneous natural sediments? (ii) Does U in natural sediments exist as U minerals or as adsorbed U(VI) on other mineral surface? (iii) What is the mechanism of U release in soil and groundwater? Is it desorption, or mineral dissolution, or both? (iv) How do water chemistry variables (pH and redox potential) and dissolved chemicals commonly found in natural water (e.g., citrate, bicarbonate, and natural organic matter) influence U release from natural sediments? And to what extent?

The objective of this study is to: (i) identify the major minerals in a natural heterogeneous sediment that host and release U, and (ii) determine the mechanisms and extent of U release under a range of water chemistry conditions relevant to natural soil water and groundwater. A sediment sample was collected, characterized, and examined using laboratory leaching experiments to investigate the effects of pH, Eh, citrate, bicarbonate, and natural organic matter on U and major element release. Our results show that carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals are major U hosting minerals, and substantial amounts of U exist as adsorbed uranyl ion. We also found U release increased with increasing pH and redox potential, and that citrate, bicarbonate, and natural organic matter promoted U release. By comparing U and major element release profiles, we concluded that U desorption is the dominant U release mechanism under most of the water chemistry conditions tested in our leaching experiments. This study demonstrated the importance of carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals as U hosting phases, and shed light on the mechanisms of U release from natural sediments to water.

## 3.2 Materials and methods

### 3.2.1 Sample collection and characterization

A sediment sample was collected on 30th August, 2012 from a site (latitude: N 46.89577624 and longitude: W 55.39293679) near St. Lawrence (Fig. 3.1), a town located in Burin Peninsula, south coast of the Island of Newfoundland, Canada, where uranium concentrations are high in sediments and some water wells according to the Department of Environment and Conservation – Government of Newfoundland and Labrador (Newfoundland and Labrador Water Resource Portal and http://maps.gov.nl.ca/water/mapbrowser/Default.aspx). The till sample was collected from a depth of 0.6 to 1 m below land surface, air dried and sieved through 0.053 mm sieve, well mixed, and stored in plastic buckets for use in all subsequent experiments. The cutoff size of 0.053 mm is recommended by the Till Protocol Working Group Canada for geochemical analysis because ore minerals are easily broken down to this size range over short distances and it contains phyllosilicates that will scavenge cations released during weathering (Lett, 1995; Levson, 2001; Nevalainen, 1989; Shilts, 1993; Tarvainen, 1995).

Mineral composition of the sediment sample was determined using X-ray diffraction (XRD) and scanning electronic microscopy equipped with energy dispersive spectroscopy (SEM-EDX). The details of the XRD and SEM-EDX analysis was described elsewhere (Alam and Cheng, in prep). The pH, organic carbon, and metal concentrations of the sample were determined using wet chemistry methods. Sediment pH was determined by mixing 5 mM $CaCl_2$ with 2.5 grams of dry sediment sample, and measuring the pH of the supernatant (Williams et al., 2003). Organic carbon content in the sediment sample was determined following the procedure described by Gregorich and Ellert (1993), i.e., a solution of 5 mM $CaCl_2$ was use to extract organic carbon from the sediment, and the extracted dissolved organic carbon (DOC) in the $CaCl_2$ solution was measured by a Shimadzu TOC-V analyzer. A five step sequential extraction procedure (detail procedure is described in Appendix 2A) (Tessier et al., 1979) was performed on the sediment sample to determine the elements (i.e., Fe, Mn, Al, Si, Mg, Ca and U) contained in each of the following five phases: exchangeable phase, carbonate minerals, Fe and Mn oxyhydroxides, organic phases and residual phases, with the extracted solutions measured by ICP-MS using synthetic calibration solutions.

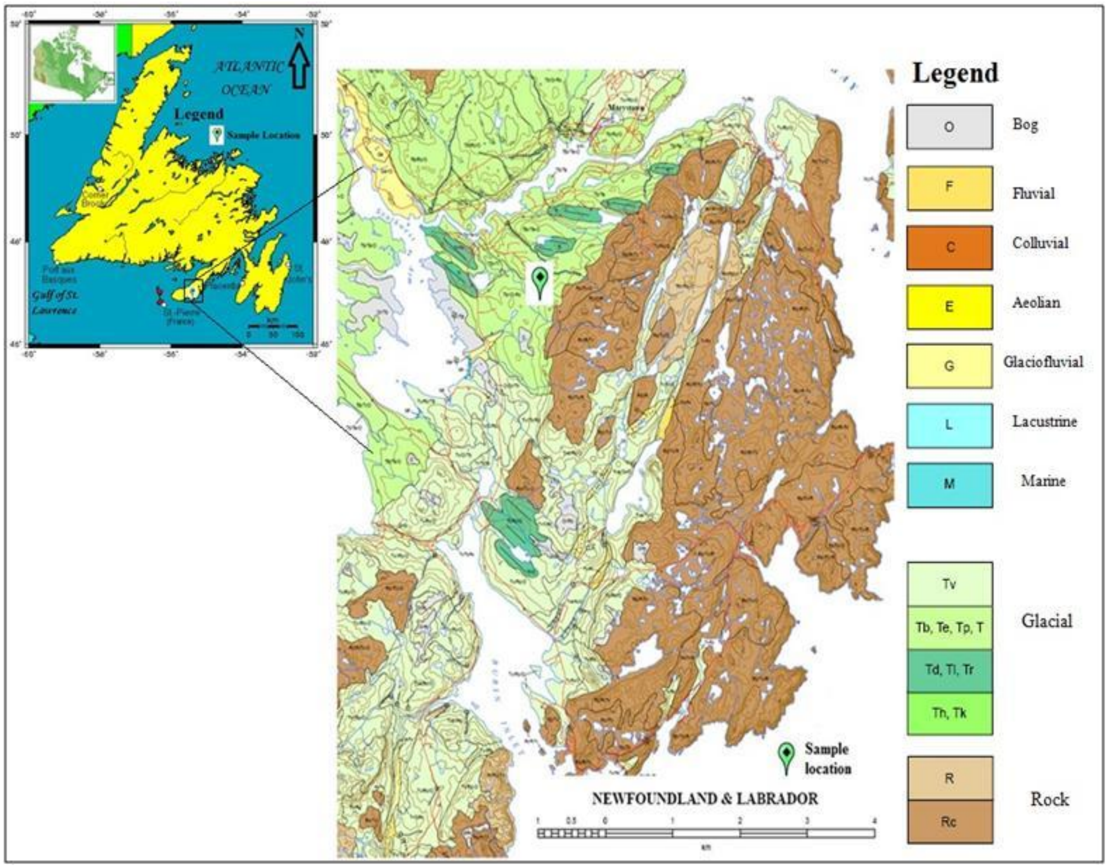


Figure 3.1: Sampling location shown on alluvial geology map (after www.nr.gov.nl.ca/nr/mines/maps/surfnl/surfnl).

### 3.2.2 Batch leaching experiments

Sodium chloride (NaCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium citrate dihydrate ($C_6H_9Na_3O_9.2H_2O$), and sodium ascorbate ($C_6H_7NaO_6$) were all analytical grade and purchased from VWR Canada. Humic acid (natural organic matter (NOM)) was obtained from Alfa Aesar. All the solutions used in our experiments were prepared by dissolving the chemicals in deionized water.

To evaluate the effects of pH, Eh, bicarbonate, and natural organic matter (NOM) on mineral dissolution and uranium release from sediment to groundwater, four types of batch leaching experiments were conducted: (i) pH experiments; (ii) Eh experiments; (iii) bicarbonate experiments, and (iv) NOM experiments. We carried out four pH experiments (pH = 3.0, 5.0, 8.0 and 10), four Eh experiments (Eh = +200 to +300 mV, pH = 3; Eh = +200 to +300 mV, pH = 10; Eh = +50 to -150 mV, pH = 3; Eh = +50 to -150 mV, pH = 10) , two bicarbonate experiments (bicarbonate concentration = 0.01 M, pH = 8; bicarbonate concentration = 0.001 M, pH = 8), and two NOM experiments (humic acid concentration = 50 mg C/L, pH = 8; humic acid concentration = 20 mg C/L, pH = 8). To prepare a sample for the leaching experiments, one gram (1.000 g) air-dried, sieved sediment sample was mixed with 40 ml background solution in a 50 ml HDPE centrifuge tube. The background solution was 0.01M NaCl solution for pH experiments, citrate or citrate + ascorbate in 0.01M NaCl solution for Eh experiments (Table 3.1), 0.01 M or 0.001 M bicarbonate in 0.01 M NaCl solution for bicarbonate experiments, and 50 mg C/L or 20 mg C/L humic acid in 0.01 M NaCl solution for NOM experiments. The pH of each sample was adjusted and maintained by adding 1 M NaOH and/or 1M HCl to the suspensions. The total volume of the NaOH + HCl solution used was very small (< 0.5 mL), so that the final volume of the solution was close to 40 mL.

Table 3.1: pH and Eh conditions of Eh experiments with various reducing agents.

| Reagents | Concentrations (M) | pH | Eh (mV) |
|---|---|---|---|
| Sodium citrate | 0.03 | 3 | +200 to +300 |
| Sodium citrate | 0.03 | 10 | +200 to +300 |
| Sodium citrate + sodium ascorbate | 0.03 + 0.06 | 3 | -150 to +50 |
| Sodium citrate + sodium ascorbate | 0.03 + 0.06 | 10 | -150 to +50 |

Twelve identical samples were prepared for each of the pH, Eh, bicarbonate, and NOM experiment. The centrifuge tubes holding the samples were capped and placed on a shaker table. At pre-determined leaching time of 0, 1, 2, 4, 8, 16 days, two replicate sample tubes were sacrificed for each experiment. The tubes were taken off from the shaker, and the pH and Eh were immediately measured using Thermo Orion Kit Star A211 Ph Bt with pH electrode (8102 ROSS; Thermo Orion) and ORP electrode (Orion Sure-Flow Comb Redox Ele). Supernatant was withdrawn from each tube, promptly filtered through 0.45 µm nylon filters, and analyzed by ICP-MS for U, Fe, Mn, Al, Si, Mg, and Ca concentrations using synthetic calibration solutions. The limit of detection

(LOD) for U, Fe, Mn, Al, Si, Mg and Ca was 0.56 $\mu gL^{-1}$, 115 $\mu gL^{-1}$, 0.17 $\mu gL^{-1}$, 5.3 $\mu gL^{-1}$, 250 $\mu gL^{-1}$, 1.2 $\mu gL^{-1}$, 126 $\mu gL^{-1}$, respectively.

## 3.3 Results and discussion

### 3.3.1 Characterization of sediment

#### 3.3.1.1 Mineralogical composition

X-ray diffraction (XRD) profile shows that quartz, albite and microcline constitutes the major mineral phases in the sediment sample (Fig. 3.2). A few unidentified small peaks in the XRD profile prove the existence of other minerals in the sediment sample. These minerals could not be identified because their quantity was below the detection limit of XRD analysis (~ 1 to 5% of the total mass) (Pecharsky and Zavalij, 2008). SEM-EDX analysis substantiated the presence of quartz, albite and microcline (potassium feldspar), and identified many other minerals (Table 3.2). Fe oxyhydroxides (0.59 wt.%) (Table 3.2 and Fig. 3.3B) and pyrites ($FeS_2$) (0.14 wt.%) (Fig. 3.3C) were identified in SEM-EDX analysis. SEM-EDX showed the presence of few coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) grains which occurs naturally with U(IV) (Fig. 3.3A). No uranium dioxide ($UO_2$) or minerals that contain U(VI) (i.e., uranyl ion) were positively identified. However, this does not exclude the possibility that uranyl ions are present in the sediment in dispersed forms (i.e., adsorbed species on mineral surfaces and/or impurities in mineral structures) that are below the detection limit of SEM-EDX, which is ~ 0.01% of the total mass.

### 3.3.1.2 pH, organic carbon, and phase distribution of uranium and major elements

The sediment had a pH value of 5.70, and soluble organic carbon content of 0.014%. The total U concentration in the sediment sample was measured as 26 mg/kg by summing each fraction from sequential extraction steps (Appendix 3A). The distribution of U in different phases is shown in Fig. 3.4. The labile phase of U amounts to 66.6% of the total U. Labile U either adsorbs to the surface of minerals as an exchangeable phase or is associated with minerals that could be easily soluble under proper conditions (Tessier et al., 1979).

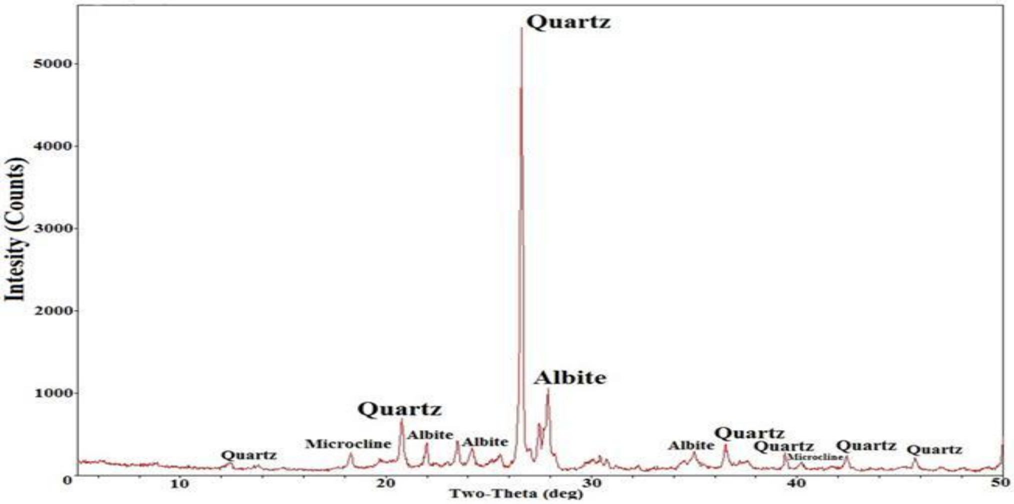


Figure 3.2: XRD profile of sediments.

Uranium bound to carbonate minerals comprises the largest pool of labile U followed by U bound to Fe-Mn oxyhydroxides, accounting for 35.4% and 21.6% of the total U, respectively. Labile U is also bound to exchangeable and organic phases, each of which amounts to 0.52% and 7.33% of the total U, respectively. Although coffinite (U(SiO4)1-x(OH) 4x) is the only U-bearing mineral identified by our SEM-EDX analysis, U was found in each step of our sequential extraction. Uranium in our sample seems to adsorb to mineral surfaces or exists as impurities in minerals. Iron oxyhydroxides, silicate minerals, and carbonates are known to absorb trace elements (e.g., U) in sediments (Chatain et al., 2005; Tessier et al., 1979). Besides the labile phases, the residual phase (mostly silicate minerals) holds a significant portion of U (33.4%). U most probably exists in the residual phase as impurities in the structure of silicate minerals, which are not easily soluble and resistant to dissolution in the first 4 steps of extraction (Tessier et al., 1979).

The total concentration of Fe, Mn, Al, Mg and Ca in the sediment sample was measured as 36.4, 0.89, 88.1, 6.29 and 5.75 g/kg, respectively by summing each fraction from sequential extraction steps (Appendix 3A). The distributions of Fe, Mn, Al, Mg and Ca in different phases are shown in Fig. 3.4. The largest pool of Fe, Mn, Al, Mg and Ca is in the residual phase (silicate minerals), accounting for 88.4%, 84.7%, 93.3%, 74.9% and 74% of the total Fe, Mn, Al, Mg and Ca, respectively. Fe bound to organic phase has highest pool of labile Fe followed by Fe bound to Fe-Mn oxyhydroxides phase, amount to 4.84% and 4.51% of the total Fe, respectively. Small amounts of Fe were bound to carbonate and exchangeable phases. Our SEM-EDX results confirmed Fe is present in a number of silicate minerals including clays, chlorite, almandine, and biotite, and Fe was also found in a few oxides and oxyhydroxides minerals including Fe oxyhydroxides, ilmenite and hematite (Table 3.2).

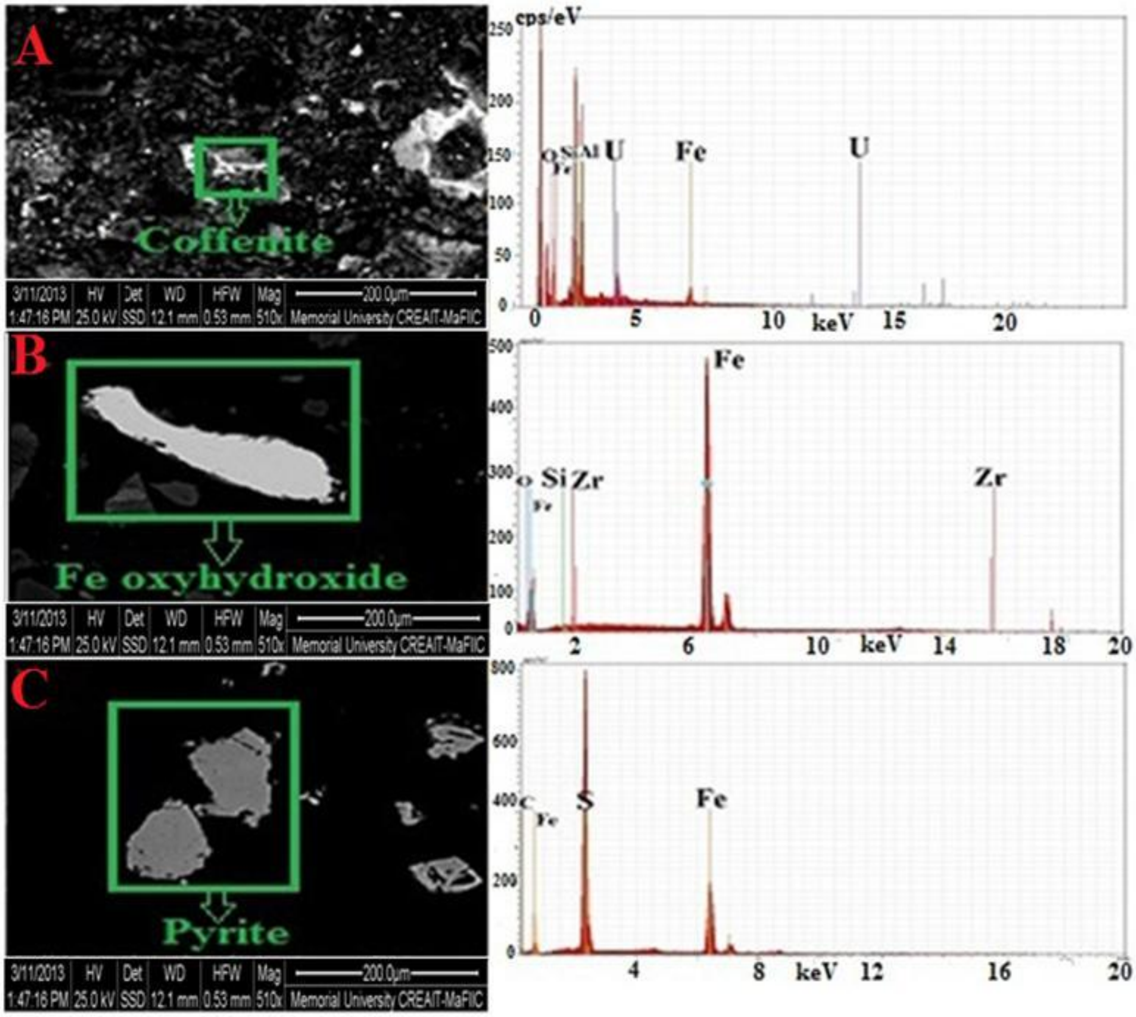


Figure 3.3: SEM images and respective EDX spectra showing (A) Coffinite; (B) iron oxyhydroxide and (C) pyrite.

Table 3.2: Modal mineralogy of sediments identified in SEM-EDX analysis.

| **Minerals** | **Weight (%)** | **Grains** |
|---|---|---|
| Quartz ($SiO_2$) | 35.46 | 10342 |
| Albite ($NaAlSi_3O_8$) | 25.89 | 10229 |
| Potassium feldspar ($KAlSi_3O_8$) | 21.64 | 9585 |
| Fe-poor Clays | 10.03 | 5553 |
| Chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.(Mg,Fe)_3(OH)_6$) | 1.81 | 1754 |
| Plagioclase feldspar excluding albite ($NaAlSi_3O_8$ – $CaAl_2Si_2O_8$) | 1.32 | 1353 |
| Fe-rich Clays (Fe spotted on clays) | 0.65 | 727 |
| Kaersutite ($NaCa_2(Mg_4Ti)Si_6Al_2O_{23}(OH)_2$) | 0.72 | 713 |
| Fe oxyhydroxides | 0.59 | 576 |
| Fine-grain-silicate | 0.19 | 465 |
| Titano-Fe-oxide | 0.32 | 286 |
| Titanite ($CaTiSiO_5$) | 0.20 | 401 |
| Rutile ($TiO_2$) | 0.24 | 196 |
| Zircon ($ZrSiO_4$) | 0.24 | 145 |
| Biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) | 0.15 | 282 |
| Ilmenite ($FeTiO_3$) | 0.16 | 131 |
| Pyrite ($FeS_2$) | 0.14 | 164 |
| Almandine ($Fe_3Al_2Si_3O_{12}$) | 0.11 | 123 |
| Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) | 0.05 | 102 |
| Calcite ($CaCO_3$) | 0.02 | 21 |
| Sphalerite ($(Zn,Fe)S$) | 0.01 | 39 |
| Galena (PbS) | 0.02 | 12 |
| Monazite ($(Ce,La)PO_4$) | 0.01 | 41 |
| Pyrrhotite ($Fe_{1-x}S$ ($x = 0$ to $0.2$)) | 0.01 | 10 |
| Bastnasite ($(Ce,La,Y)CO_3F$)) | 0.01 | 8 |
| Hematite ($Fe_2O_3$, $\alpha$-$Fe_2O_3$) | 0.00 | 7 |
| Chalcopyrite ($CuFeS_2$) | 0.00 | 5 |
| Coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) | 0.00 | 2 |
| Cr-Spinel ($Mg(Al,Cr)_2O_4$) | 0.00 | 1 |
| Kozoite ($(Nd,La,Sm,Pr)(CO_3)(OH)$) | 0.00 | 1 |
| CaOH-Fe | 0.00 | 1 |

Mn bound to exchangeable phase exhibited highest pool of Mn followed Mn bound to organic and Fe-Mn oxyhydroxides phases, accounting for 5.12%, 3.94% and 3.84%, respectively. A small amount of Mn was found in the carbonate phase. No manganese minerals were identified by SEM-EDX analysis, probably because the quantity of Mn was below the detection limit of SEM-EDX analysis. Similar to Fe, Al bound to organic phase has highest pool of labile Al followed by Al bound to Fe-Mn oxyhydroxides phase, amounts to 3.2% and 2.69% of the total Al, respectively.

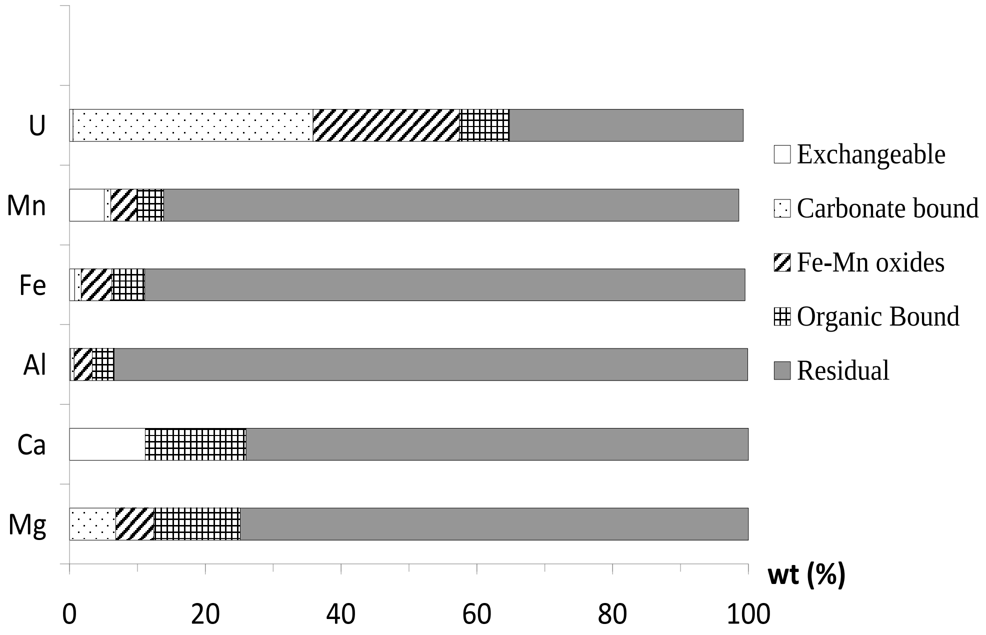


Figure 3.4: Weight percentage of U, Mn, Fe, Al, Ca and Mg in various phases of sediments.

Small amounts of Al were bound to carbonate and exchangeable phases. Al was also identified in a number of silicateminerals including albite, almandine, biotite, clay, feldspar and kaersutite (Table 3.2). Al oxyhydroxides were not detected in SEM-EDX analysis. The largest pool of labile phase Mg and Ca is the organic bound phase, amounts to 12.7% and 14.9% of total Mg and Ca, respectively. No Mg was found in the exchangeable phase whereas 11.14% of total Ca is in the exchangeable phase. Mg bound to carbonate minerals and Fe-Mn oxyhydroxides, amounts to 6.8% and 5.6% of total Mg, respectively, whereas no Ca was found in carbonate or Fe-Mn oxyhydroxides phases. Mg was identified by SEM-EDX in a few minerals including biotite, chlorite, kaersutite and Cr-spinal, while no Mg carbonate mineral was identified. Ca was identified in a number of minerals including apatite, plagioclase feldspar, kaersutite and titanite. Although no Ca was found in the carbonate phase of sequential extraction, a few grains of calcite were identified in SEM-EDX analysis (Table 3.2). Total Si and phase distribution of Si could not be determined due to the use of HF and formation of volatile SiF4 gas when extracting the residual phase. We however conclude, based on our SEM-EDX results that the majority of Si in the sediment sample exists in silicate minerals (e.g., albite, clays, feldspar, chlorite, quartz).

### 3.3.2 Batch leaching experiments

#### 3.3.2.1 Effects of pH

pH strongly influenced U release from the sediment to water. With increasing pH, much more U was released (Fig. 3.5). At low pH, U release was very low: maximum U concentration in water was 4.25, 2.0 and 5.65 µg/L, respectively at pH 3, 5 and 8. At pH 10, release of U was much higher: maximum U concentration was 22 µg/L. At pH 3, U concentration in water reached its maximum at t = 1 day, gradually decreased from t = 1 to 4 day, and reached a steady state concentration of 1.93 µg/L after day 4. The decrease in U concentration during day 1 to 4 is probably due to U re-adsorption to mineral surface. At pH 5, U concentration in water increased during the first day of leaching and was steady at 1.77 µg/L after day 1. At pH 8, U concentration increased steadily during the whole leaching period, reached its maximum of 5.65 µg/L at day 16. At pH 10, U concentration increased gradually until day 8 and became stabilized at ~22 µg/L afterwards.

pH significantly influenced mineral dissolution, as indicated by changes in major elements (Fe, Mn, Al, Si, Mg and Ca) released with changing pH (Fig. 3.6a to 3.6f). With increase in pH, Fe and Si concentrations increased, while the concentrations of Mn, Al, Mg, and Ca decreased. At pH 3 and 5, Fe release was low: maximum Fe release was 271 and 491 µg/L, respectively, indicating major Fe minerals in the sediment (i.e., Fe oxyhydroxides and Fe-containing silicate minerals) are stable at low pH. At pH 8 and 10, Fe concentrations were much higher: maximum Fe release was 2987 and 3760 µg/L, respectively, indicating significant dissolution of Fe minerals. The release of Mn was much higher at low pH (3 and 5) than at high pH (8 and 10).

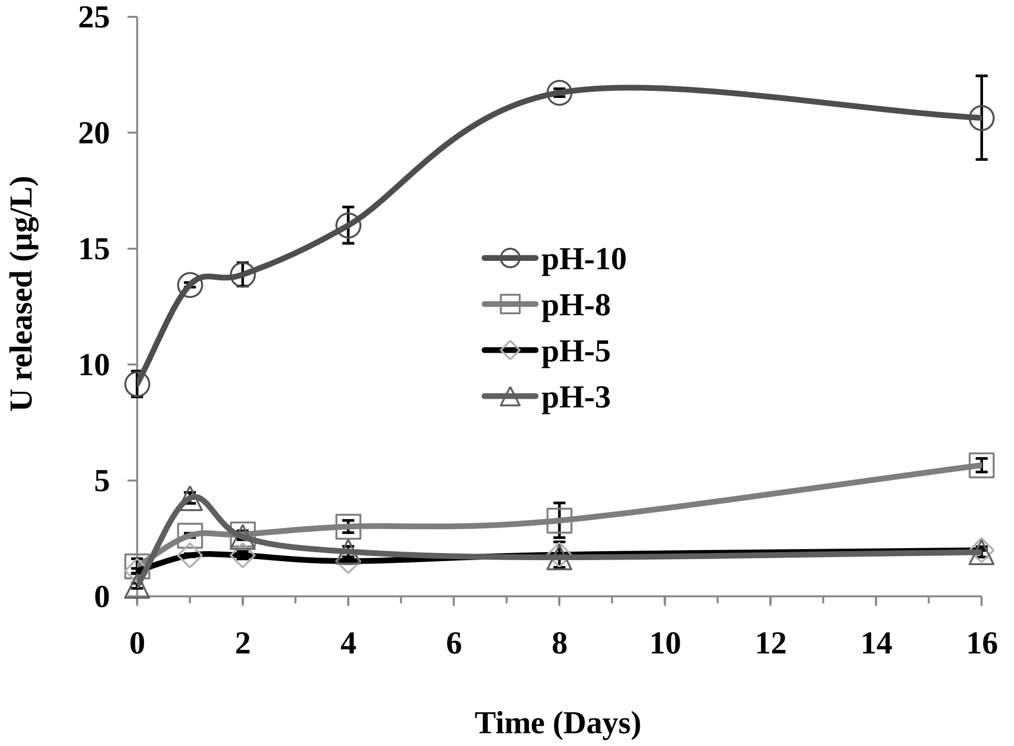
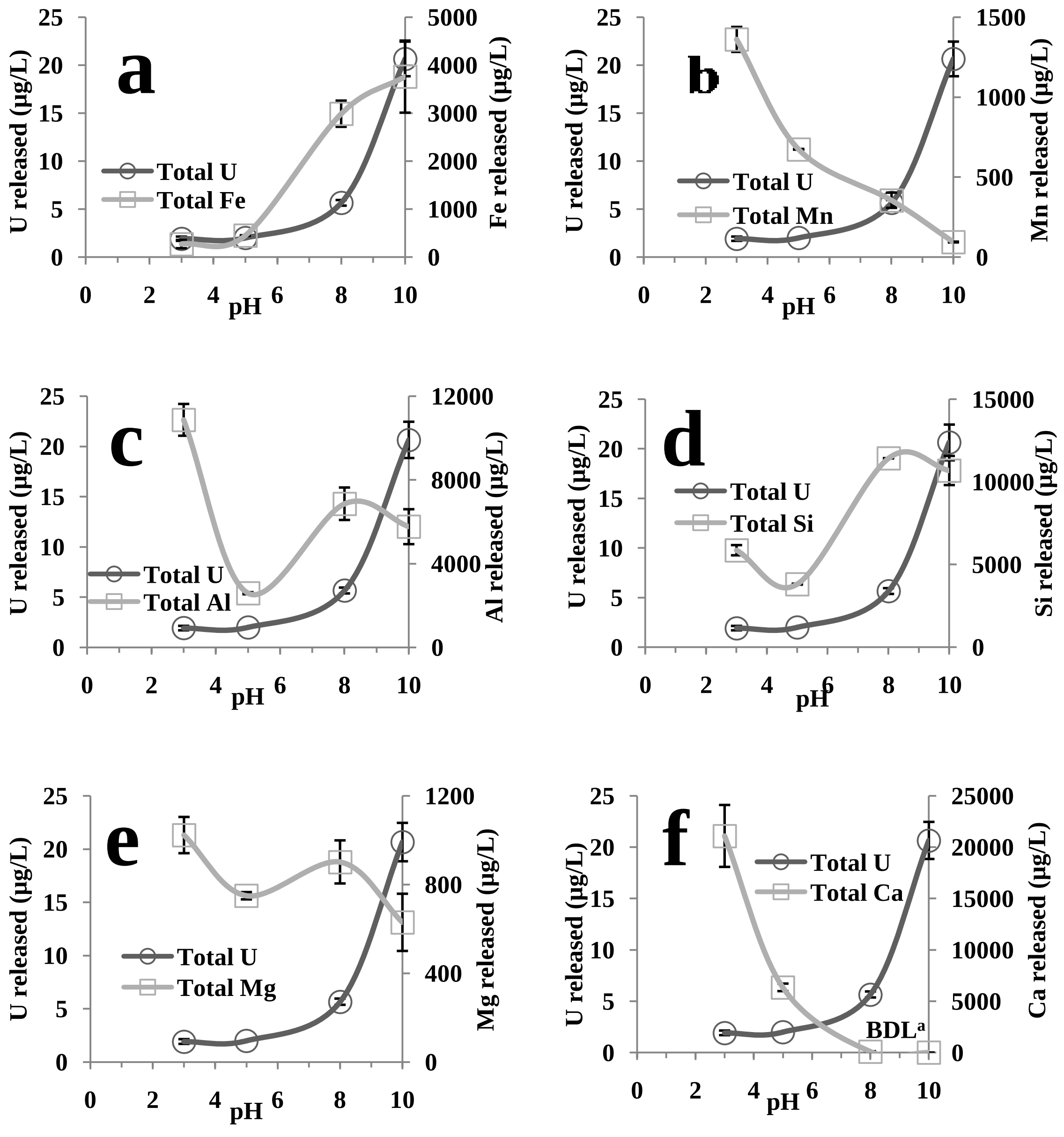


Figure 3.5: Effects of pH on U release.

At low pH, Mn release was due to desorption of the exchangeable Mn and dissolution of Mn-carbonate minerals. At high pH (8 and 10), exchangeable Mn and Mn-carbonate minerals were stable, so were Mn oxyhydroxides and Mn-bearing silicate minerals, resulting in low Mn release. The release of Al from sediments to water was highest at pH 3, moderate at pH 8 and 10, and lowest at pH 5. The high Al release at pH 3 was the result of desorption of exchangeable Al, dissolution of Al-carbonate minerals, and probably Al oxyhydroxides. At high pH of 8 and 10, exchangeable Al and carbonate minerals were stable. Al release was presumably due to dissolution of silicate minerals, and probably Al oxyhydroxides (Acker and Bricker, 1992; Amram and Ganor, 2005). At pH 5, silicate minerals, carbonate minerals, Al oxyhydroxides, and exchangeable (adsorbed) Al were stable, resulting in low Al release. Si release was higher at high pH (8 and 10) than that of at low pH (3 and 5). Si in water could be either from silicate minerals or silica ($SiO_2$) (Brady and Walther, 1990; Rimstidt, 1997).

Our results showed solubility of these minerals increased with increasing pH. Mg release was highest at pH 3, moderate at pH 5 and 8, and lowest at pH 10. The high Mg release at pH 3 was due to dissolution of Mg-carbonate minerals. With increase in pH, carbonate minerals became more stable, and Mg release was mainly due to dissolution of silicate minerals. Ca release was the highest at pH 3. As pH increased, Ca release decreased. At high pH 10, water Ca concentration was lower than below detection limit (~126 µg/L). At low pH (3 and 5), Ca release was due to desorption of exchangeable Ca, because calcium carbonate was not present in the sediment based on our sequential extraction  Although silicate minerals hold most of the Ca, they were not released at high pH (8 and 10).



[a]Below detection limit

*Release of Ca was below detection limit of 126 µg L-[1] at pH 10

Figure 3.6: Effects of pH on the release of U, and the trend of U release with Fe, Mn, Al, Si, Mg and Ca release at t = 16 days. a: U vs Fe; b: U vs Mn; c: U vs Al; d: U vs Si; e: U vs Mg and f: U vs Ca.

U release from the sediment to water was due to U desorption from mineral surface and/or dissolution of U bearing minerals. If all the exchangeable-phase U in our leaching experiments were desorbed, water U concentration would be 3.4 µg/L (calculated based on exchangeable-phase U concentration (0.13 mg/kg) measured by sequential extraction, and the sediment mass (1 g) and water volume (40 mL) used in our experiments). Measured U concentration in water in all our experiments was above 3.4 µg/L (4.25, 5.65, and 21.72 µg/L at pH 3, 8 and 10, respectively) except for pH 5 where U concentration was 2 µg/L, suggesting it is possible that both desorption of exchangeable U and mineral dissolution are involved in U release in these experiments. When pH increased from 3 to 10, U release increased 5 folds, Fe release and Si release also increased (5 and 2 fold, respectively), while the release of all other major elements decreased (Fig. 3.6a to 3.6f). These results suggest dissolution of Fe-bearing and Si-bearing minerals might have contributed to U release. Both Fig. 3.6a and 3.6d show the most of Fe and Si is released between pH 6 to 8, whereas most U is released between pH of 8 to 10. These suggest that U is probably concentrated in specific, minor U-silicate phases that only become destabilized above pH of 8. By examining the release profile of U, Fe and Si, we found that the pattern of U release was similar to that of Fe and Si, especially at high pH (8, 10), and that at pH above 5, the amount of U released (as indicated by its concentration in water) was strongly correlated to the amount of Fe and Si released (Appendix 3B (Fig. 3B.1 to 3B.4)). These results imply that at high pH, dissolution of Fe-bearing minerals (i.e., Fe oxyhydroxides and/or Fe-containing silicate minerals) can contribute to U release, while at low pH, release of exchangeable U (i.e., U desorption from mineral surface) is the dominant mechanism of U release.

### 3.3.2.2 Effects of redox potential (Eh) and citrate

Redox potential (Eh) significantly influenced U release from sediment to water. At a fixed pH (3 or 10), U release was much higher at high Eh than that at lower Eh (Fig. 3.7). When redox potential was in the range of +200 to +300 mV, after 16 days of leaching, 166.8 µg/L (at pH 10) and 122.9 µg/L (at pH 3) U were released, whereas at low redox potential (Eh = +50 to -150 mV), 80.3 µg/L (at pH 10) and 36.35 µg/L (at pH 3) U were released after 16 days of leaching.

Redox potentials also have strong influence on mineral dissolution, as indicated by its influence on major elements (Fe/Mn/Al/Si/Mg/Ca) release (Fig. 3.8a to 3.8l). Fe concentration in water was much higher under reducing conditions than that under oxidizing conditions. Under reducing conditions (Eh = +50 to -150 mV), 41000 µg/L (at pH 10) and 23763 µg/L (at pH 3) Fe were released after 16 days of leaching, whereas under oxidizing conditions (Eh = +200 to +300 mV), 31015 µg/L (at pH 3) and 14046 µg/L (at pH 10) Fe were released. The increase in Fe release with decreasing Eh suggests reductive dissolution is a major mechanism of Fe mineral dissolution (Ahmed et al., 2004; Bhattacharya et al., 1997; Nickson et al., 2000), and that Fe oxyhydroxides are the major mineral accountable for  Fe release in our experiments. In our Eh experiments, Fe released at both pH 3 and 10 were much higher than that in our pH experiments, even at high Eh (compare Fig. 3.6 to Fig. 3.8). The much higher Fe release at high Eh experiments was due to the high concentration (0.03 mol/L) of citrate used.

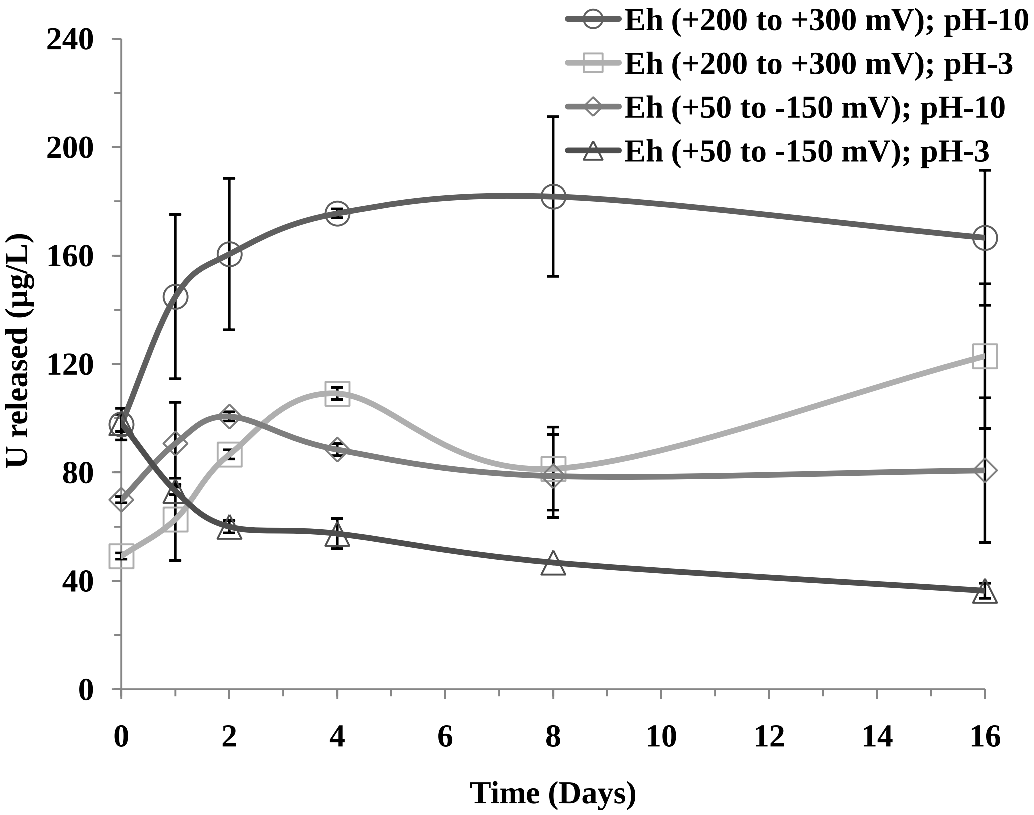


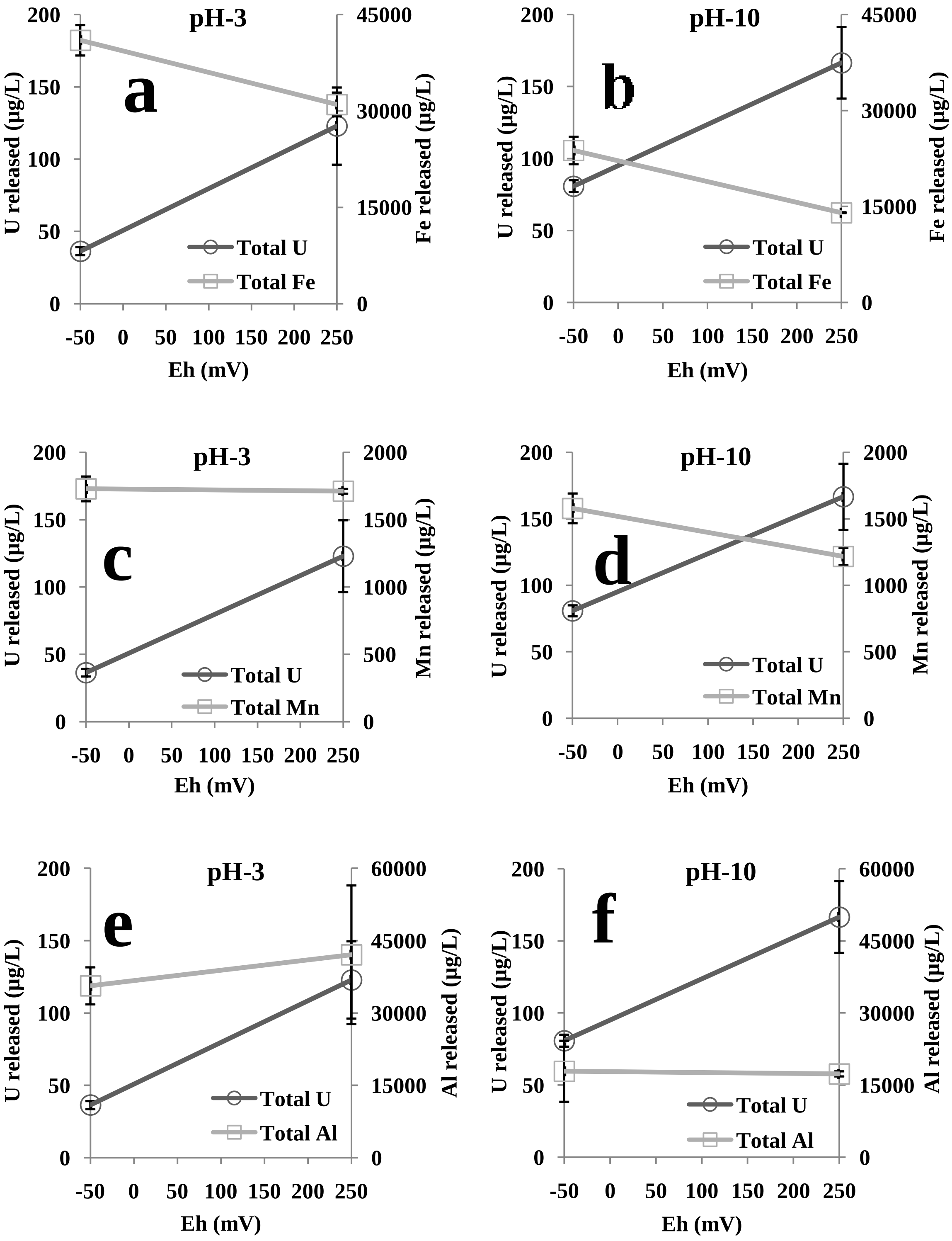
Figure 3.7: Effects of Eh on U release.

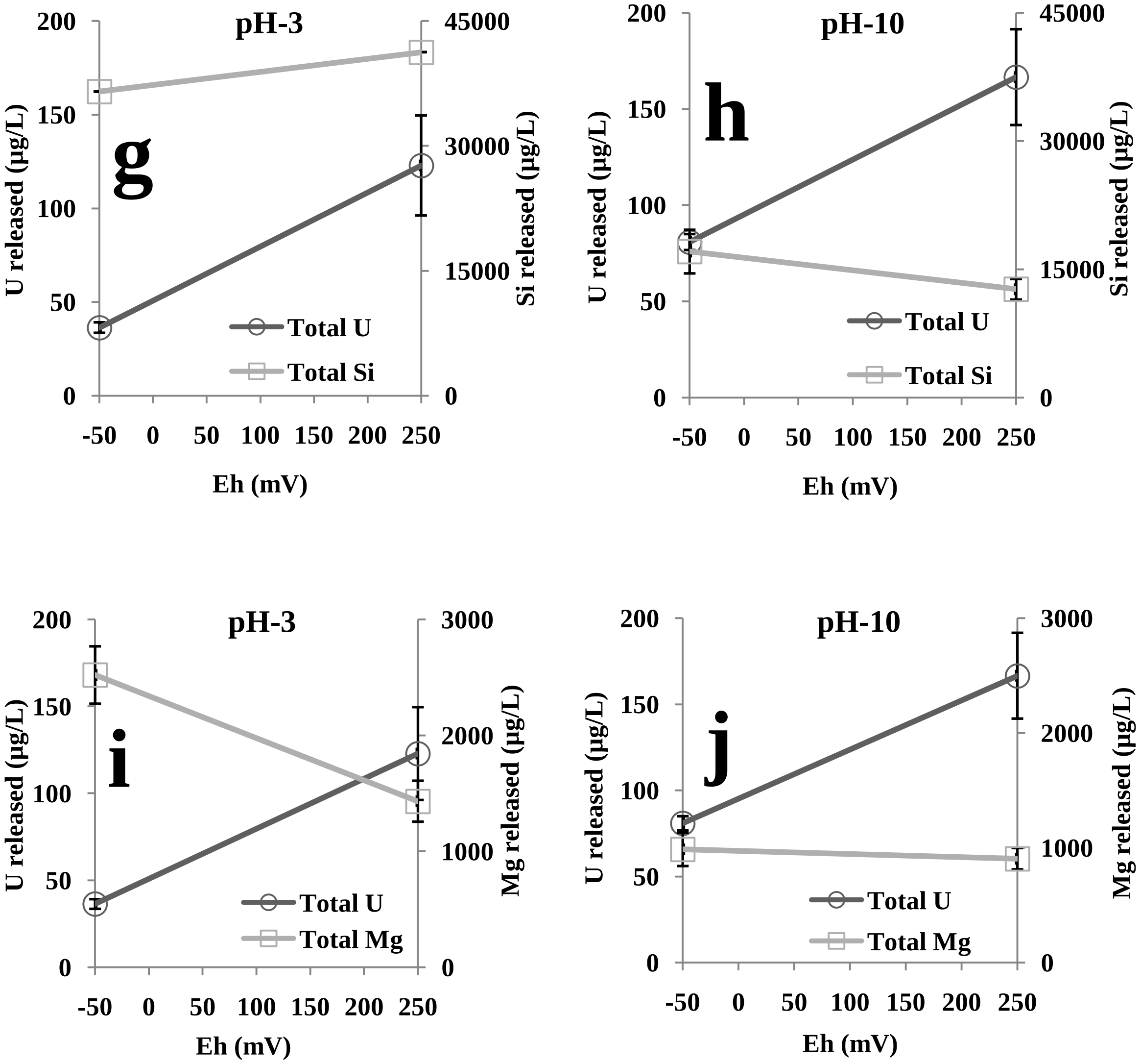
Citrate forms soluble Fe-citrate complexes and therefore promotes Fe mineral dissolution (Engelmann et al., 2003; Francis and Dodge, 1993). Mn release at pH 3 was not influenced by Eh, while at pH 10, Mn release increased slightly with decreasing Eh. These results show at low pH, Mn release was mainly due to desorption of exchangeable-phase Mn, while at high pH, reductive dissolution of Mn minerals (Mn oxyhydroxides and Mn-bearing silicates) was the major Mn release mechanism. Al and Si release from the sediment does not seem to be strongly influenced by Eh. At pH 3, Al and Si release increased slightly with increasing Eh, while at pH 10, Al release did not change with changing Eh, and Si release decreased slightly with increasing Eh. Al and Si release in our experiments was mainly due to the dissolution of silicate minerals. Silicate minerals dissolution is not influenced by redox potential, therefore, it is not surprising Si and Al release was not strongly influenced by Eh. Mg release decreased with increasing Eh at pH 3, while at pH 10, Mg release was insensitive to Eh. At pH 3, dissolution of Fe- and Mn-oxyhydroxides could have contributed to Mg release, as substantial amount of Mg was stored in the Fe- and Mn-oxyhydroxides (Fig. 3.4). As previously discussed, dissolution of Fe- and Mn-oxyhydroxides decreased with increasing Eh. At pH 10, Mg release was probably mainly due to dissolution of silicate minerals, therefore Mg release was not influenced by Eh.

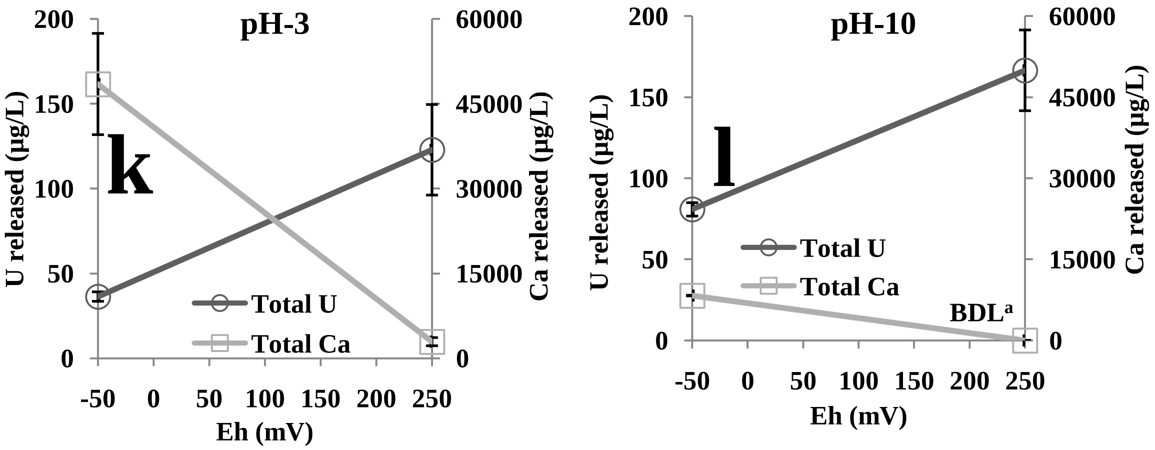
In all our Eh experiments, U water concentration after 16 days of leaching was higher than the expected U concentration if all and only the exchangeable-phase U were released (3.4 µg/L). Under oxidizing conditions, 122 µg/L (at pH 3) and 166.8 µg/L U (at pH 10) were released; under reducing conditions, 36.35 µg/L (at pH 3) and 80.3 µg/L (at pH 10) U were released. These results indicate besides desorption of exchangeable U, other mechanisms (e.g., mineral dissolution) must have contributed to U release. At a fixed pH (3 or 10), U release increased with increasing Eh, while the release of most major elements either decreased or was insensitive to Eh change (Fig. 3.8a to 3.8l), indicating mechanisms other than mineral dissolution were involved in U release. In our

Eh experiments, U released at both pH 3 and 10 were much higher than that in our pH experiments (compare Fig. 3.6 to Fig. 3.8). Citrate, which was present in the leaching solutions in our Eh experiments, can form low-adsorbing aqueous complexes with U(VI) (Bailey et al., 2005; Huang et al., 1998; Pasilis and Pemberton, 2003) and enhances U release from sediments to water. Citrate facilitated the dissolution of Fe- and Al-containing minerals (compare Fig. 3.6 and Fig. 3.8) by forming aqueous Fe and Al complexes, which additionally increased the release of U associated with these minerals.

By examining the release profile of U and each major element, we found that at high Eh, U release pattern was similar to that of each major element and there was a positive and reasonably high correlation between U concentration and major element concentration (except Ca at pH 3) (Appendix 3C (Fig. 3C.1 and 3C.2)). These results show that U release was related to mineral dissolution. At pH 10, dissolution of Fe- and Mn-oxydroxides and silicate minerals contributed to U release, while at pH 3, in addition to Fe- and Mn-oxydroxides and silicate minerals, carbonate minerals contributed.


a
pH-3
U released (µg/L)
Fe released (µg/L)
200
150
100
50
0
45000
30000
15000
0
-50
0
50
100
150
200
250
Eh (mV)
Total U
Total Fe
b
pH-10
U released (µg/L)
Fe released (µg/L)
Total U
Total Fe
Eh (mV)
c
pH-3
U released (µg/L)
Mn released (µg/L)
2000
1500
1000
500
0
Total U
Total Mn
Eh (mV)
d
pH-10
U released (µg/L)
Mn released (µg/L)
Total U
Total Mn
Eh (mV)
e
pH-3
U released (µg/L)
Al released (µg/L)
60000
45000
30000
15000
0
Total U
Total Al
Eh (mV)
f
pH-10
U released (µg/L)
Al released (µg/L)
Total U
Total Al
Eh (mV)


pH-3
g
U released (µg/L)
Si released (µg/L)
200
150
100
50
0
45000
30000
15000
0
-50
0
50
100
150
200
250
Eh (mV)
Total U
Total Si
pH-10
h
U released (µg/L)
Si released (µg/L)
Total U
Total Si
Eh (mV)
pH-3
i
U released (µg/L)
Mg released (µg/L)
3000
2000
1000
0
Total U
Total Mg
Eh (mV)
pH-10
j
U released (µg/L)
Mg released (µg/L)
Total U
Total Mg
Eh (mV)



[a]Below detection limit

*Release of Ca was below detection limit of 126 µg $L^{-1}$ at pH 10

Figure 3.8: Effects of Eh on the release of U, and the trend of U release with Fe, Mn, Al, Si, Mg and Ca release at t = 16 days. a: U vs Fe at pH 3; b: U vs Fe at pH 10; c: U vs Mn at pH 3; d: U vs Mn at pH 10; e: U vs Al at pH 3; f: U vs Al at pH 10; g: U vs Si at pH 3; h: U vs Si at pH 10; i: U vs Mg at pH 3; j: U vs Mg at pH 10; k: U vs Ca at pH 3 and l: U vs Ca at pH 10.

We also found that at low Eh, the pattern of U release was different from each of the major elements: U concentration in water was high (70 to 100 µg/L) at the beginning of leaching, but decreased afterwards, while major element concentration in water increased steadily during the entire leaching process (Appendix 3C (Fig. 3C.3 and 3C.4)). The high U concentration at the beginning of leaching demonstrated mineral dissolution contributed to initial U release. As the leaching process progressed, U concentration in water decreased, although major element concentration in water continued to increase, indicating mineral dissolution. The decoupling of U release and mineral dissolution was demonstrated by the low $r^2$ value and/or negative correlation between U concentration and major element concentration (Appendix 3C (Fig. 3C.3 and 3C.4)). The decrease in U concentration in water can be attributed to reductive precipitation of U(VI). Under reducing conditions (i.e., low Eh), U(VI) was reduced to U(IV) and precipitated as U(IV) minerals with very low solubility; therefore the concentration of U in water in our low Eh leaching experiments decreased after the initial spike in U concentration.

### 3.3.2.3 Effects of bicarbonate

Bicarbonate greatly enhanced U release from the sediment. Uranium concentration in water after 16 days of leaching was 114.8, 10.8 and 5.6 µg/L, respectively for the 0.01 M, 0.001M, and the non-bicarbonate treatment experiment (Fig. 3.9). The influence of bicarbonate on major element release, however, was less significant. When bicarbonate concentration increased from near zero to 0.01 M, U release increased 20 fold, yet major element release decreased either moderately (Mn and Si) or slightly (Fe, Al, and Mg) (Fig. 3.10a to 3.10e).

By examining the release profile of U and major elements, we found that in the 0.001 M bicarbonate treatment, the pattern of U release and that of major elements was different (Appendix 3D (Fig. 3D.1)), and there was no correlation between U concentration and major element concentration in water (low $r^2$, (Appendix 3D (Fig. 3D.1)). We also found that in the 0.01 M bicarbonate treatments, U concentration and the concentration of each major element reached to its maximum during the first day of leaching, then stayed around that concentration during the remaining leaching process (Appendix 3D (Fig. 3D.2)). Therefore, the correlation between U release and mineral dissolution cannot be assessed by linear regression.

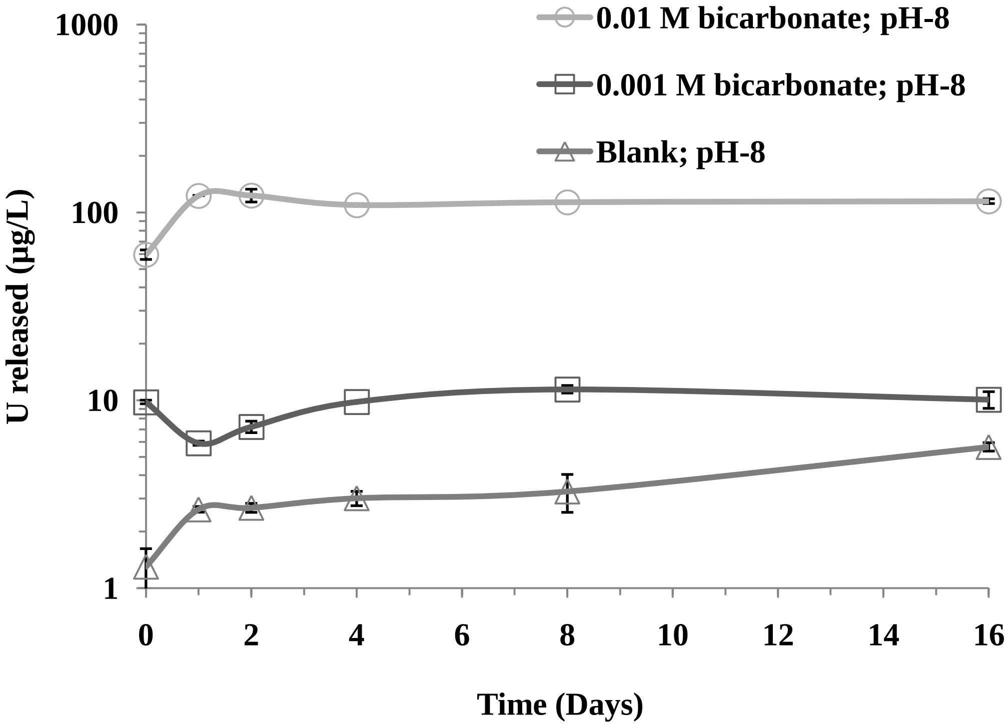
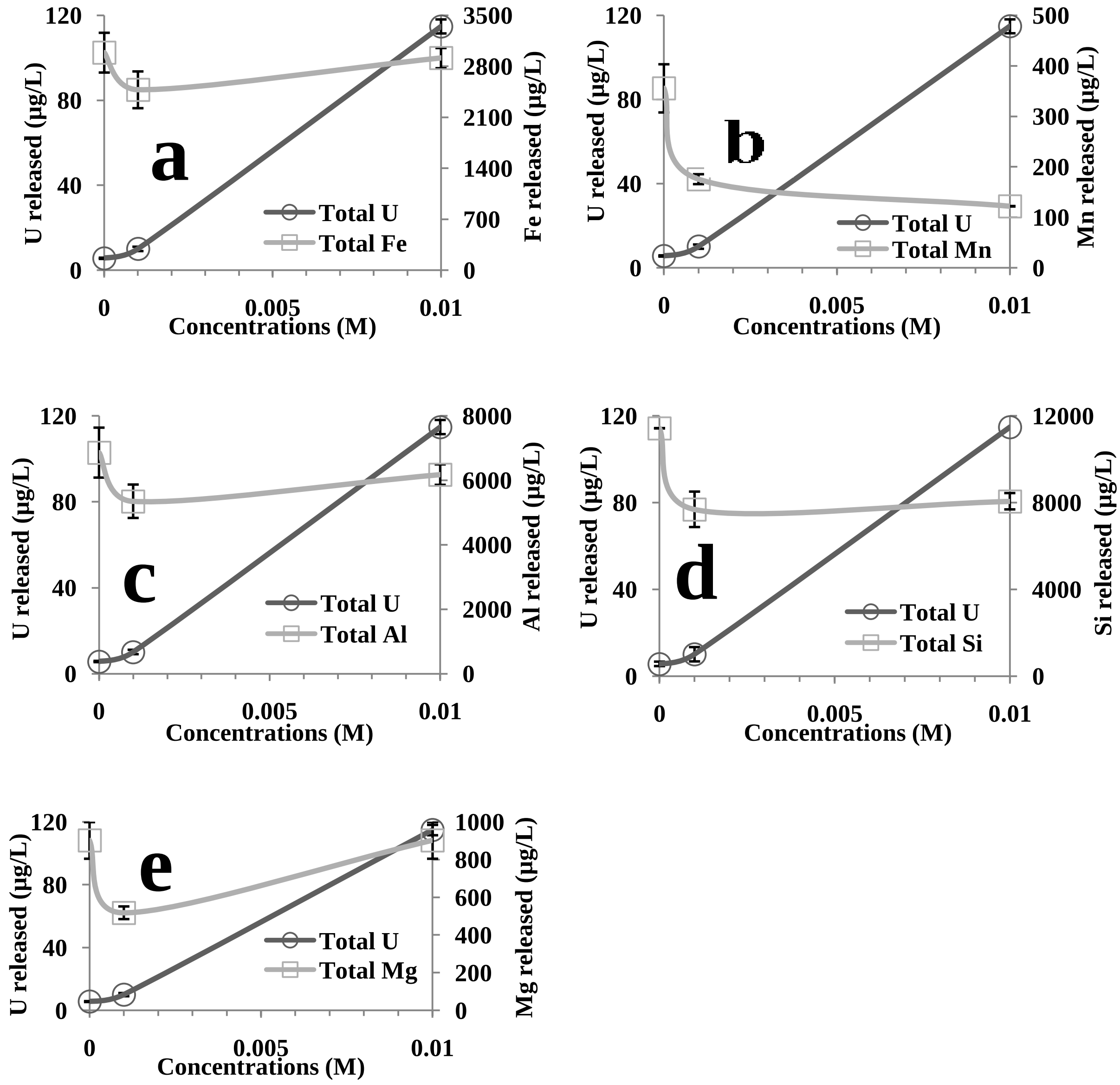


Figure 3.9: Effects of bicarbonate on U release.



*Release of Ca was below detection limit of 126 µg $L^{-1}$ at pH 10

Figure 3.10: Effects of bicarbonate on the release of U, and the trend of U with Fe, Mn, Al, Si and Mg release at t=16 days. a: U vs Fe; b: U vs Mn; c: U vs Al; d: U vs Si and e: U vs Mg.

Major element release in the 0.01 M bicarbonate treatment was very close to or even lower than that in non-bicarbonate treatment (Fig. 3.10a to 3.10e), indicating the increased U release in the presence of bicarbonate was due to increased U desorption, rather than increase in mineral dissolution. At bicarbonate concentration of 0.01 M, U released to water was as high as 114.8 µg/L, far exceeding the expected U concentration if all the exchangeable-phase U was desorbed (3.4 µg/L). This, however, does not necessarily mean that mineral dissolution has to contribute to U release. Previous studies showed that carbonate can influence U adsorption by forming U-carbonate complexes. Depending on the type of complexes formed, carbonate can either increase or decrease U adsorption: formation of ternary surface complexes at near neutral pH increases U adsorption (Barnett et al., 2002), while formation of aqueous complexes ($UO_2CO_3$, $UO_2(CO_3)_2^{2-}$, and $UO_2\ (CO_3)_3^{4-}$) decreases U adsorption (Baborowski and Bozau, 2006; Barnett et al., 2002; Grenthe and Lagerman, 1991; Nguyen Trung et al., 1992; Regenspurg et al., 2009). In our leaching experiments with added bicarbonate, the pH was high (8), therefore high U release can be attributed to enhanced U desorption due to the formation of aqueous U-carbonate complexes, which substantially shifted U adsorption equilibrium.

### 3.3.2.4 Effects of natural organic matter (NOM)

NOM promoted U release from the sediment. After 16 days of leaching, 21.2, 12.4 and 5.6 µg/L uranium were released respectively in the presence of 50 mg C/L, 20 mg C/L and non-NOM treatments (Fig. 3.11). NOM also influenced mineral dissolution, but in a different manner: with increasing NOM concentration, release of major elements either decreased (Mn, Al, Si, and Mg), or increased marginally (Fe, from 3000 to 3244 µg/L) (Fig. 3.12a to 3.12e). Our observed decrease in Mn, Al, Si, and Mg release with increasing NOM concentration is consistent with previous reports that NOM can reduce the dissolution of silicate minerals (Jones and Tiller, 1999; Tombácz et al., 2004).

The decrease in silicate mineral dissolution is due to adsorption of negatively charged NOM to mineral surface, which neutralizes the positive charges of metal ions on mineral surface and therefore reduces mineral solubility (Gu et al., 1994; Specht et al., 2000). The slight increase in Fe release at higher NOM concentrations is probably related to the decrease in Eh (Fig. 3.12a), which promoted reductive dissolution of Fe oxyhydroxides (Gu et al., 2005).

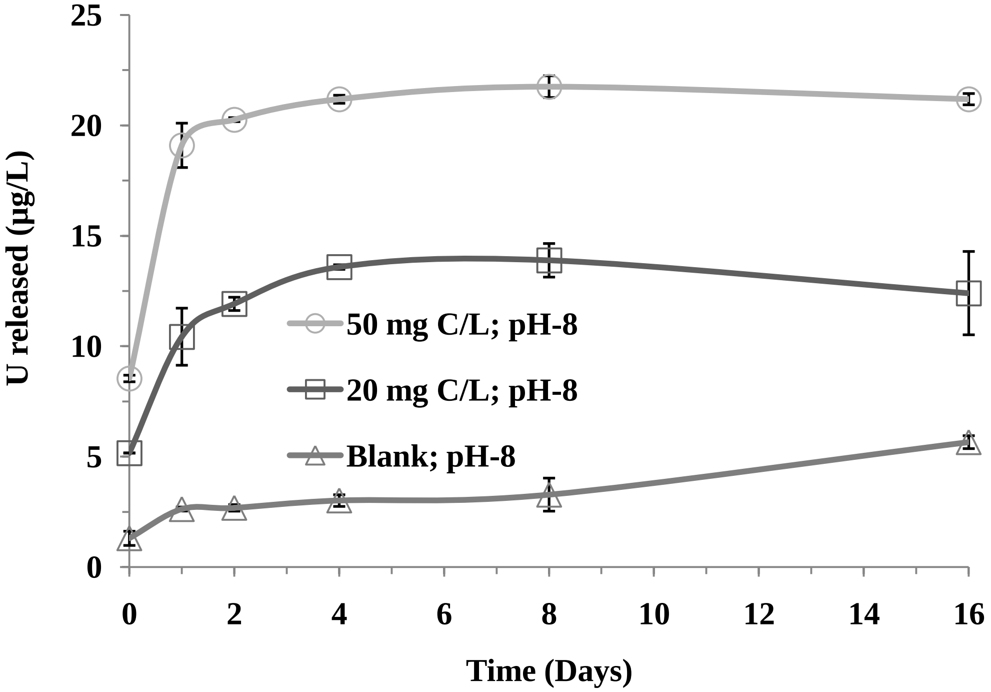
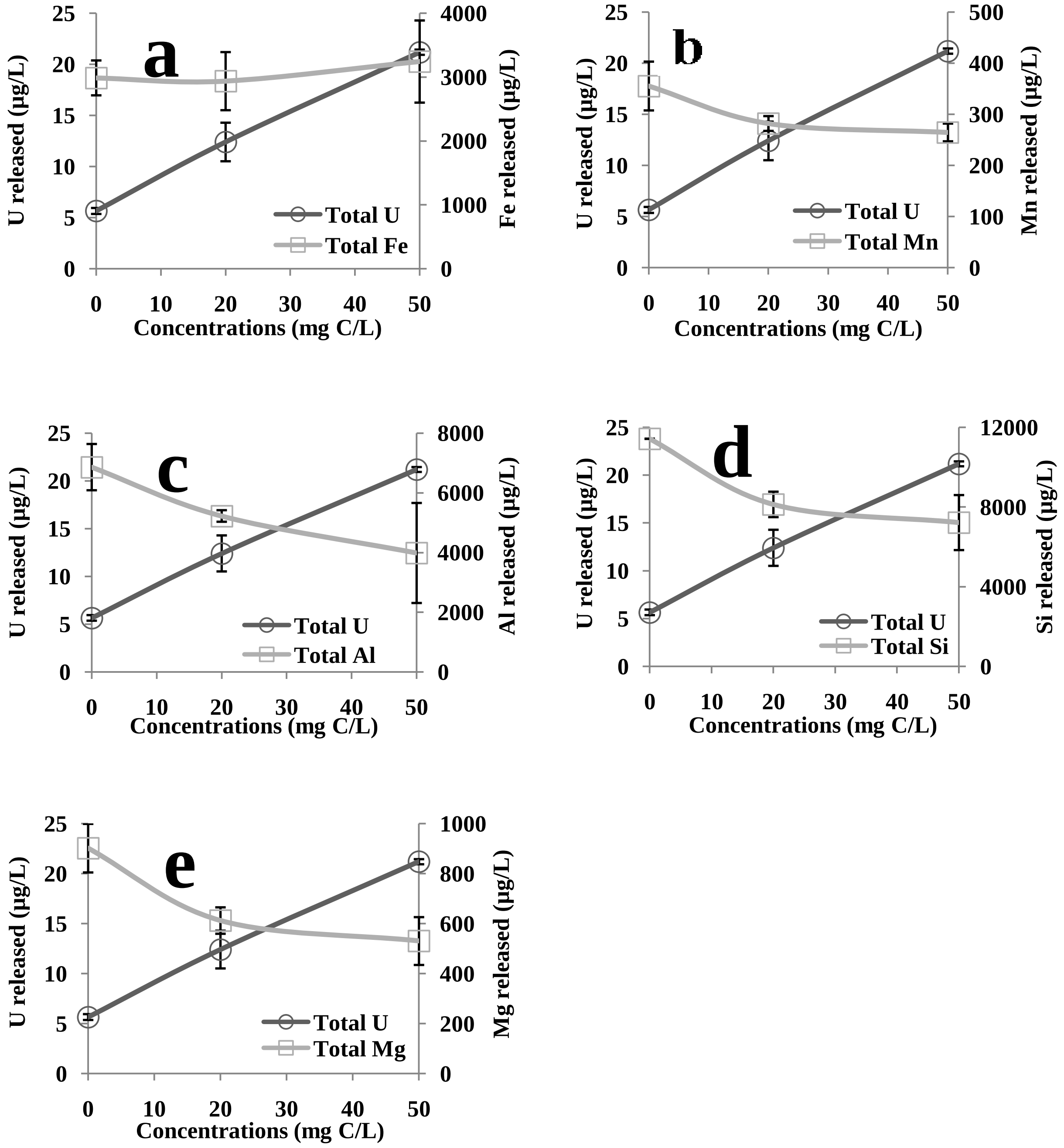


Figure 3.11: Effects of NOM on U release.

U released in our NOM experiments (21.8 and 13.9 µg/L) are above the expected U concentration if all and only the exchangeable U are released (3.4 µg/L), indicating U release could be due to both desorption of exchangeable U and mineral dissolution. The profile of U and major element release in the presence NOM shows that U concentration and the concentration of each major element reached to its maximum during the first a few days of leaching, and stayed around that maximum concentration during the remaining leaching process. Therefore, the correlation between U release and mineral dissolution cannot be assessed by linear regression (Appendix 3E (Fig. 3E.1 and 3E.2)).



*Release of Ca was below detection limit of 126 µg $L^{-1}$ at pH 10

Figure 3.12: Effects of NOM on the release of U, and the trend of U with Fe, Mn, Al, Si and Mg at t=16 days. a: U vs Fe; b: U vs Mn; c: U vs Al; d: U vs Si and e: U vs Mg.

Based on the observation that release of major elements in NOM treatments was lower than that in non-NOM treatment (Fig. 3.12a to 3.12e), we concluded that the increased U release in the NOM treatments was due to increased U desorption, rather than increase in mineral dissolution. NOM influences U release via a number of mechanisms: (i) NOM competes with U(VI) for sorption sites on oxides and clay minerals, which increases U desorption (Bednar et al., 2007); (ii) NOM forms low-adsorbing aqueous complexes with U(VI), also increases U desorption (Lenhart and Honeyman, 1999); (iii) NOM reduces Eh, which reduces U(VI) to U(IV) and therefore reduces U release (Gu et al., 2005). However, reduction in Eh could also promote reductive dissolution of Fe(III) minerals and may increase U release from Fe oxyhydroxides. In our experiments, higher NOM concentrations resulted in higher U release. The decrease in Eh (Appendix 3F (Fig. 3F.1)) and its influence on Fe oxyhydroxides dissolution (Fig. 3.12a) and U release was limited, even at a high NOM concentration of 50 mg/L. Competition for surface sites and formation of low adsorbing aqueous complexes dominated U-NOM interactions and increase U release.

## 3.4 Summary and conclusions

Carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals are the major U hosting phases in our natural sediment sample. Water chemistry conditions significantly influence the extent of U release from these minerals: U release increases with increasing pH and redox potential, and that citrate, bicarbonate, and natural organic matter can all promote U release. U release from natural sediments to water is a complicated process that involves a number of interactive geochemical reactions including: U desorption from mineral surface, dissolution of U-bearing minerals, formation of aqueous U complexes, and reductive precipitation of U. Although dissolution of Fe-containing minerals (Fe oxyhydroxides and silicate minerals) could be a key mechanism for U release at high pH, U desorption from mineral surfaces, promoted by formation of low-adsorbing aqueous U complexes, is the dominant U release mechanism under most of the water chemistry conditions tested in our leaching experiments. Under reducing conditions, reductive precipitation of U is an important mechanism that impedes U release.

## Acknowledgements

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# Chapter 4. Summary and conclusions

## 4.1 Summary and conclusions

Mineral dissolution and arsenic (As) and uranium (U) desorption from mineral surfaces play key roles in controlling As and U contamination in subsurface environment. To predict and control As and U contamination, knowledge of release mechanisms and extent of release under water chemistry conditions relevant to natural soil water and groundwater is essential. The role of silicate minerals in groundwater As contamination was explored (Chapter 2). A sediment sample was collected, characterized, and examined with batch leaching experiments. SEM-EDX and XRD analysis showed that silicate minerals make up the bulk of the sediment (98%), and that arsenic mainly exists in dispersed forms in the sediment, i.e., they are either adsorbed onto mineral surface or incorporated into mineral structure as impurities (Tessier et al., 1979). Sequential extraction results showed silicate minerals and Fe oxyhydroxides are the major As-hosting phases in my natural sediment sample, holding 75% and 16% of the total As, respectively. My batch leaching experiment showed that at relatively low pH (e.g., 3~8), desorption was the main As release mechanism. At high pH (e.g., 10), mineral dissolution considerably increased and became the main As release mechanism. My siderophore experiments showed dissolution of both Fe oxyhydroxides and Al-bearing minerals contributed to As release. Eh experiments results showed that at high Eh (+200 to +350 mV), in the presence of Fe/Al chelator (i.e., citrate), significant dissolution of Fe/Mn oxyhydroxides and silicate minerals occurred and resulted in As release. I also discovered that lower Eh (+50 mV to -150 mV) promoted dissolution of Fe oxyhydroxides coating and silicate minerals, and that both Fe oxyhydroxides and silicate minerals contributed to As release. Overall, my results indicate that dissolution of Fe oxyhydroxides and silicate minerals is an important mechanism controlling As release, and that high pH, the presence of Fe and Al chelators, and extensive dissolution of Fe oxyhydroxide coating promote silicate mineral dissolution and As release. Since silicate minerals are usually the most abundant components in natural sediments, and large amount of As are associated with these minerals, contribution from dissolution of silicate minerals to groundwater As contamination could be substantial.

I investigated the mechanisms of U release from a heterogeneous natural sediment and the influence of water chemistry on U release (Chapter 3). SEM- EDX along with XRD analysis was carried out to identify mineral composition of the sediment. And batch leaching experiments were performed to investigate U release mechanism and the effects of water chemistry on U and major element release. SEM-EDX, XRD and sequential extraction showed that carbonate minerals, Fe-Mn oxyhydroxides, and silicate minerals are the major U hosting minerals, and substantial amounts of U exist as absorbed uranyl ion. Water chemistry significantly influences the mechanism and extent of U release: at high pH (8 and 10), U release was high and dissolution of Fe-bearing minerals (i.e., Fe oxyhydroxides and/or Fe-containing silicate minerals) contributed to U release. At low pH (3 and 5), U release was low and desorption of exchangeable U (i.e., U desorption from mineral surface) was the dominant mechanism of U release. Redox potential (Eh) has strong influence on U release: at high Eh (+200 to +300 mV), U release pattern was similar to that of major elements; indicating U release was related to mineral dissolution. At low Eh (-150 to +50 mV), U release was low and the pattern of U release and major element release was different, indicating reductive precipitation of U. Citrates, bicarbonates, and natural organic matter are commonly found in natural soil pore water and groundwater. I discovered citrate and bicarbonate greatly facilitated U release due to the formation of low-adsorbing aqueous U complexes, and natural organic matter moderately enhanced U release via the same mechanism. By analyzing the trend and pattern of U and major element release, I concluded that U desorption is the dominant U release mechanism under most of the water chemistry conditions tested in my leaching experiments, although mineral dissolution can be important at high pH.

This research provides new insights into the importance of silicate minerals both as an As storage phase and as a potential source of As contamination in groundwater. The importance of major U hosting minerals in a heterogeneous natural sediment was identified and the geochemical reactions and water chemistry conditions affecting As and U release are determined.

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# Appendix 2A: Sequential extraction procedures for the speciation of particulate trace metals

Methods adopted and developed by CREAIT lab at Memorial University of Newfoundland, and adopted from Tessier et al. (1979)

(A) Exchangeable

0.5g of sample with 8 ml of 1M $MgCl_2$ (pH 7.0) was agitated in a 50 ml centrifuge tube for 1 hour. Mixture was centrifuged for 30 minutes. Supernatant was separated from residue into a labeled teflon jar. The supernatant was evaporated to dryness on a hot plate. 2 ml of 8N $HNO_3$ was added to the residue and warmed until the residue dissolves completely. Supernatant was transferred into a clean snap seal and marked up to 30g with nanopure water. Supernatant was analyzed for trace metals. 8 ml of nanopure water was added to the residue in the centrifuge tube, and centrifuged and discard the nanopure.

(B) Bound to Carbonates

To the residue from (A), 8 ml of 1 M NaOAC (adjusted to pH 5 with HOAC) was added and agitated for 5 hrs. Mixture was centrifuged for 30 mins. Supernatant was separated from residue into a labeled teflon jar. The supernatant was evaporated to dryness on a hot plate. 2 ml of 8N $HNO_3$ was added to the residue and warmed until the residue dissolves completely. Supernatant was transferred into a clean snap seal and marked up to 30g with nanopure water. Supernatant was analyzed for trace metals.

(C) Fe-Mn Oxides

To the residue in (B) 15 ml of 0.04M $NH_2OH.HCl$ (in 25% (v/v) HOAC) was added. Mixture was placed at 96 ± $3^0$C for 6 hrs with occasional agitation. Mixture was centrifuged for 30 minutes. Supernatant was separated from residue into a labeled teflon jar. The supernatant was evaporated to dryness on a hot plate. 2 ml 8N $HNO_3$ was added to the residue and warmed until the residue dissolves completely. Supernatant was transferred into a clean snap seal and marked up to 30g with nanopure water. Supernatant was analyzed for trace metals.

(D) Bound to Organic Matter

To the residue from (C) 3 ml of 0.02M $HNO_3$ and 5 ml of 30% $H_2O_2$ (adjust pH to 2 with $HNO_3$) were added. The mixture was heated to 85 ± $2^0$C for 2 hrs. with occasional agitation. 3 ml of 0.02M $HNO_3$ was again added to the mixture. 5 ml of 3.2M $NH_4OAC$ in 20% (v/v) $HNO_3$ was added to the mixture and diluted to 20 ml with nanopure and agitated continuously for 30 minutes. Mixture was centrifuged for 30 minutes. Supernatant was separated from residue into a labeled teflon jar. The supernatant was evaporated to dryness on a hot plate. 2 ml 8N $HNO_3$ was added to the residue and warmed until the residue dissolves completely. Supernatant was transferred into a clean snap seal and marked up to 30g with nanopure water. Supernatant was analyzed for trace metals.

(E) Residual

Residue from (D) was transferred to a teflon jar. 2 ml of 8N $HNO_3$ and 1 ml HF in closed cap were added to the mixture and heated on a hot plate until completely dissolved. Cap was removed and evaporated to dryness and added 2 ml of 8N $HNO_3$ and evaporated to dryness. Another 2 ml of 8N $HNO_3$ was added and evaporated to dryness. This step was repeated. 2 ml 8N $HNO_3$ was added to the residue and warmed until the residue dissolves completely. Supernatant was transferred into a clean snap seal and marked up to 30g with nanopure water. Supernatant was analyzed for trace metals.

## Reference

Tessier, A., Campbell, P.G., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry 51, 844-851.

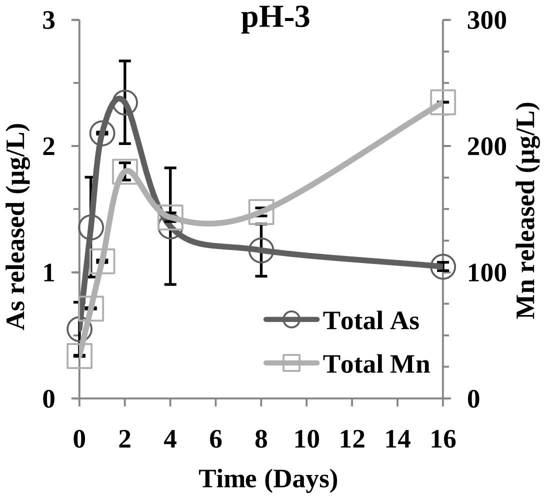
# Appendix 2B: Tabulated sequential extraction data of As

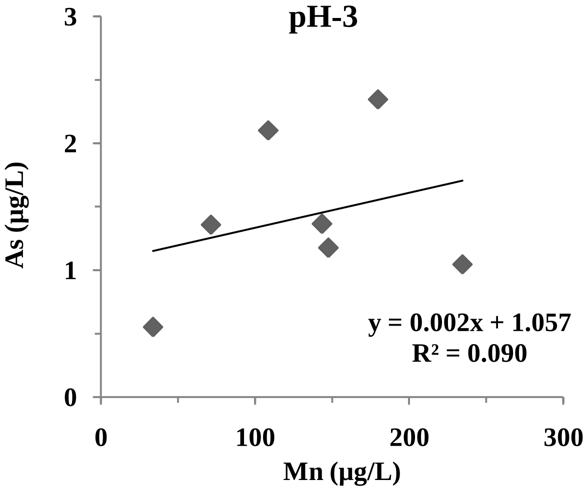
| Steps | Mg (mg/kg) & (%) | Ca (mg/kg) & (%) | Al (mg/kg) & (%) | Si (mg/kg) & (%) | Fe (mg/kg) & (%) | Mn (mg/kg) & (%) | As (mg/kg) & (%) |
|---|---|---|---|---|---|---|---|
| Exchangeable | BDL[a] | 6 ± 0.6 (0.1 %) | 1.03 ± 0.20 (0.004 %) | BDL[a] | 1.17 ± 0.37 (0.005 %) | 0.08 ± 0.02 (0.013 %) | 0.44 ± 0.01 (2.35 %) |
| Carbonate Bound | 4846.56 ± 337.58 (61 %) | BDL[a] | 274.94 ± 15.73 (0.71 %) | 127.6 ± 22.68 | 169 ± 38.9 (0.69 %) | 9.67 ± 1.39 (1.67 %) | 0.35 ± 0.04 (1.62 %) |
| Fe-Mn Oxides | 145.5 ± 5.33 (2 %) | BDL[a] | 1394 ± 19.78 (3.50 %) | 491 ± 17.61 | 1118 ± 11.20 (4.56 %) | 209.45 ± 2.29 (36.15 %) | 3.02 ± 0.002 (15.99 %) |
| Organic Bound | 75.2 ± 0.01 (1 %) | 315.68 ± 40.45 (5.9 %) | 284.5 ± 8.17 (0.75 %) | 358.64 ± 40.45 | 315.68 ± 14.46 (1.13 %) | 10.17 ± 0.15 (1.76 %) | 1.02 ± 0.01 (5.44 %) |
| Residual | 2904.51 ± 36.36 (36 %) | 5159.92 ± 4987.77 (94 %) | 36690.56 ± 1157.53 (95 %) | NA[b] | 22990.53 ± 246.63 (93.62 %) | 350.03 ± 0.84 (60.14 %) | 14.42 ± 0.29 (75 %) |
| Total extracted | 7971.81 (100 %) | 5481.61 (100 %) | 38645.78 (100 %) | NA[b] | 24555.61 (100 %) | 579.41 (100 %) | 19.26 (100 %) |

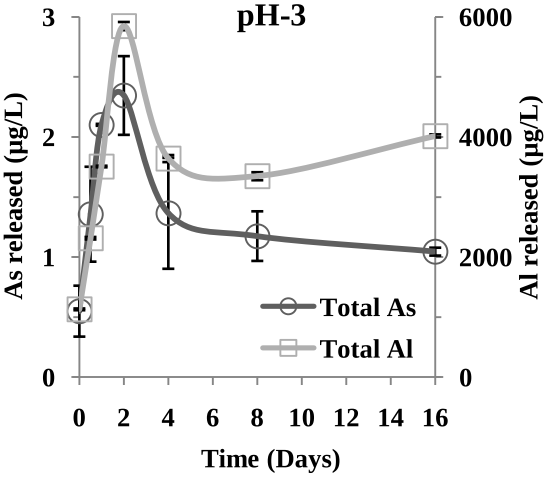
[a] Below detection limit

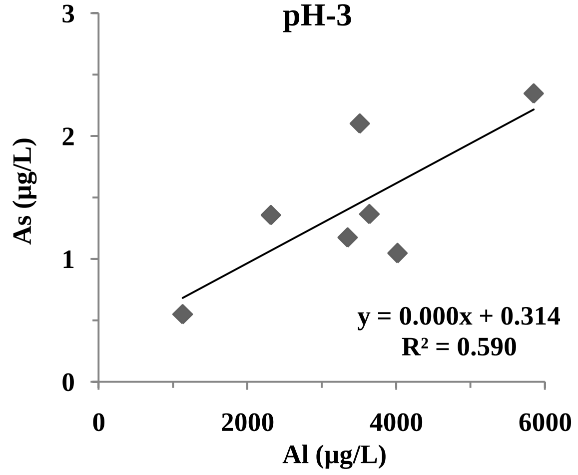
[b] Not available

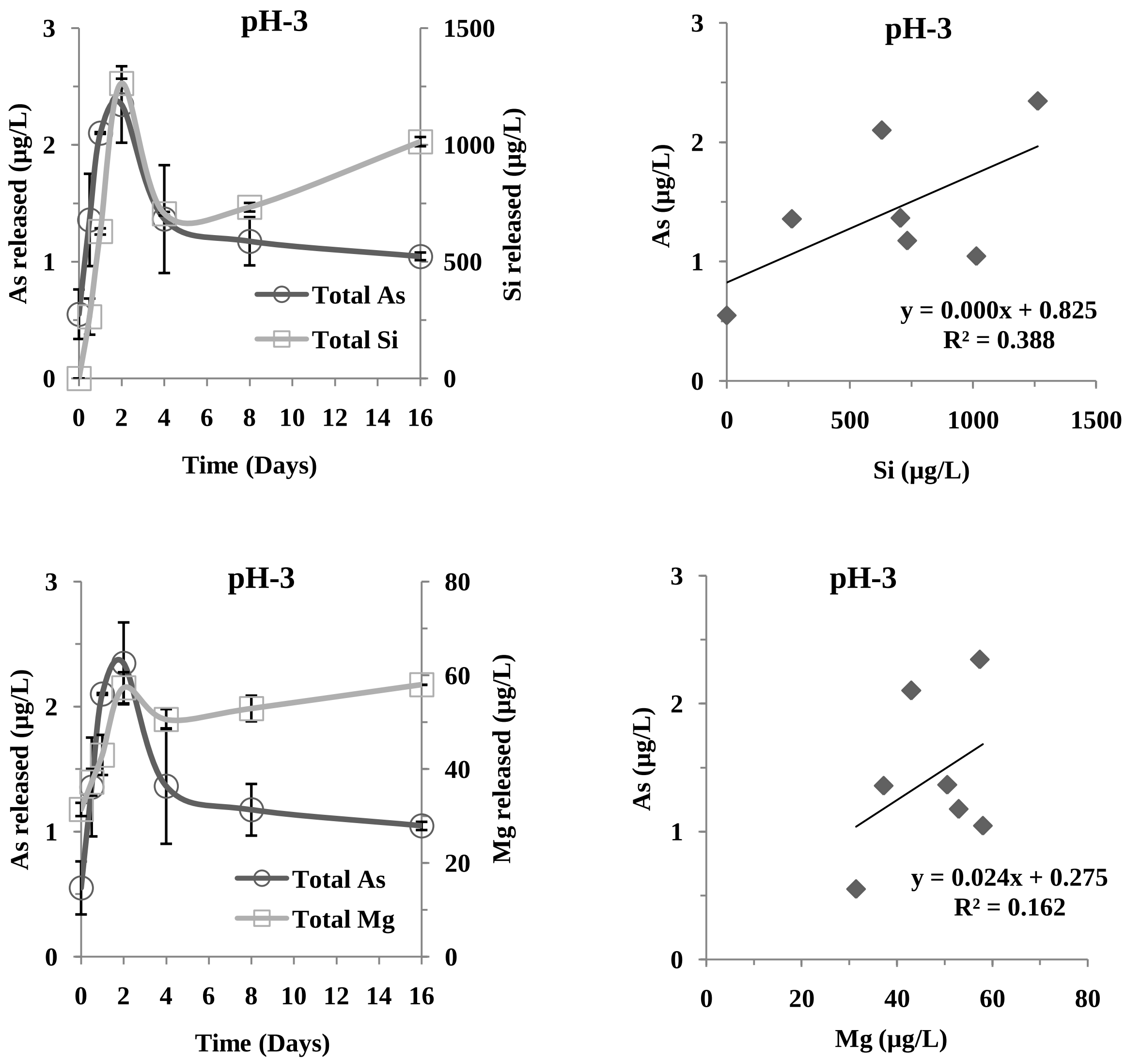
## Appendix 2C: Effects of pH on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg.





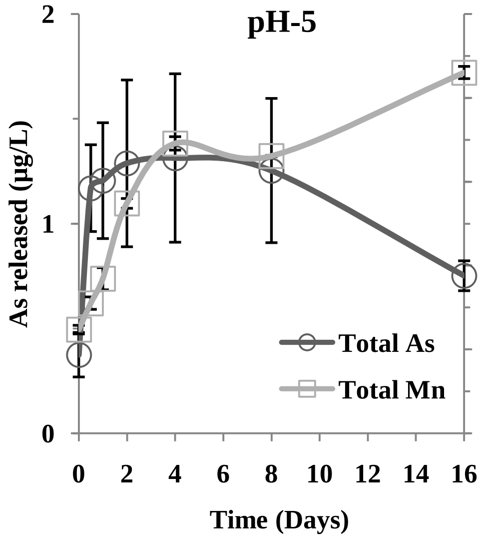


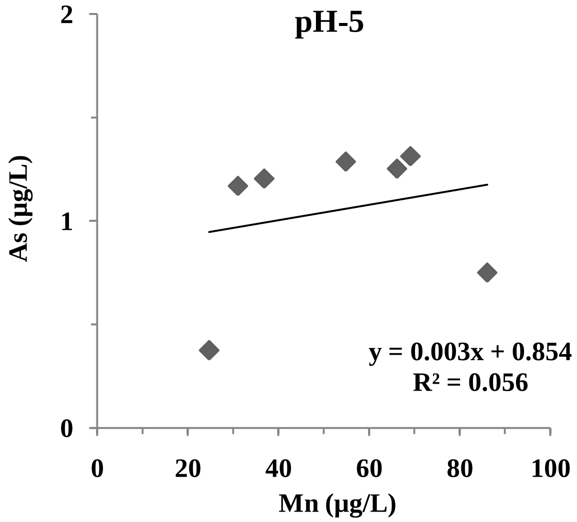


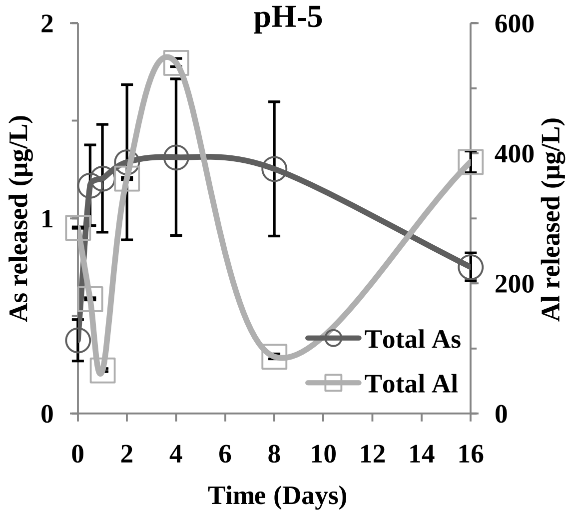


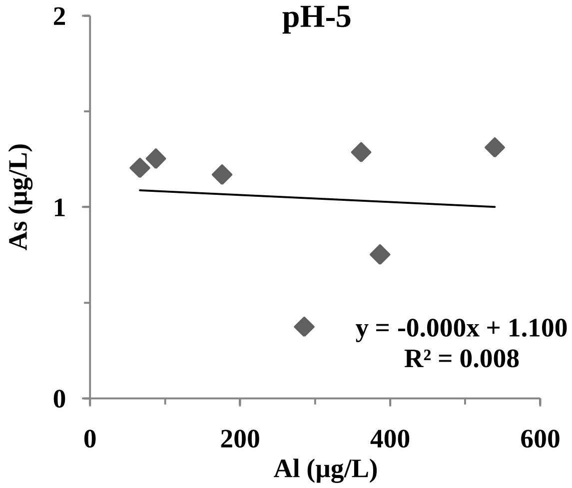
*Release of Fe was below detection limit of 0.0115 mg $L^{-1}$ at pH = 3

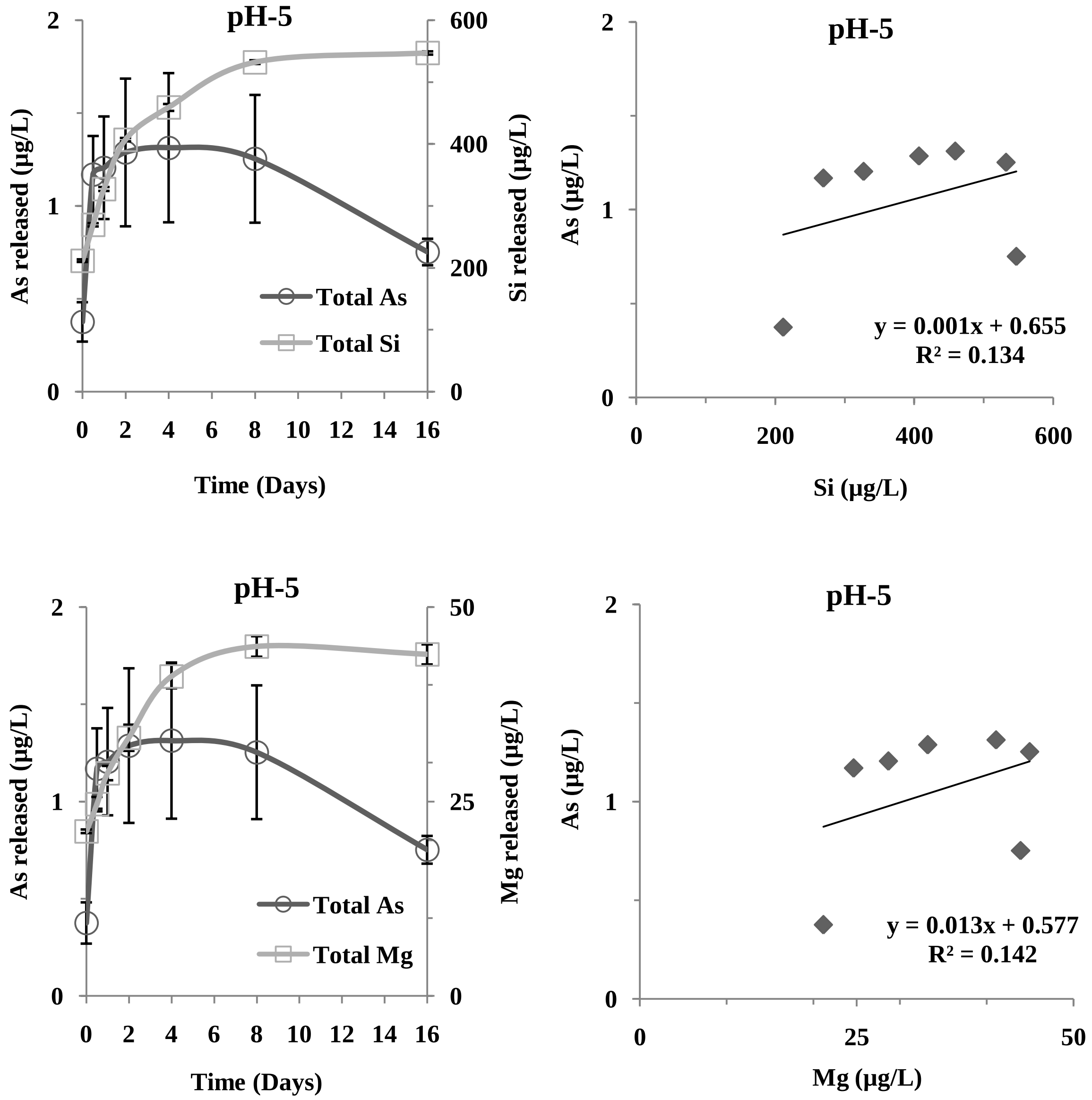
Figure 2C.1: Effects of pH on the release of As, Mn, Al, Si and Mg with time and correlation of As with Mn, Al, Si and Mg at pH = 3.


pH-5
As released (µg/L)
Mn released (µg/L)
2
1
0
100
80
60
40
20
0
0 2 4 6 8 10 12 14 16
Time (Days)
Total As
Total Mn


pH-5
As (µg/L)
2
1
0
0 20 40 60 80 100
Mn (µg/L)
y = 0.003x + 0.854
R² = 0.056

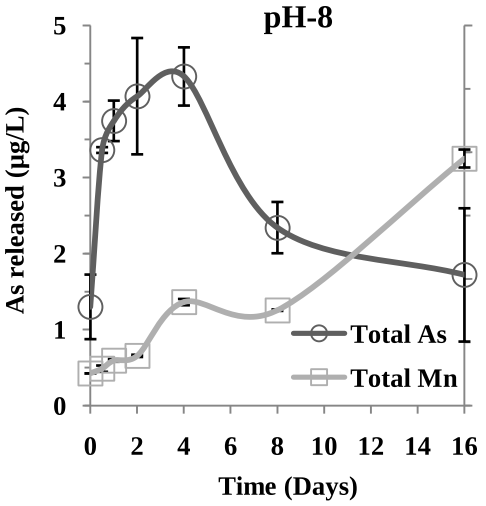

pH-5
As released (µg/L)
Al released (µg/L)
2
1
0
600
400
200
0
0 2 4 6 8 10 12 14 16
Time (Days)
Total As
Total Al

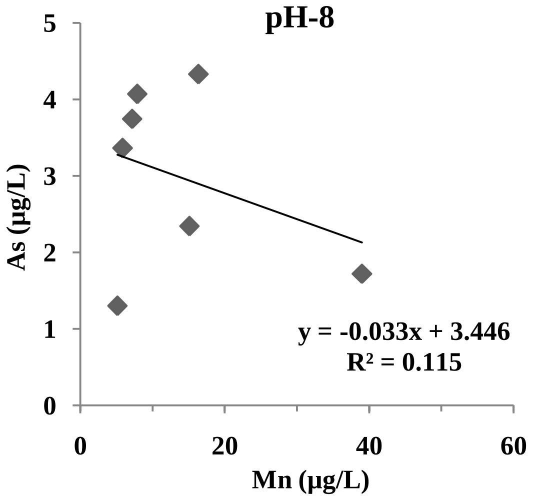

pH-5
As (µg/L)
2
1
0
0 200 400 600
Al (µg/L)
y = -0.000x + 1.100
R² = 0.008

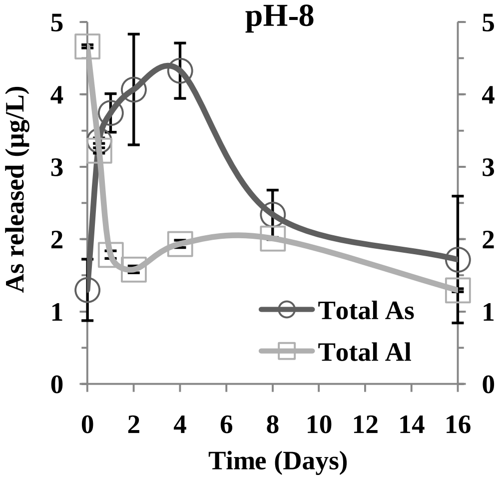


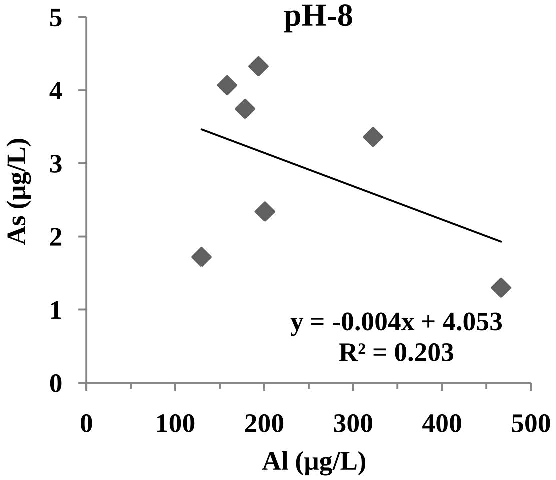
*Release of Fe was below detection limit of 0.0115 mg L$^{-1}$ at pH = 5

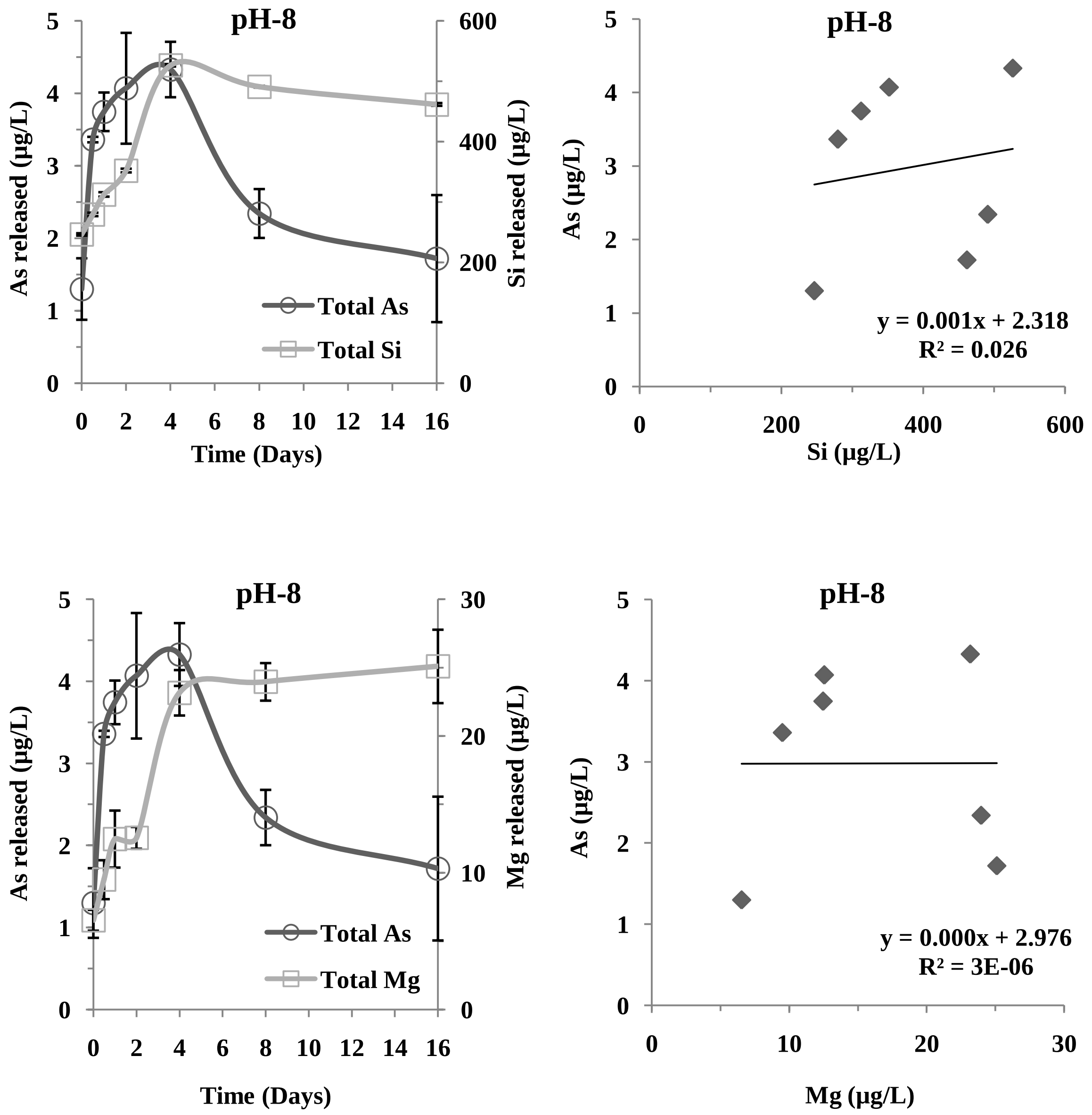
Figure 2C.2: Effects of pH on the release of As, Mn, Al, Si and Mg with time and correlation of As with Mn, Al, Si and Mg at pH = 5.


pH-8
As released (µg/L)
Mn released (µg/L)
Time (Days)
Total As
Total Mn
0
1
2
3
4
5
0
20
40
60
0
2
4
6
8
10
12
14
16


pH-8
As (µg/L)
Mn (µg/L)
y = -0.033x + 3.446
R² = 0.115
0
1
2
3
4
5
0
20
40
60

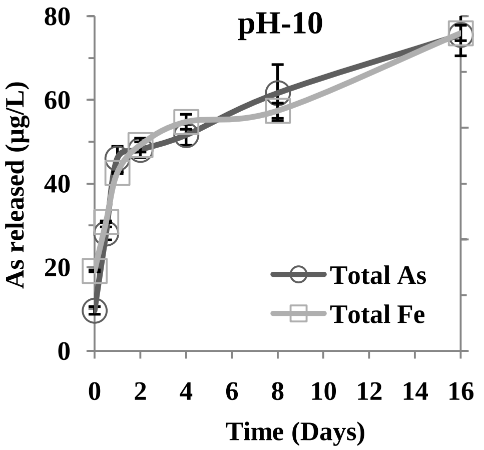

pH-8
As released (µg/L)
Al released (µg/L)
Time (Days)
Total As
Total Al
0
1
2
3
4
5
0
100
200
300
400
500
0
2
4
6
8
10
12
14
16

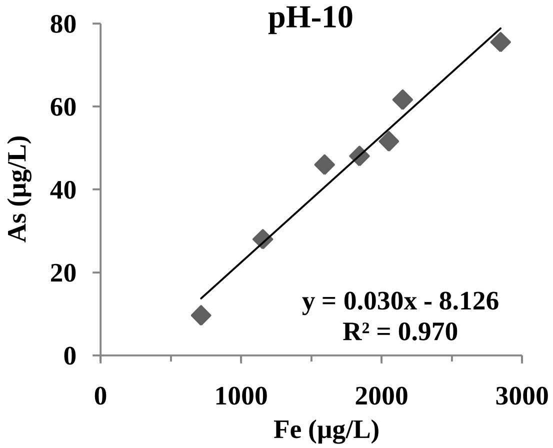

pH-8
As (µg/L)
Al (µg/L)
y = -0.004x + 4.053
R² = 0.203
0
1
2
3
4
5
0
100
200
300
400
500

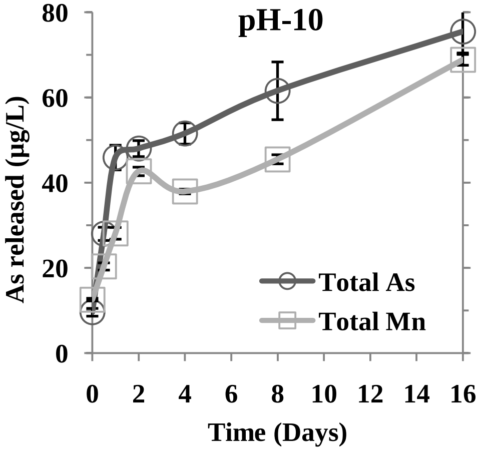


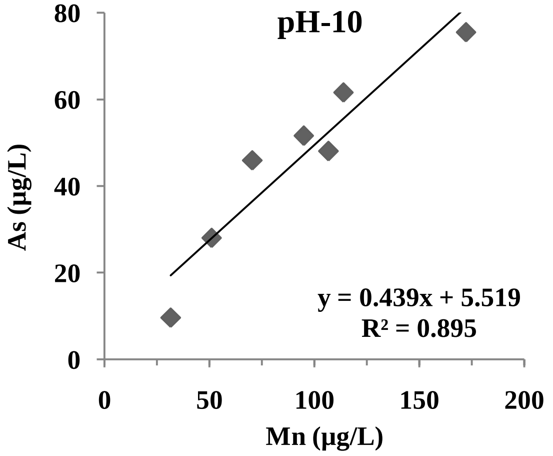
*Release of Fe was below detection limit of 0.0115 mg L$^{-1}$ at pH = 8

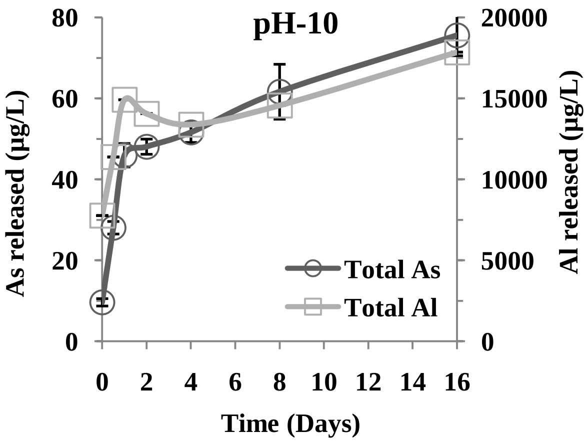
Figure 2C.3: Effects of pH on the release of As, Mn, Al, Si and Mg with time and correlation of As with Mn, Al, Si and Mg at pH = 8.

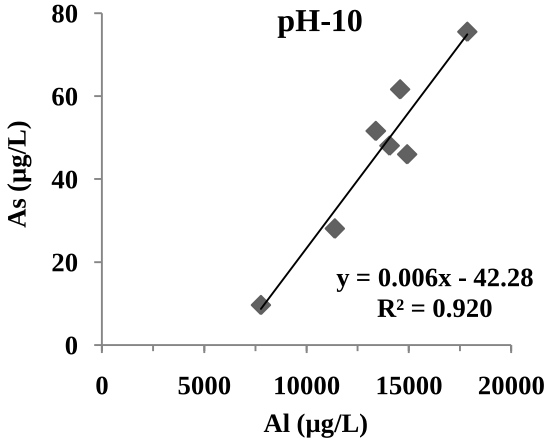

pH-10
As released (µg/L)
Fe released (µg/L)
Time (Days)
Total As
Total Fe
0
20
40
60
80
0
1000
2000
3000
0 2 4 6 8 10 12 14 16


pH-10
As (µg/L)
Fe (µg/L)
y = 0.030x - 8.126
R² = 0.970
0
20
40
60
80
0 1000 2000 3000


pH-10
As released (µg/L)
Mn released (µg/L)
Time (Days)
Total As
Total Mn
0
20
40
60
80
0
50
100
150
200
0 2 4 6 8 10 12 14 16


pH-10
As (µg/L)
Mn (µg/L)
y = 0.439x + 5.519
R² = 0.895
0
20
40
60
80
0 50 100 150 200


pH-10
As released (µg/L)
Al released (µg/L)
Time (Days)
Total As
Total Al
0
20
40
60
80
0
5000
10000
15000
20000
0 2 4 6 8 10 12 14 16


pH-10
As (µg/L)
Al (µg/L)
y = 0.006x - 42.28
R² = 0.920
0
20
40
60
80
0 5000 10000 15000 20000

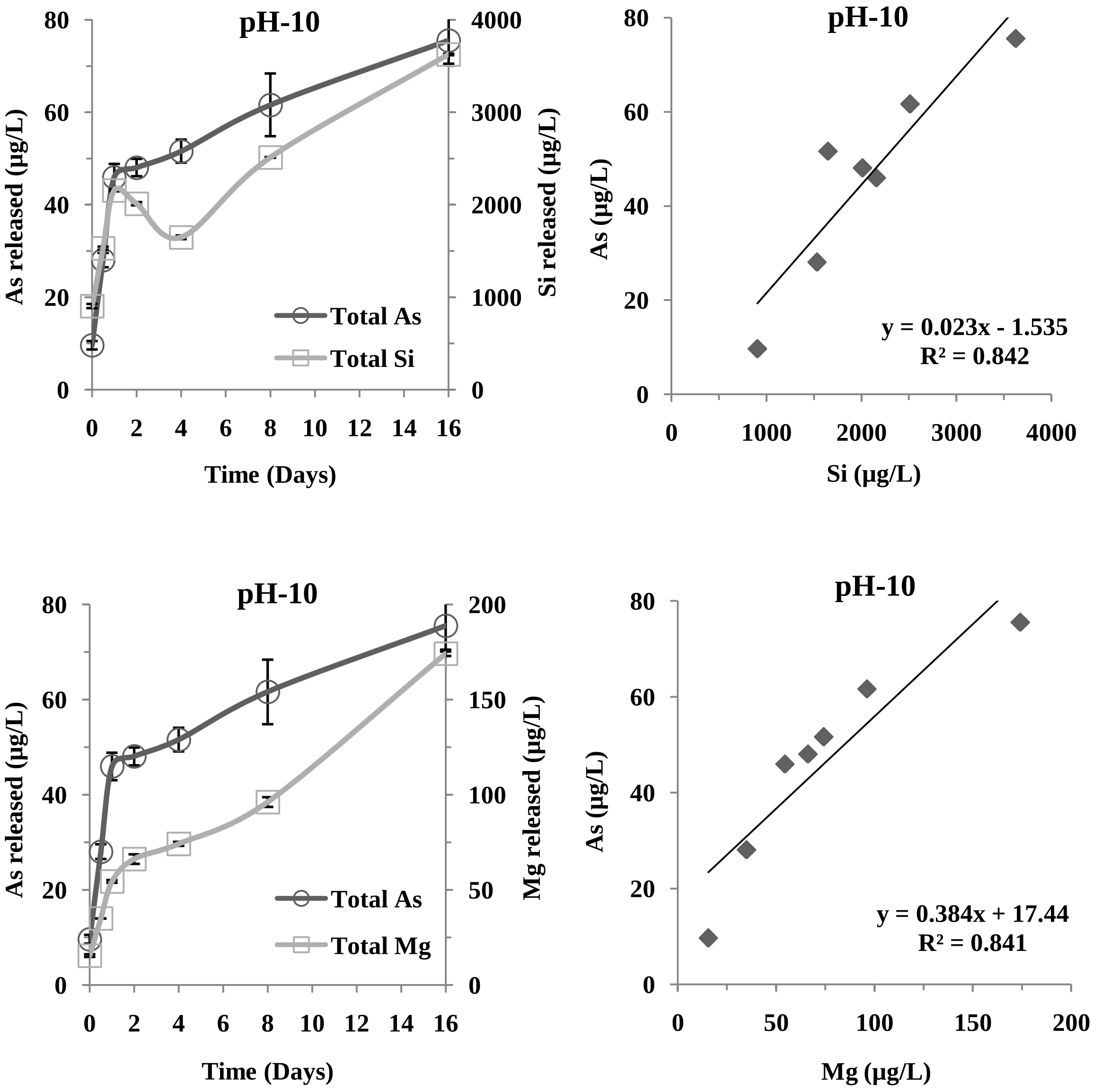
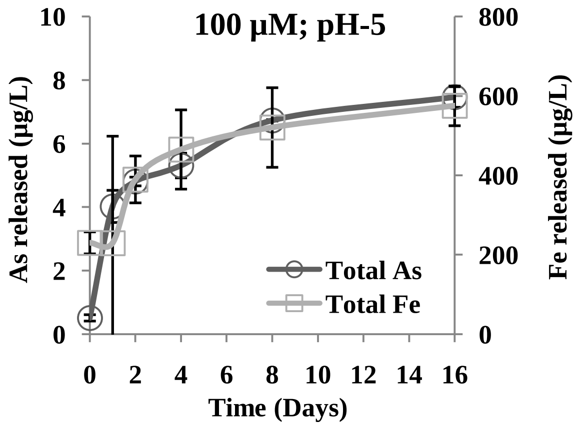
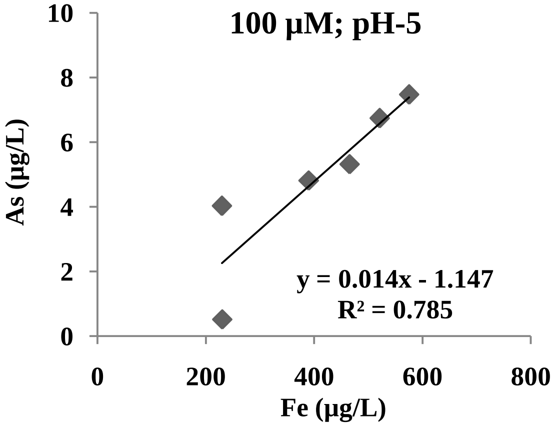
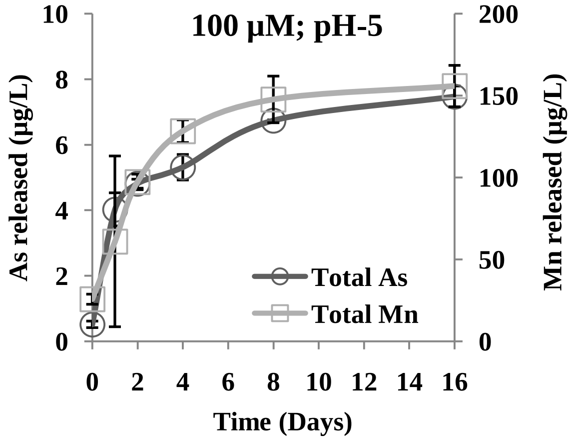


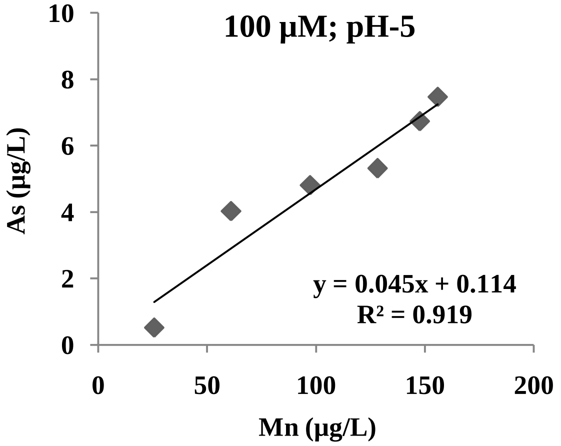
Figure 2C.4: Effects of pH on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg at pH = 10.

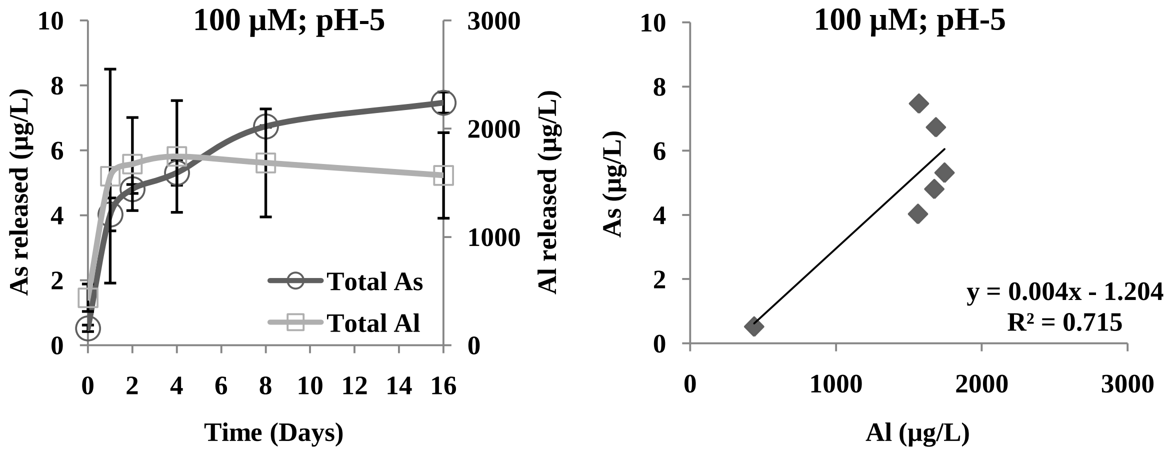
# Appendix 2D: Effects of siderephore concentrations on the release of As, Fe, Mn, Al and Si with time and correlation of As with Fe, Mn, Al and Si.





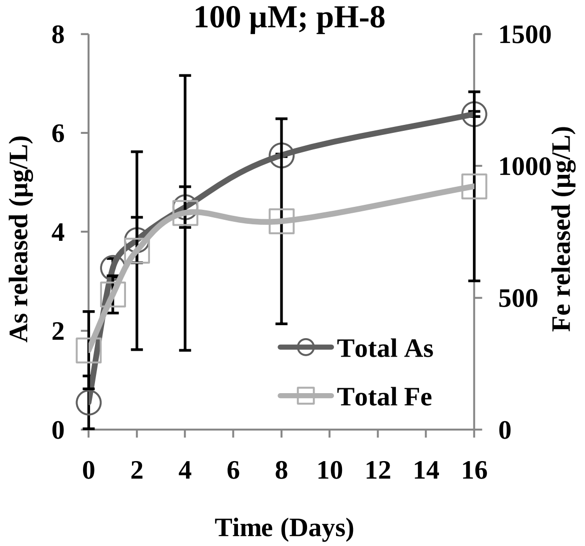


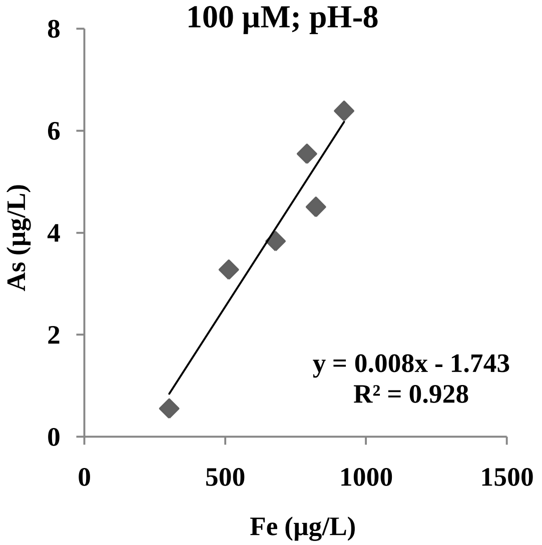


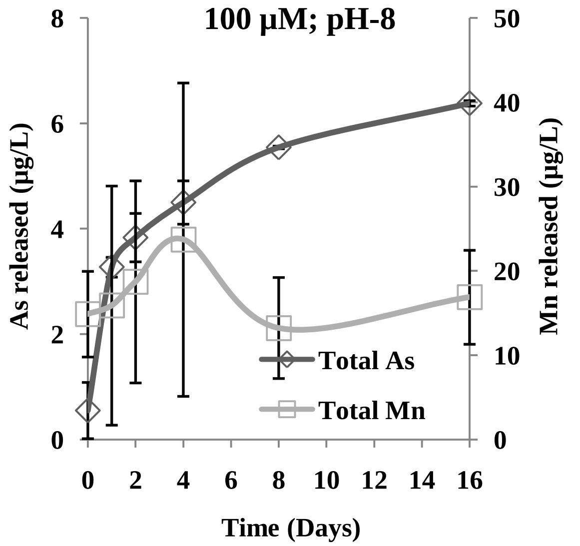


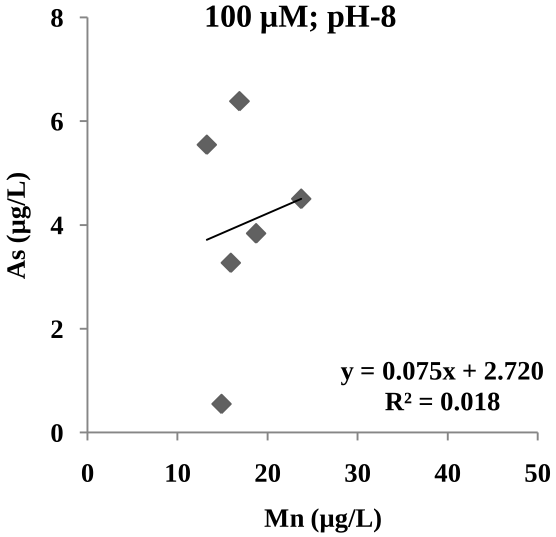
* Release of Mg was below detection limit of 3.35 µg $L^{-1}$, and release of Si was below detection limit of 731.30 µg $L^{-1}$ at 100 µM siderophore and pH = 5

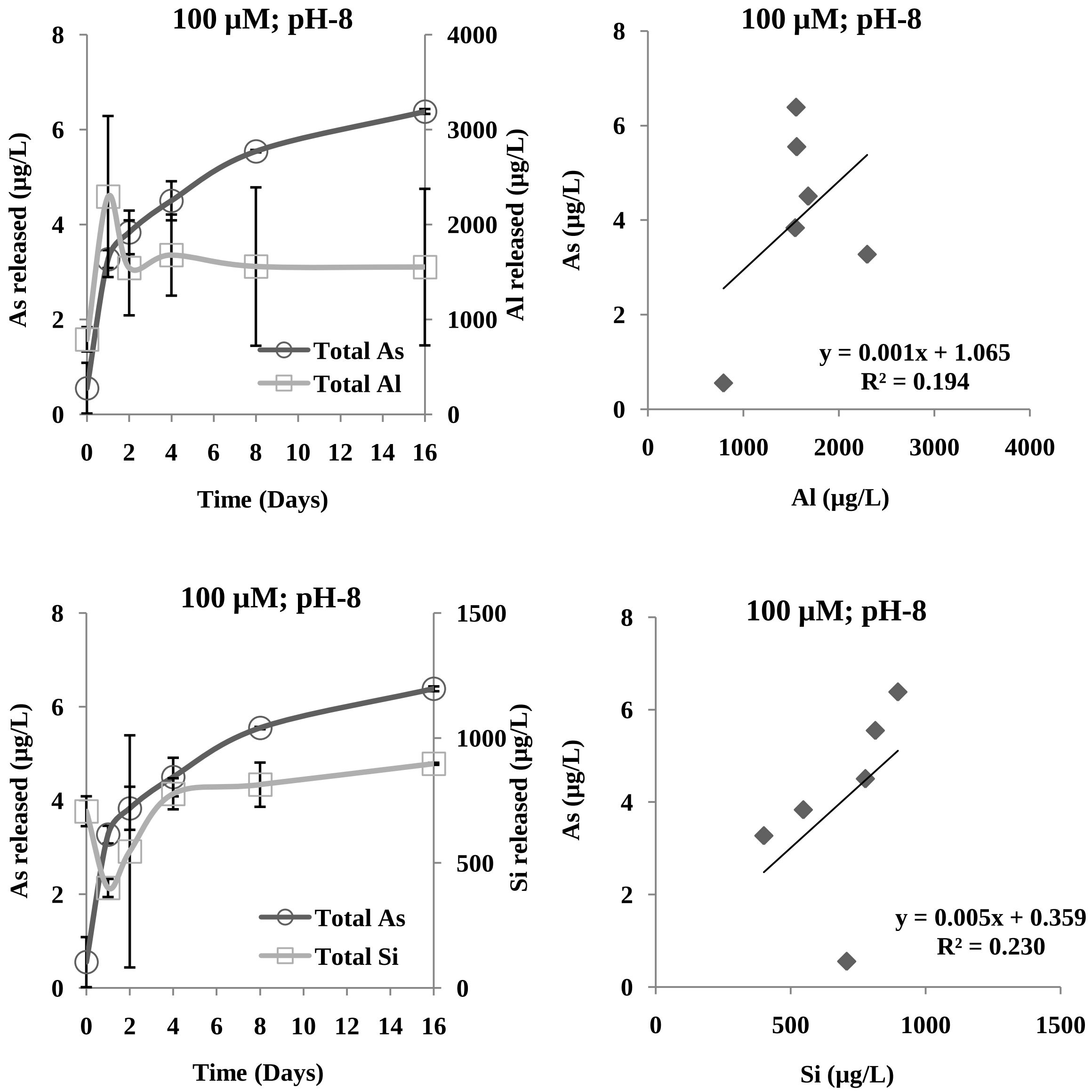
Figure 2D.1: Effects of siderophore concentrations on the release of As, Fe, Mn and Al with time and correlation of As with Fe, Mn and Al at 100 µM siderophore and pH = 5.


100 µM; pH-8
As released (µg/L)
Fe released (µg/L)
Time (Days)
Total As
Total Fe
0
2
4
6
8
0
500
1000
1500
0
2
4
6
8
10
12
14
16


100 µM; pH-8
As (µg/L)
Fe (µg/L)
y = 0.008x - 1.743
R² = 0.928
0
2
4
6
8
0
500
1000
1500

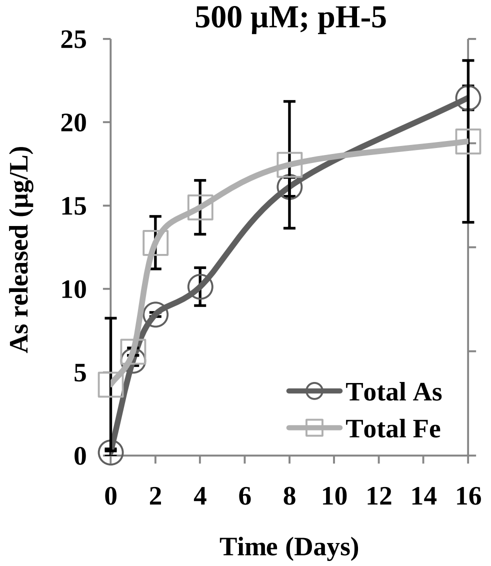

100 µM; pH-8
As released (µg/L)
Mn released (µg/L)
Time (Days)
Total As
Total Mn
0
2
4
6
8
0
10
20
30
40
50
0
2
4
6
8
10
12
14
16

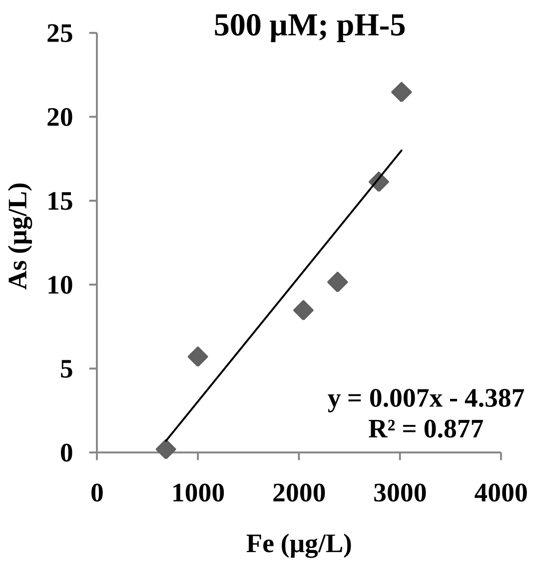

100 µM; pH-8
As (µg/L)
Mn (µg/L)
y = 0.075x + 2.720
R² = 0.018
0
2
4
6
8
0
10
20
30
40
50

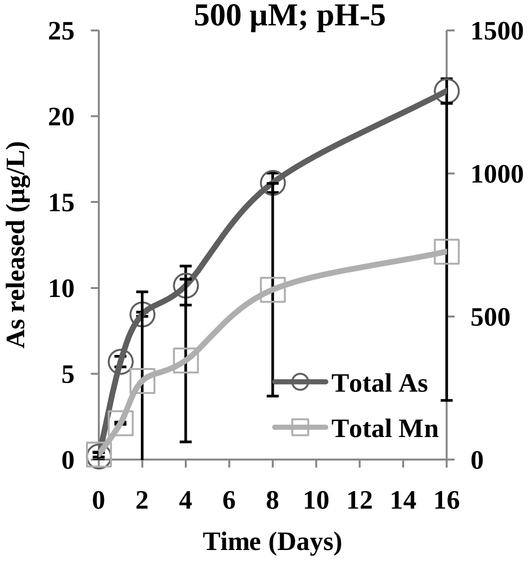


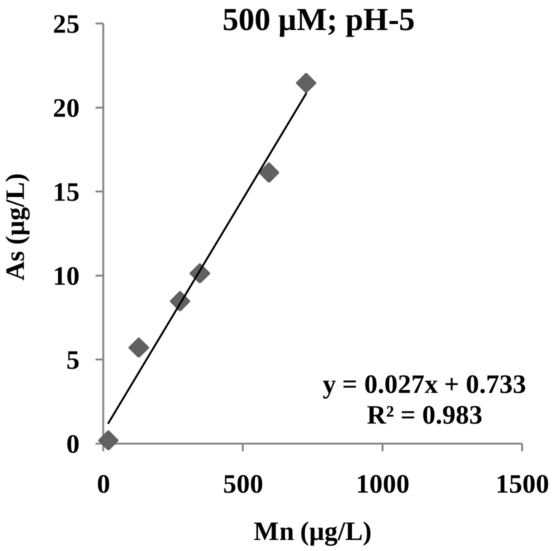
* Release of Mg was below detection limit of 3.35 µg $L^{-1}$ at 100 µM siderophore and pH = 8

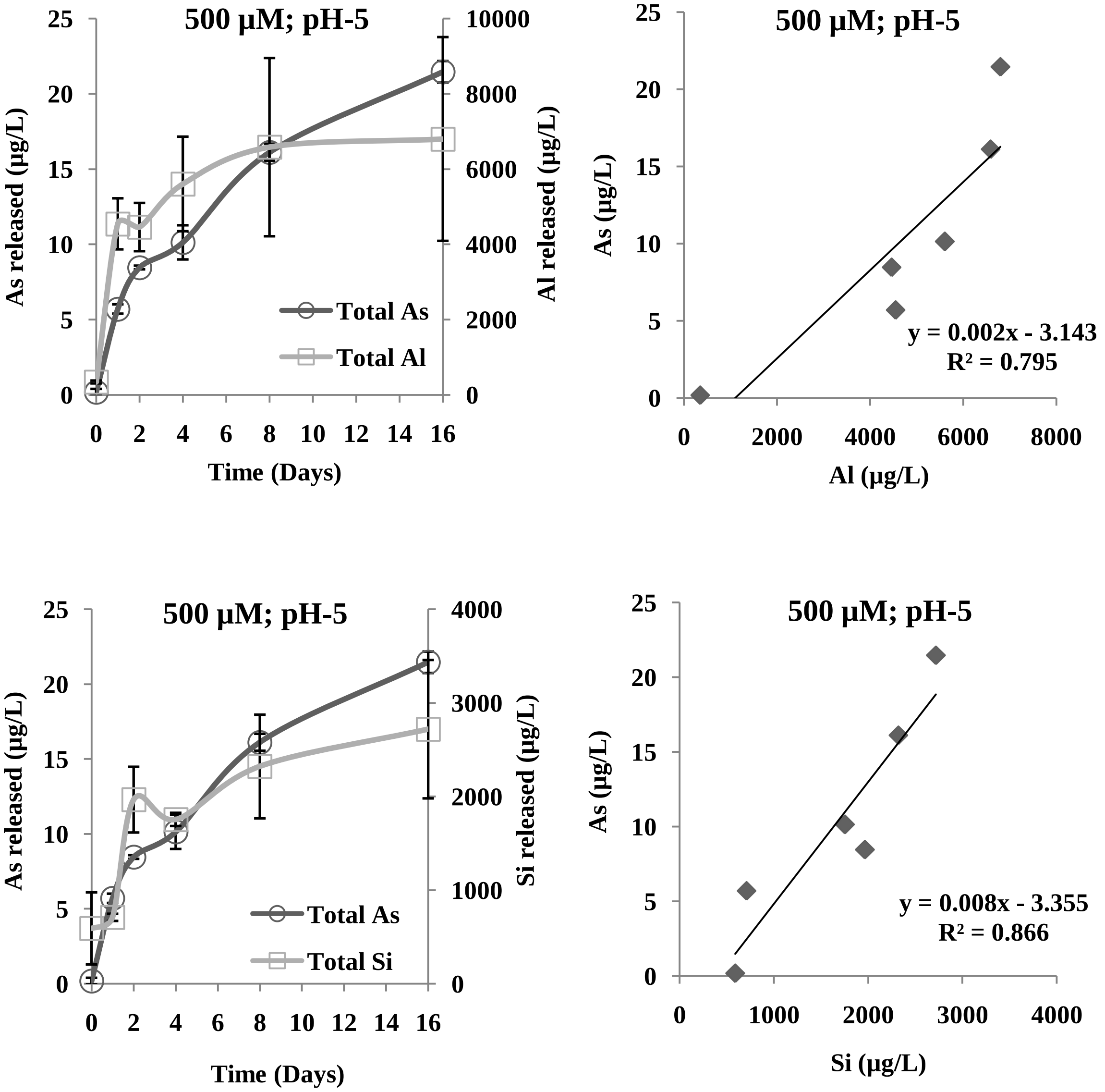
Figure 2D.2: Effects of siderophore concentrations on the release of As, Fe, Mn, Al and Si with time and correlation of As with Fe, Mn, Al and Si at 100 µM siderophore and pH = 8.


500 µM; pH-5


500 µM; pH-5

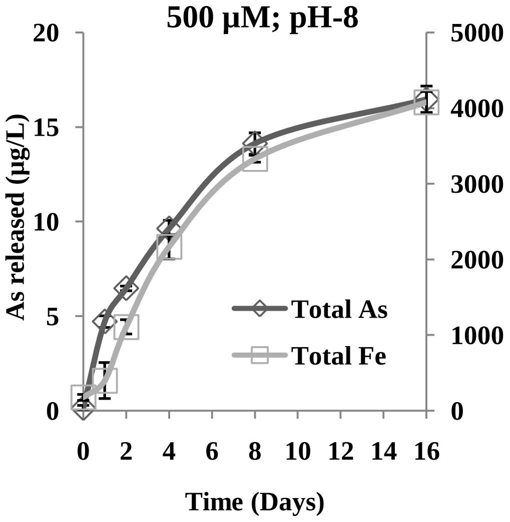

500 µM; pH-5

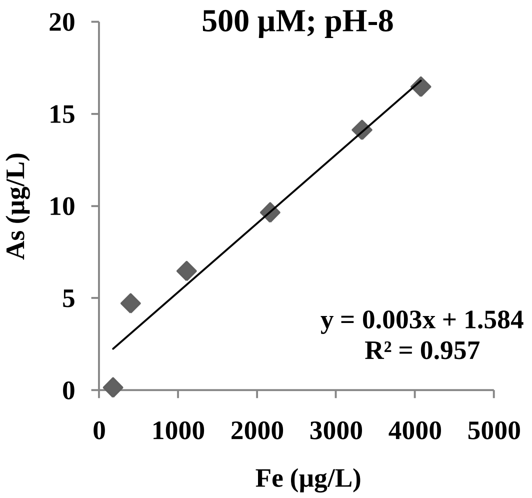

500 µM; pH-5

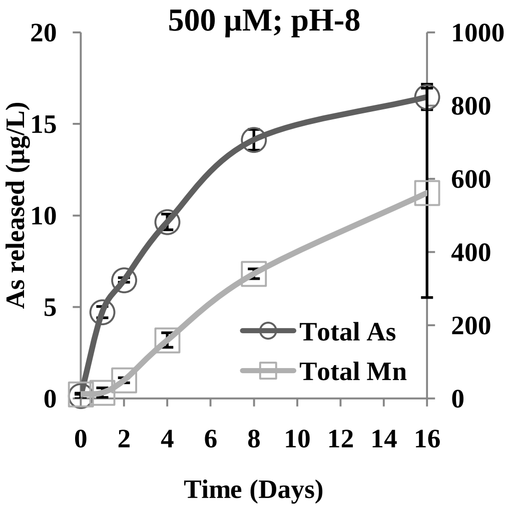


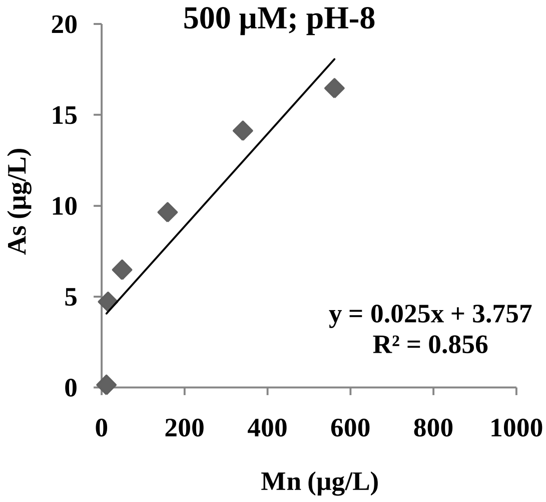
* Release of Mg was below detection limit of 3.35 µg $L^{-1}$ at 500 µM siderophore and pH = 5

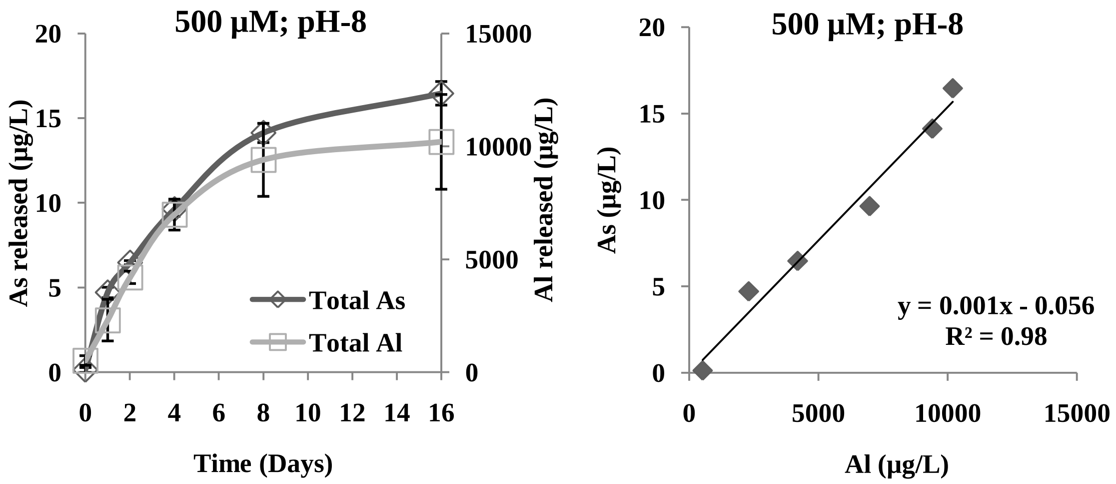
Figure 2D.3: Effects of siderophore concentrations on the release of As, Fe, Mn, Al and Si with time and correlation of As with Fe, Mn, Al and Si at 500 µM siderophore and pH = 5.


500 µM; pH-8
As released (µg/L)
Fe released (µg/L)
Time (Days)
0
5
10
15
20
0
1000
2000
3000
4000
5000
0
2
4
6
8
10
12
14
16
Total As
Total Fe


500 µM; pH-8
As (µg/L)
Fe (µg/L)
0
5
10
15
20
0
1000
2000
3000
4000
5000
y = 0.003x + 1.584
R² = 0.957


500 µM; pH-8
As released (µg/L)
Mn released (µg/L)
Time (Days)
0
5
10
15
20
0
200
400
600
800
1000
0
2
4
6
8
10
12
14
16
Total As
Total Mn

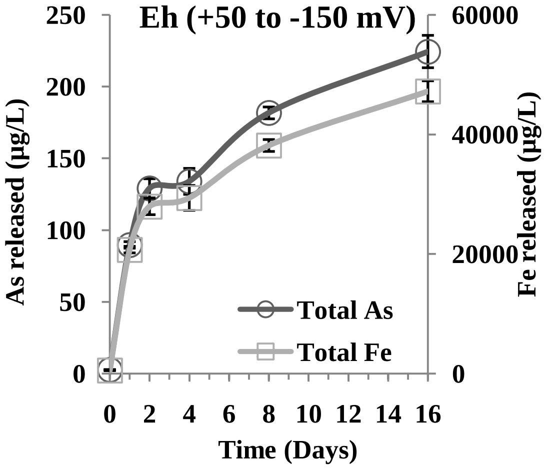

500 µM; pH-8
As (µg/L)
Mn (µg/L)
0
5
10
15
20
0
200
400
600
800
1000
y = 0.025x + 3.757
R² = 0.856

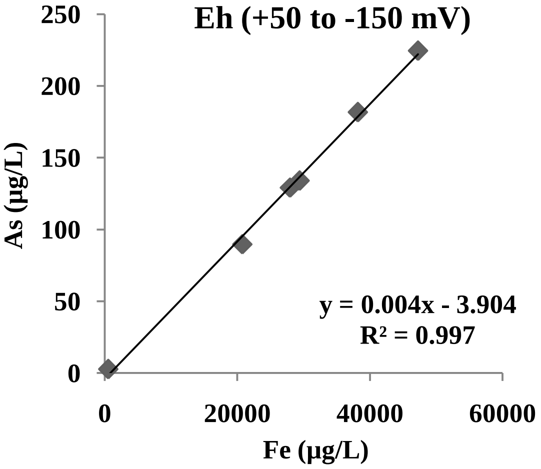


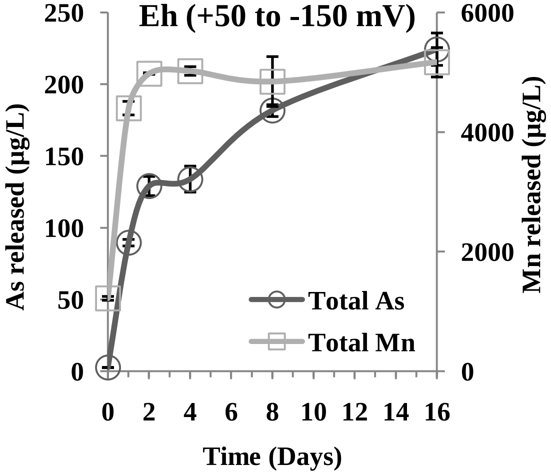
* Release of Mg was below detection limit of 3.35 µg $L^{-1}$, and release of Si was below detection limit of 731.30 µg $L^{-1}$ at 500 µM siderophore and pH = 8

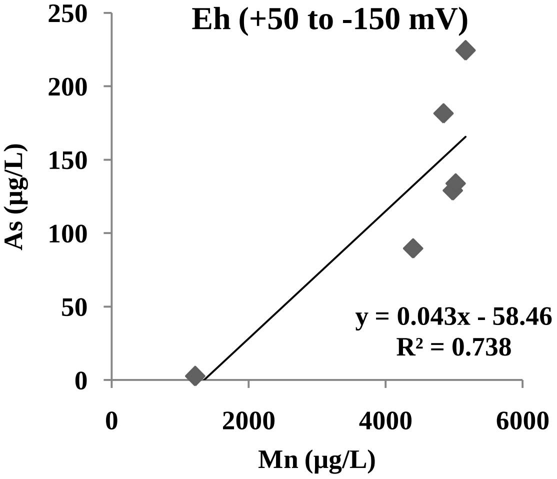
Figure 2D.4: Effects of siderophore concentrations on the release of As, Fe, Mn and Al with time and correlation of As with Fe, Mn and Al at 500 µM siderophore and pH = 8.

# Appendix 2E: Effects of Eh on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg.









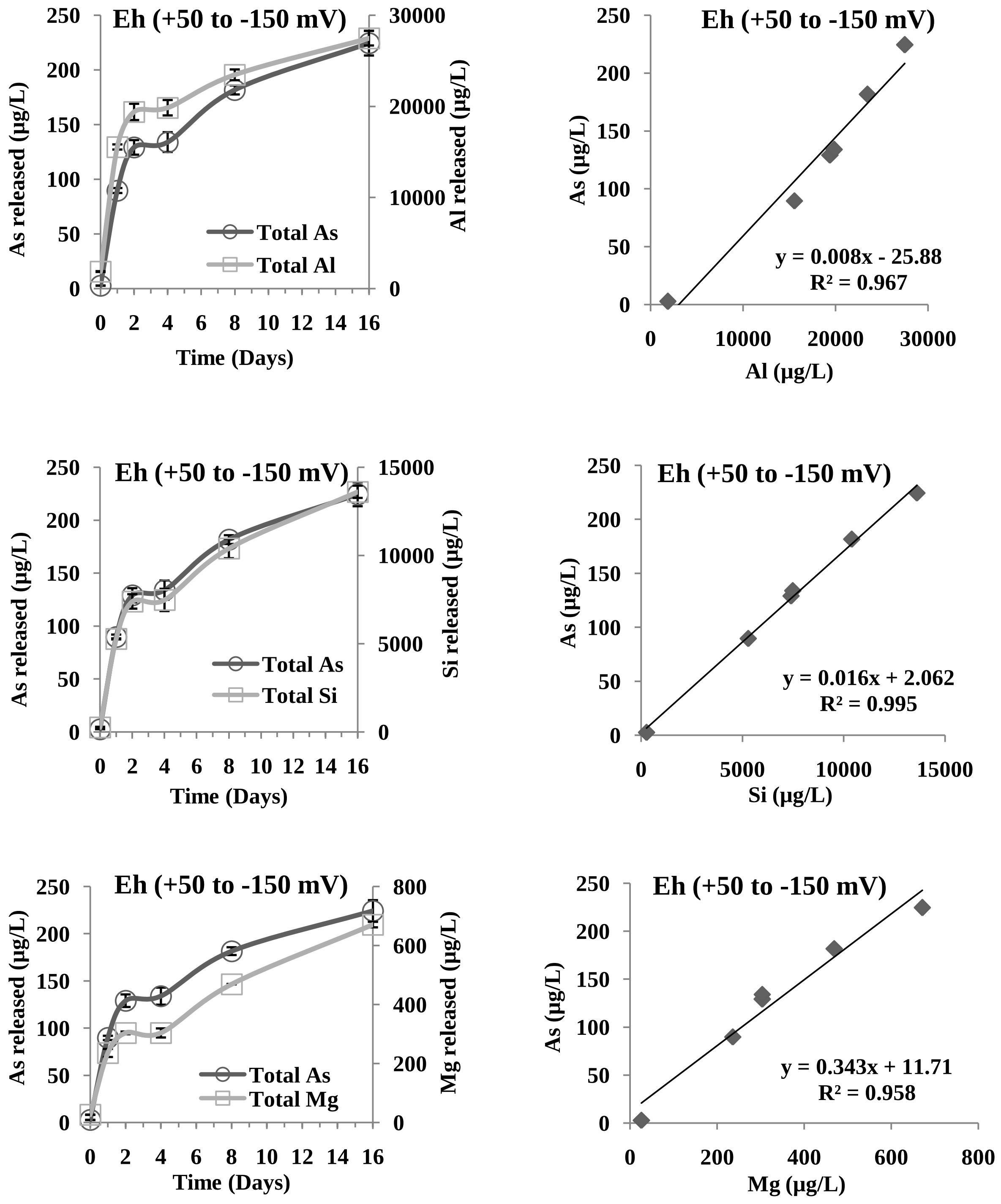
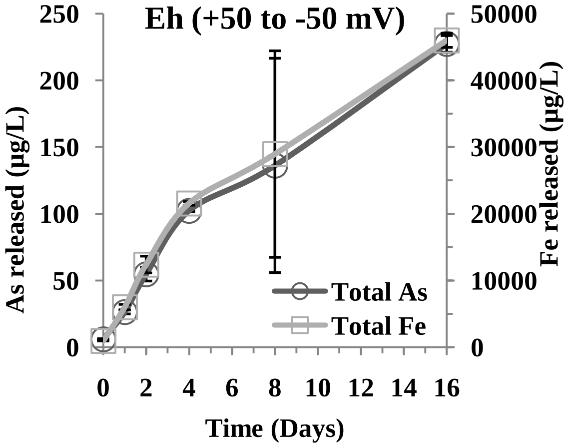
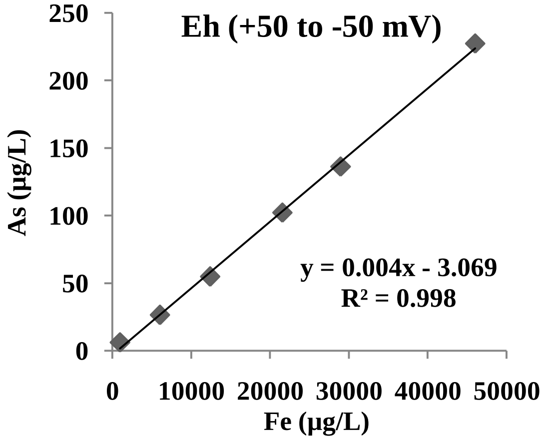
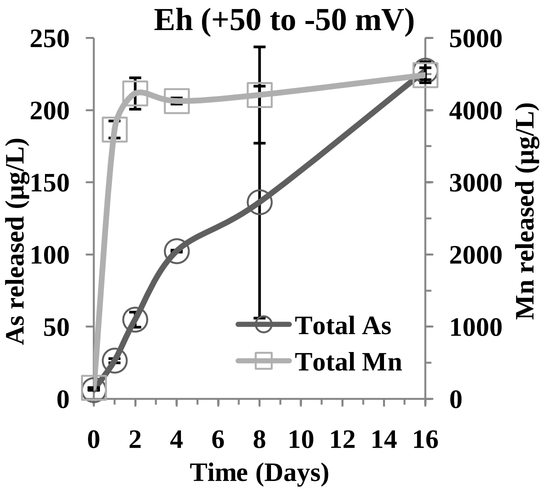
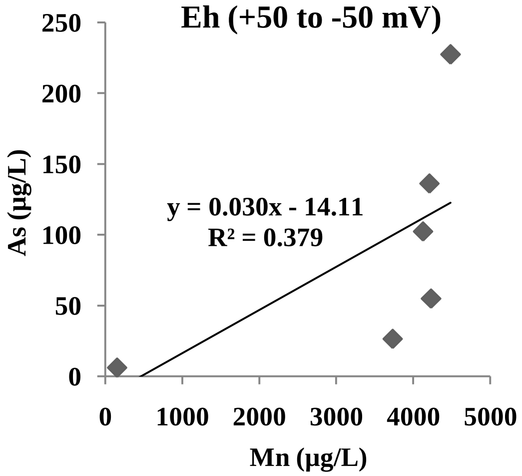


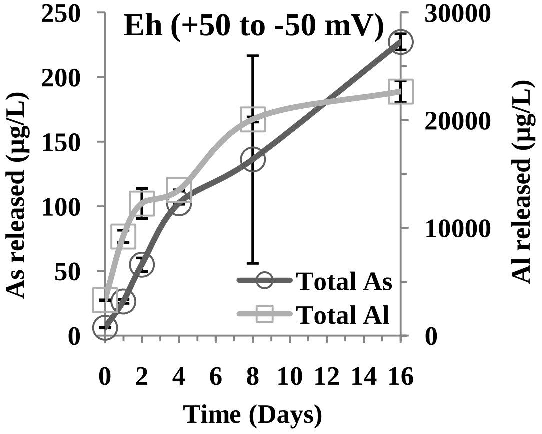
Figure 2E.1: Effects of Eh on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg at Eh = +50 to -150 mV.

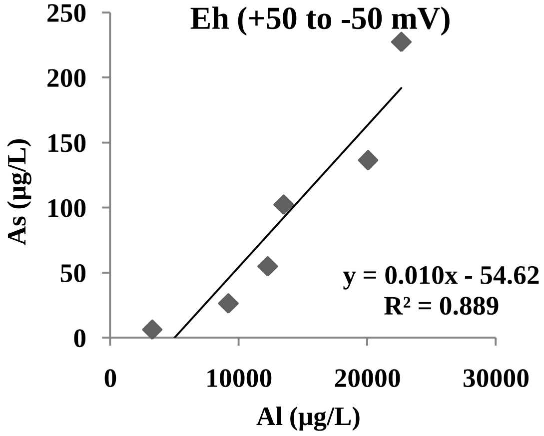

Eh (+50 to -50 mV)
As released (µg/L)
Fe released (µg/L)
Time (Days)
0
50
100
150
200
250
0
10000
20000
30000
40000
50000
0
2
4
6
8
10
12
14
16
Total As
Total Fe


Eh (+50 to -50 mV)
As (µg/L)
Fe (µg/L)
y = 0.004x - 3.069
R² = 0.998
0
50
100
150
200
250
0
10000
20000
30000
40000
50000


Eh (+50 to -50 mV)
As released (µg/L)
Mn released (µg/L)
Time (Days)
0
50
100
150
200
250
0
1000
2000
3000
4000
5000
0
2
4
6
8
10
12
14
16
Total As
Total Mn


Eh (+50 to -50 mV)
As (µg/L)
Mn (µg/L)
y = 0.030x - 14.11
R² = 0.379
0
50
100
150
200
250
0
1000
2000
3000
4000
5000


Eh (+50 to -50 mV)
As released (µg/L)
Al released (µg/L)
Time (Days)
0
50
100
150
200
250
0
10000
20000
30000
0
2
4
6
8
10
12
14
16
Total As
Total Al


Eh (+50 to -50 mV)
As (µg/L)
Al (µg/L)
y = 0.010x - 54.62
R² = 0.889
0
50
100
150
200
250
0
10000
20000
30000

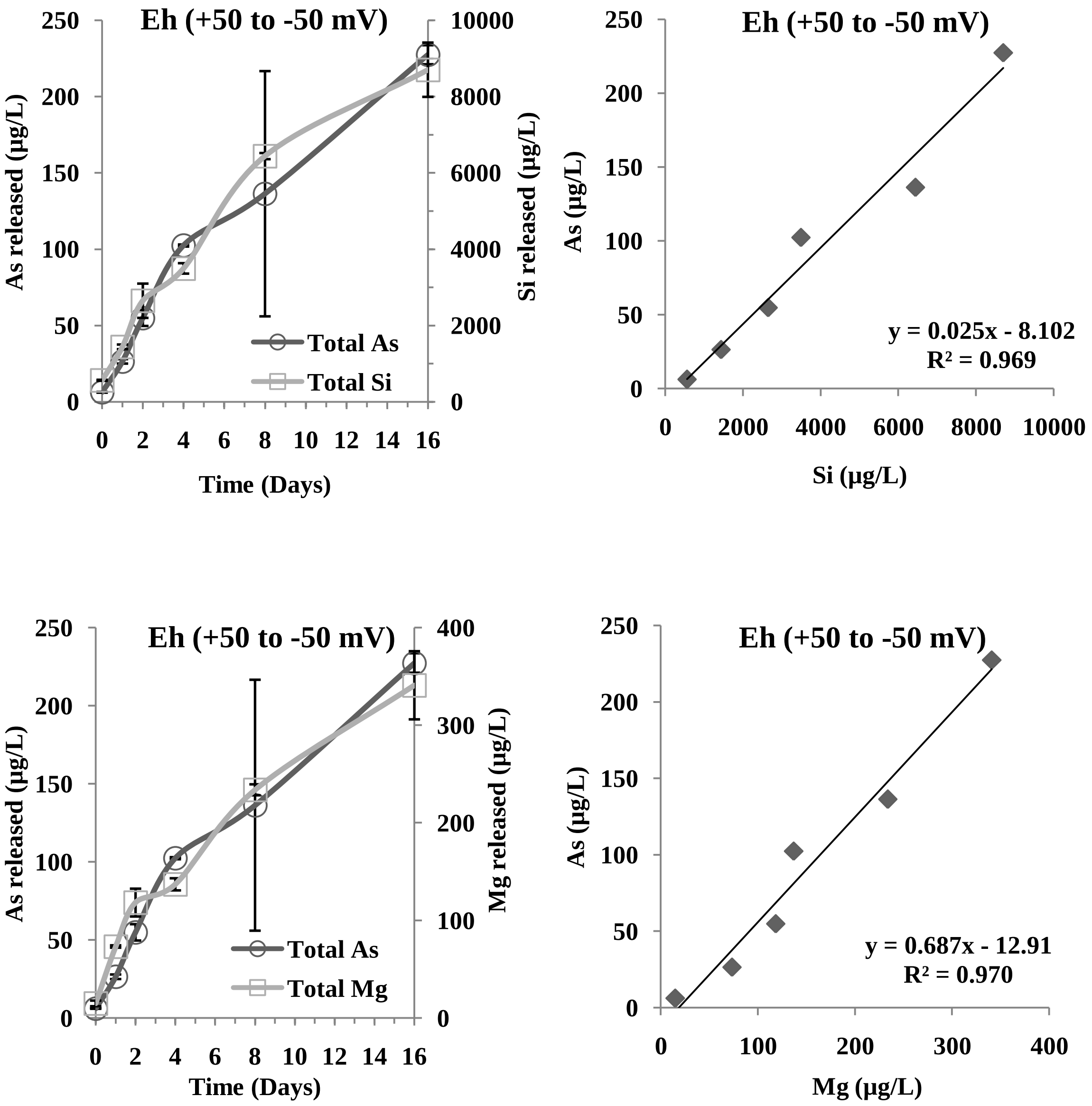
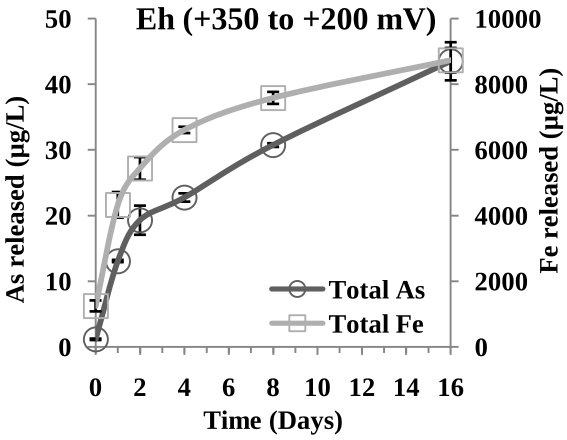
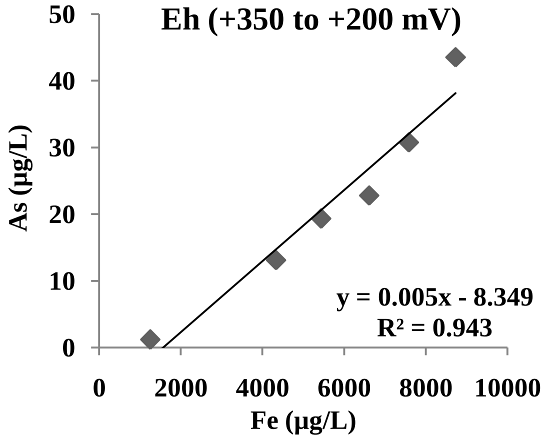
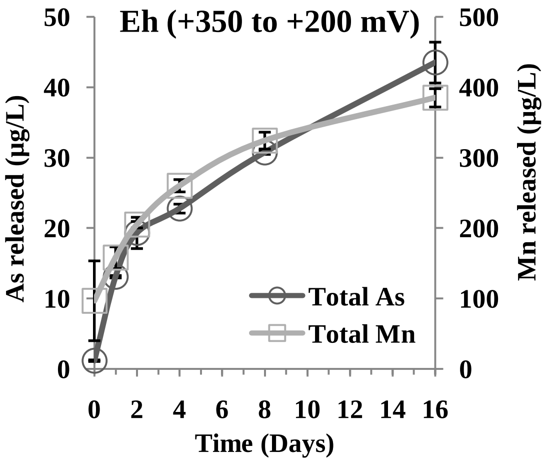
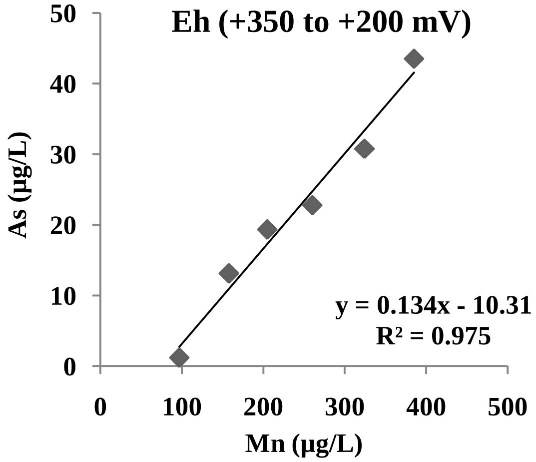


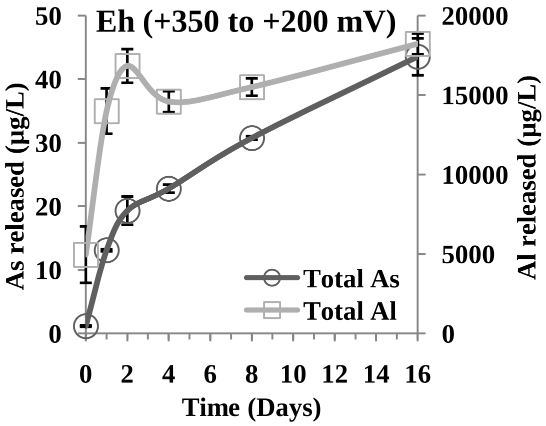
Figure 2E.2: Effects of Eh on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg at Eh = +50 to -50 mV.

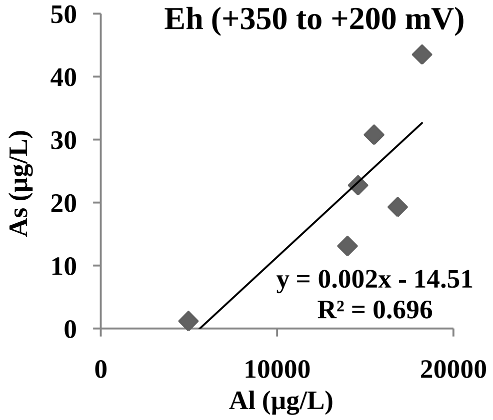

Eh (+350 to +200 mV)
As released (µg/L)
Fe released (µg/L)
Time (Days)
0 2 4 6 8 10 12 14 16
0 10 20 30 40 50
0 2000 4000 6000 8000 10000
Total As
Total Fe


Eh (+350 to +200 mV)
As (µg/L)
Fe (µg/L)
0 2000 4000 6000 8000 10000
0 10 20 30 40 50
y = 0.005x - 8.349
R² = 0.943


Eh (+350 to +200 mV)
As released (µg/L)
Mn released (µg/L)
Time (Days)
0 2 4 6 8 10 12 14 16
0 10 20 30 40 50
0 100 200 300 400 500
Total As
Total Mn


Eh (+350 to +200 mV)
As (µg/L)
Mn (µg/L)
0 100 200 300 400 500
0 10 20 30 40 50
y = 0.134x - 10.31
R² = 0.975


Eh (+350 to +200 mV)
As released (µg/L)
Al released (µg/L)
Time (Days)
0 2 4 6 8 10 12 14 16
0 10 20 30 40 50
0 5000 10000 15000 20000
Total As
Total Al


Eh (+350 to +200 mV)
As (µg/L)
Al (µg/L)
0 10000 20000
0 10 20 30 40 50
y = 0.002x - 14.51
R² = 0.696

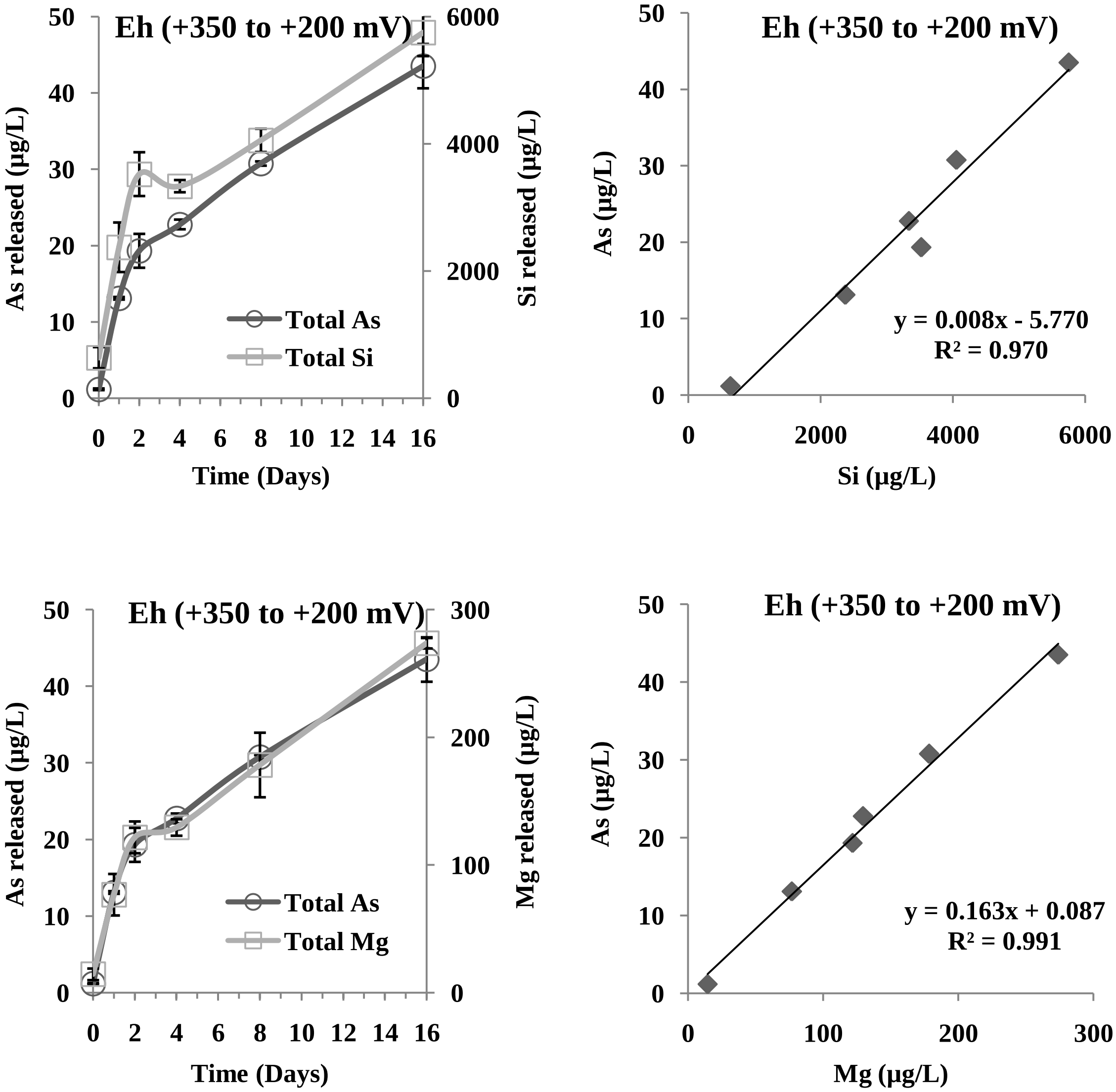
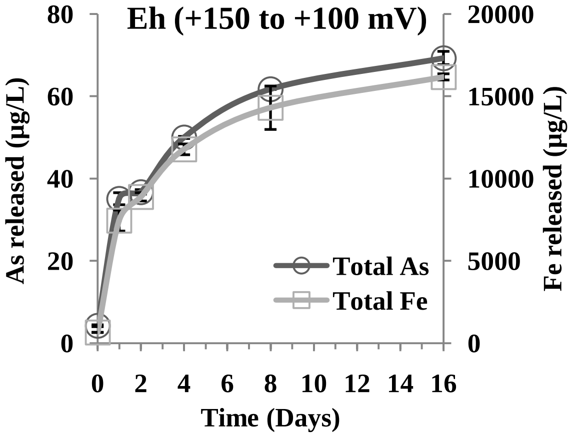
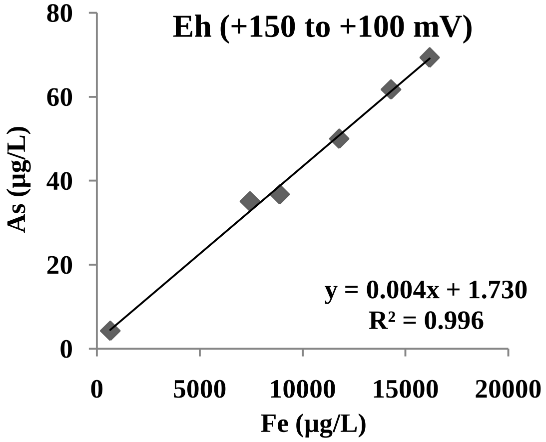
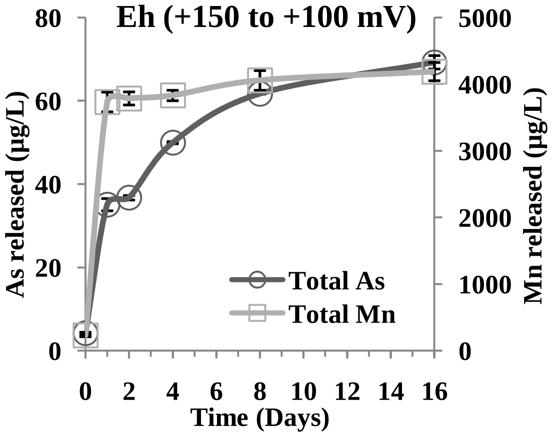
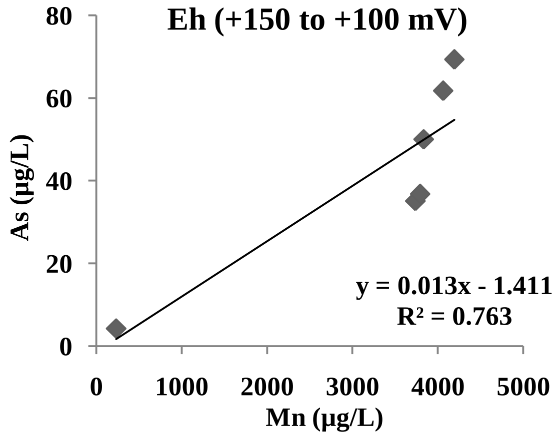


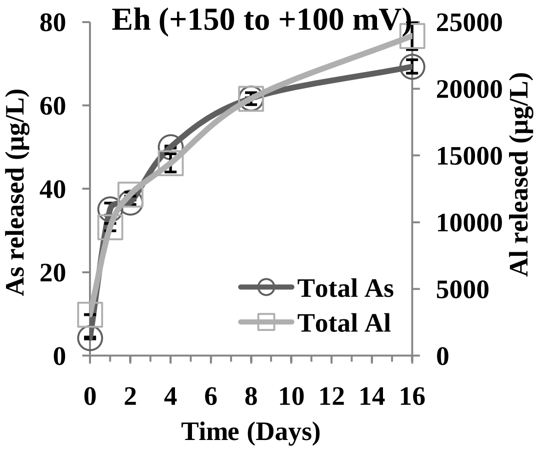
Figure 2E.3: Effects of Eh on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg at Eh = +350 to + 200 mV.

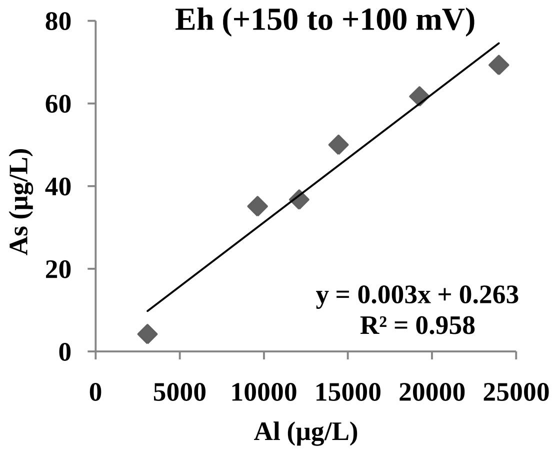

Eh (+150 to +100 mV)
As released (µg/L)
Fe released (µg/L)
Time (Days)
Total As
Total Fe
0
20
40
60
80
0
5000
10000
15000
20000
0 2 4 6 8 10 12 14 16


Eh (+150 to +100 mV)
As (µg/L)
Fe (µg/L)
y = 0.004x + 1.730
R² = 0.996
0
20
40
60
80
0 5000 10000 15000 20000


Eh (+150 to +100 mV)
As released (µg/L)
Mn released (µg/L)
Time (Days)
Total As
Total Mn
0
20
40
60
80
0
1000
2000
3000
4000
5000
0 2 4 6 8 10 12 14 16


Eh (+150 to +100 mV)
As (µg/L)
Mn (µg/L)
y = 0.013x - 1.411
R² = 0.763
0
20
40
60
80
0 1000 2000 3000 4000 5000


Eh (+150 to +100 mV)
As released (µg/L)
Al released (µg/L)
Time (Days)
Total As
Total Al
0
20
40
60
80
0
5000
10000
15000
20000
25000
0 2 4 6 8 10 12 14 16


Eh (+150 to +100 mV)
As (µg/L)
Al (µg/L)
y = 0.003x + 0.263
R² = 0.958
0
20
40
60
80
0 5000 10000 15000 20000 25000

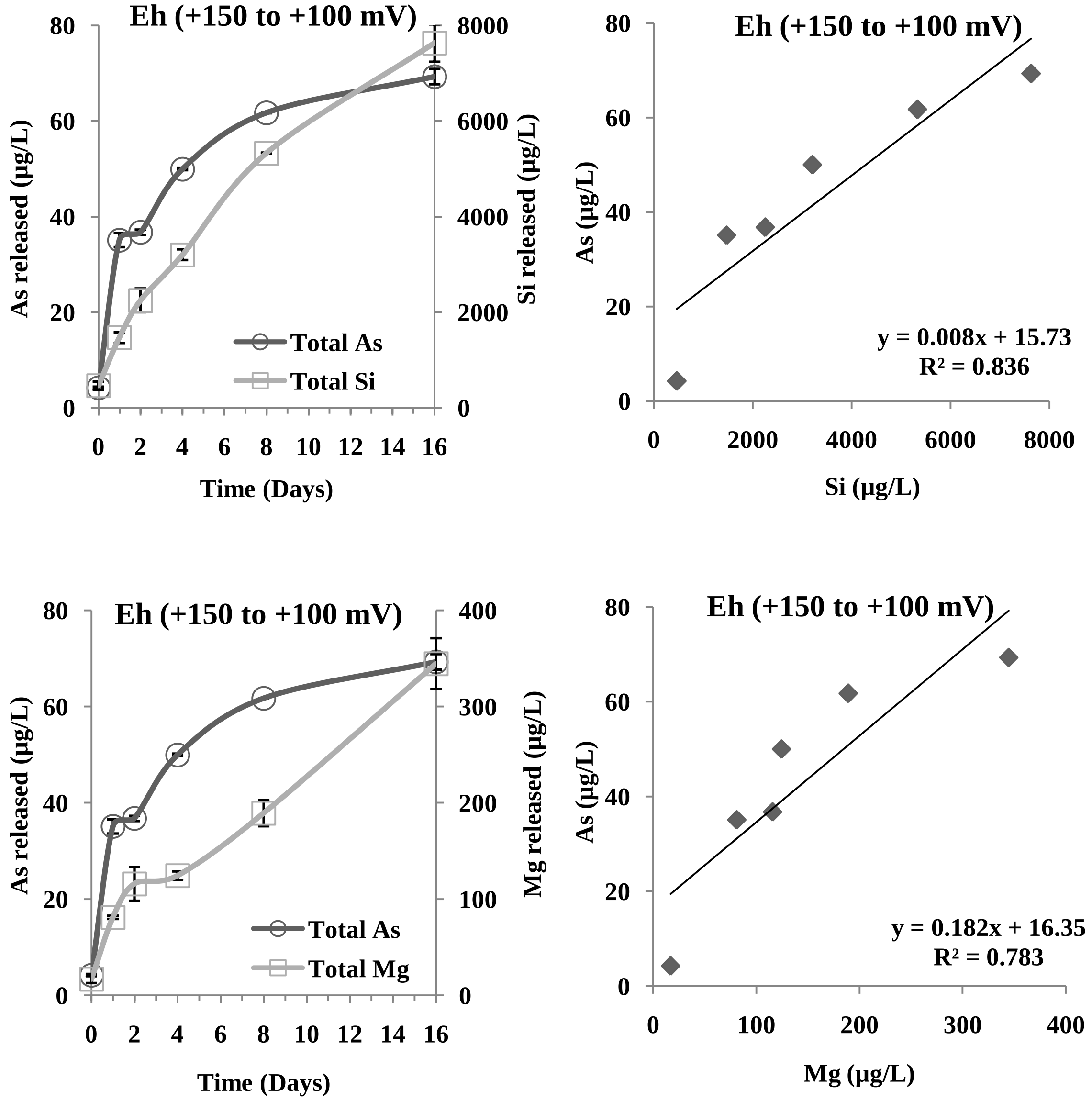


Figure 2E.4: Effects of Eh on the release of As, Fe, Mn, Al, Si and Mg with time and correlation of As with Fe, Mn, Al, Si and Mg at Eh = +150 to + 100 mV.

# Appendix 3A: Tabulated sequential extraction data of U

| Steps | Mg (mg/kg) & % | Ca (mg/kg) & % | Al (mg/kg) & % | Si (mg/kg) & % | Fe (mg/kg) & % | Mn (mg/kg) & % | U (mg/kg) & % |
|---|---|---|---|---|---|---|---|
| Exchangeable | NA[b] | 638 ± 30 | 143.5 ± 14.65 (0.16 %) | 52.47 ± 13.65 (6.58 %) | 271.4 ± 8.4 (0.75 %) | 45.46 ± 1.82 (5.12 %) | 0.14 ± 0.011 (0.52 %) |
| Carbonate bound | 156 ± 1.5 | BDL[a] | 454.67 ± 41.27<br>(0.51 %) | 265.54 ± 24.53<br>(33.32 %) | 351.5 ± 23.8<br>(0.97 %) | 8.48 ± 0.17<br>(0.95 %) | 9.18 ± 0.3<br>(35.36 %) |
| Fe-Mn oxides | 130 ± 113 | BDL[a] | 2371.75 ± 51.32<br>(2.7 %) | 72.06 ± 11.29<br>(9.04 %) | 1637.77 ± 130.66<br>(4.51 %) | 34.08 ± 0.51<br>(3.84 %) | 5.6 ± 0.2<br>(21.58 %) |
| Organic bound | 294 ± 6.25 | 852 ± 15 | 2813 ± 86.51<br>(3.2 %) | 111.5 ± 16.35<br>(13.99 %) | 1755.5 ± 11.20<br>(4.84 %) | 35 ± 0.30<br>(3.94 %) | 1.9 ± 0.05<br>(7.33 %) |
| Residual | 1730 ± 92 | 4245 ± 196.25 | 82215 ± 100<br>(93.3 %) | 295.26 ± 61.47<br>(37.05 %) | 32081 ± 181.41<br>(88.43 %) | 752.56 ± 12.56<br>(84.7 %) | 8.95 ± 0.2<br>(34.46 %) |
| Total extracted | NA[b] | NA[b] | 88097.67 | 796.86 | 36278.95 | 888.15 | 25.95 |

[a] Below detection limit

[b] Not available

# Appendix 3B: Effects of pH on the release of U, Fe and Si with time and correlation of U with Fe and Si.

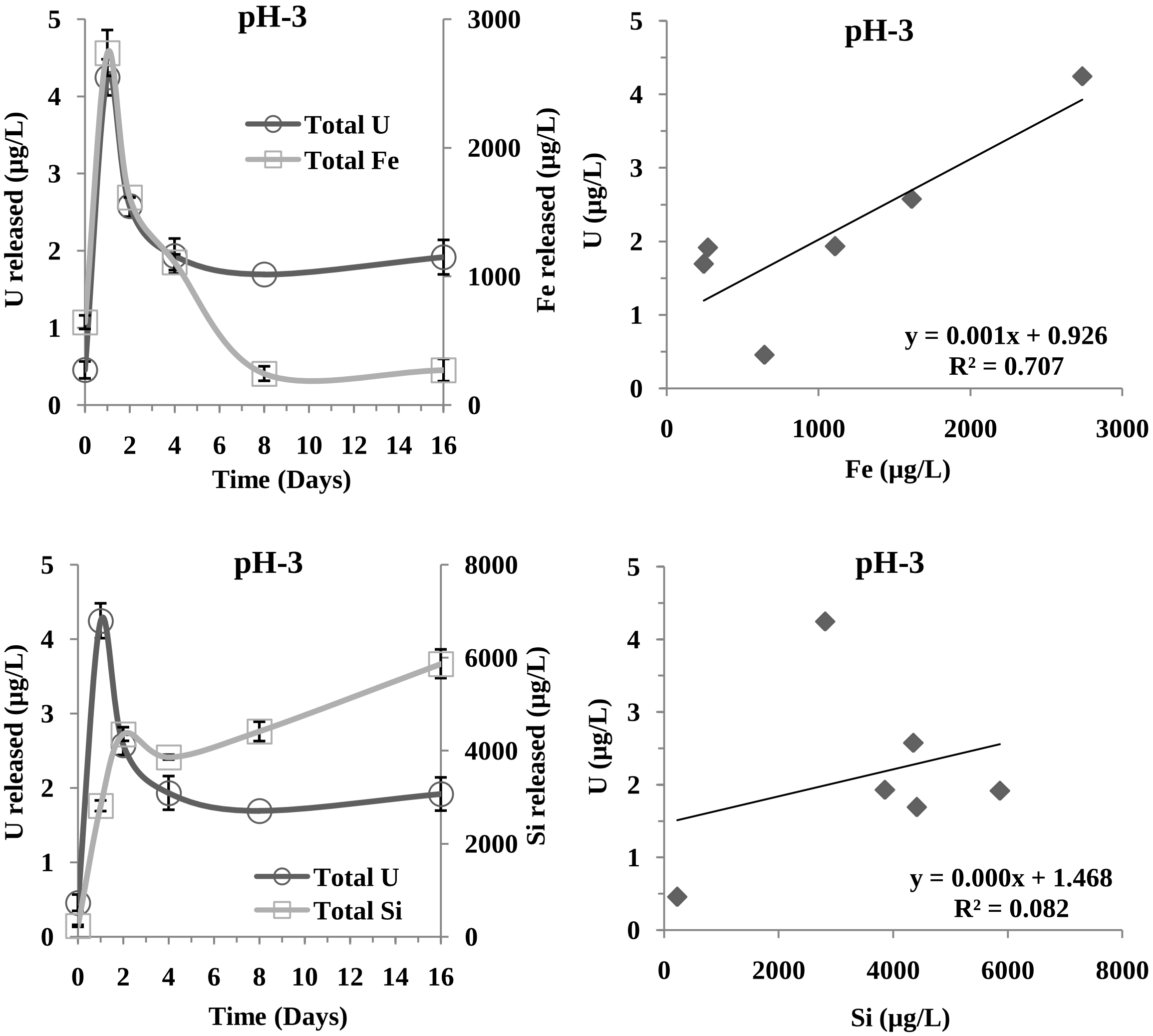


Figure 3B.1: Effects of pH on the release of U, Fe and Si with time and correlation of U with Fe and Si at pH = 3.

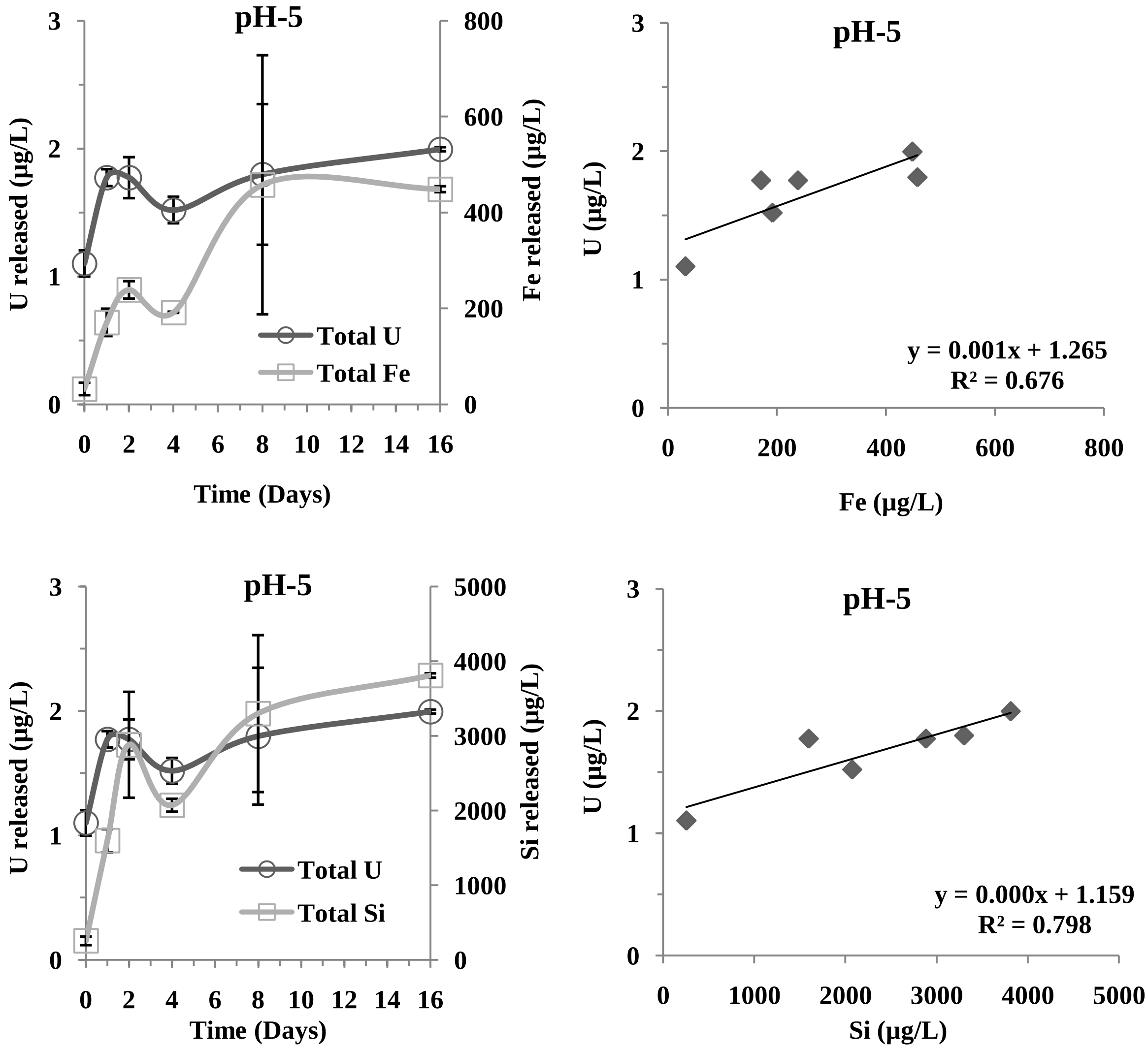


Figure 3B.2: Effects of pH on the release of U, Fe and Si with time and correlation of U with Fe and Si at pH = 5.

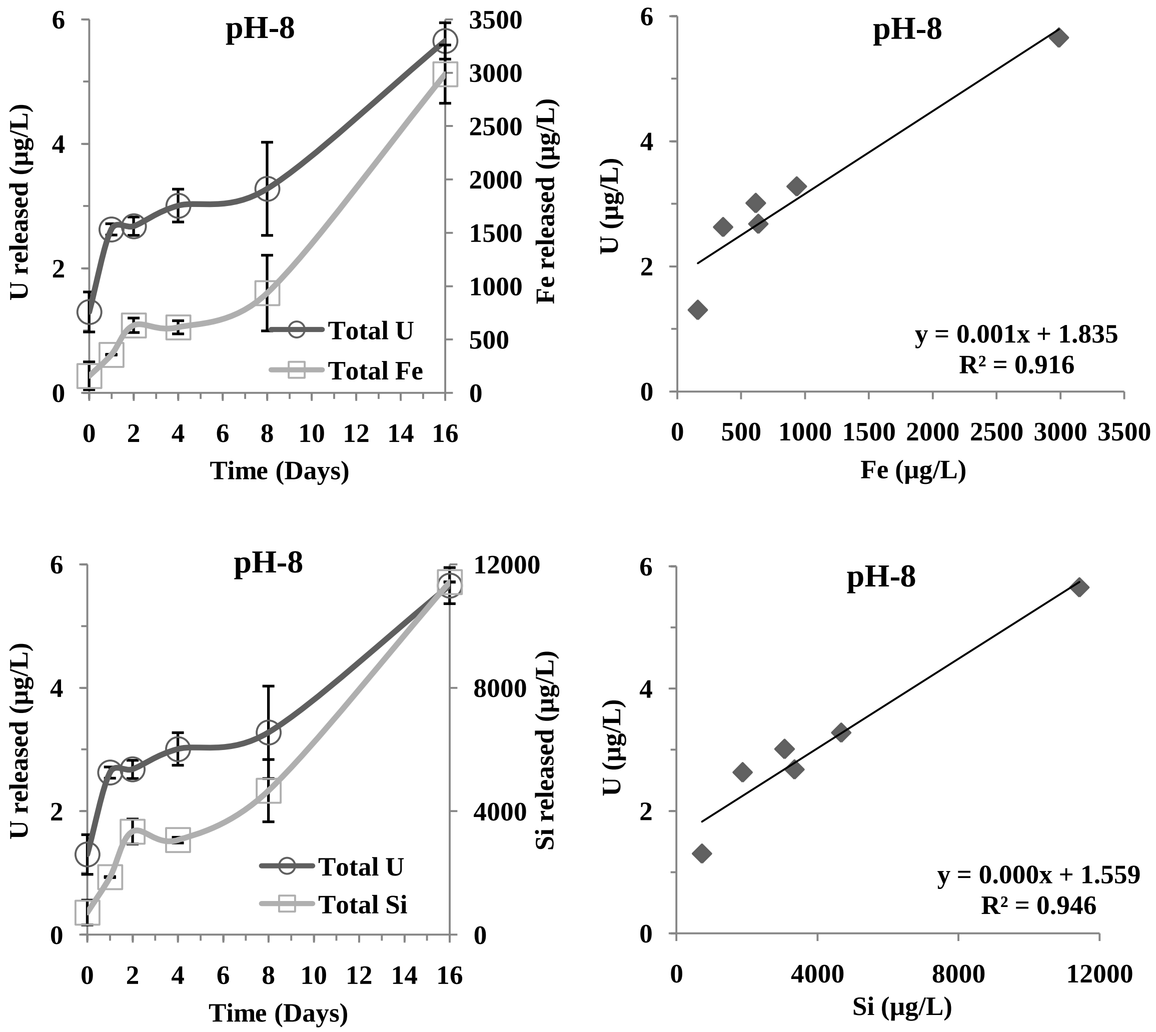


Figure 3B.3: Effects of pH on the release of U, Fe and Si with time and correlation of U with Fe and Si at pH = 8.

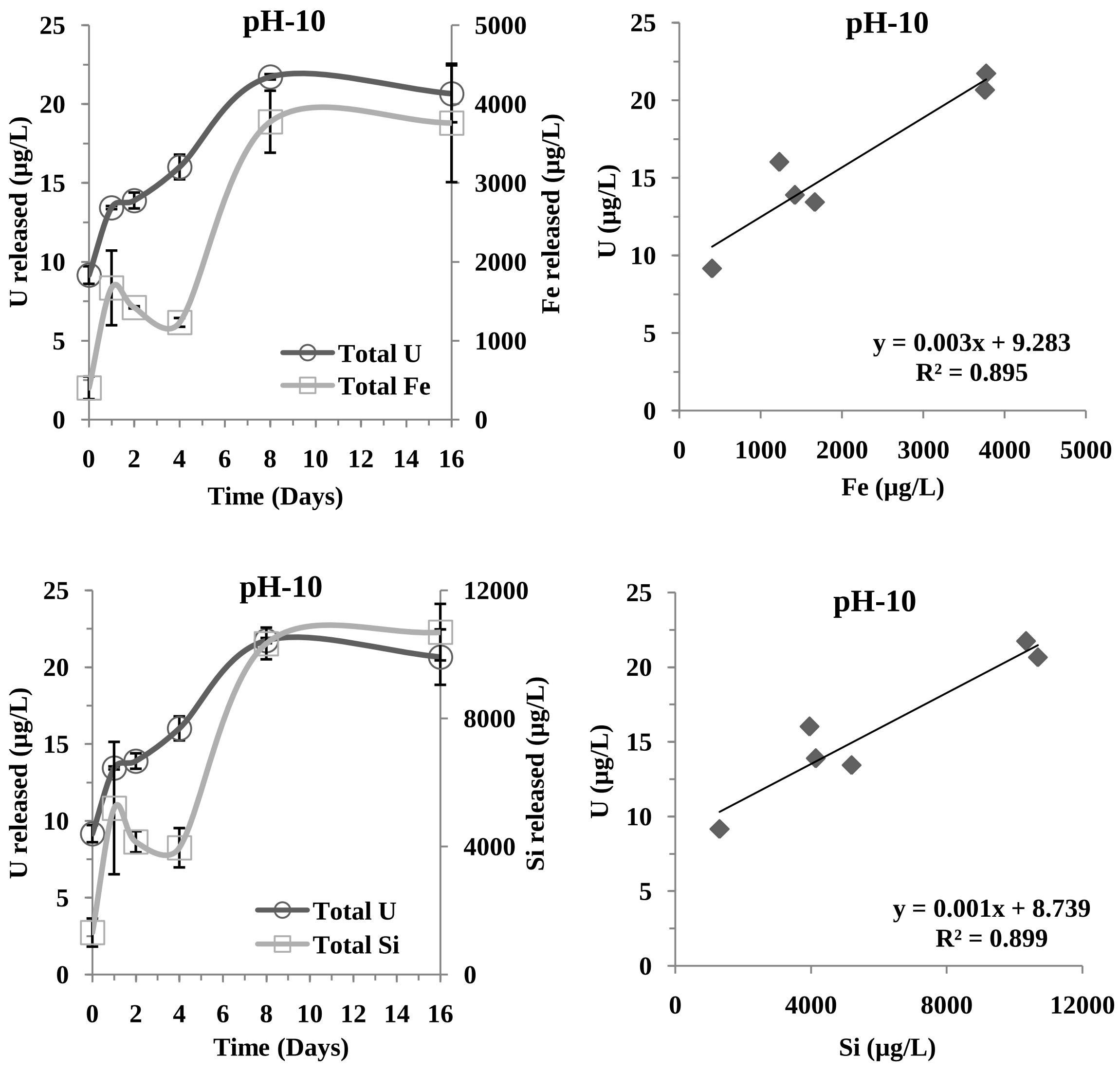
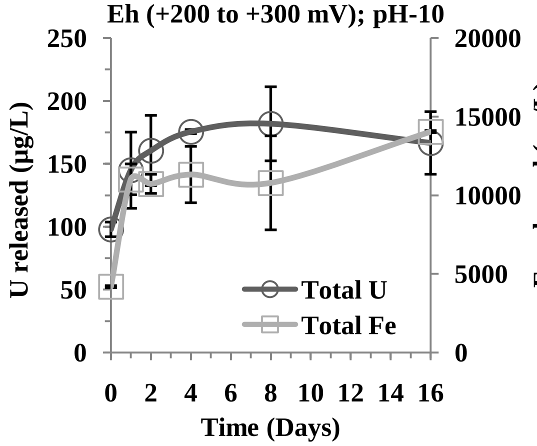
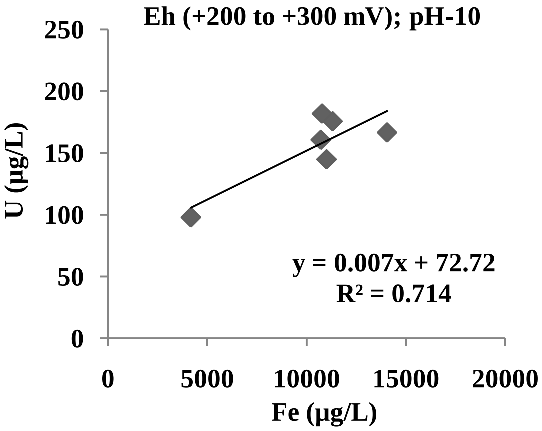
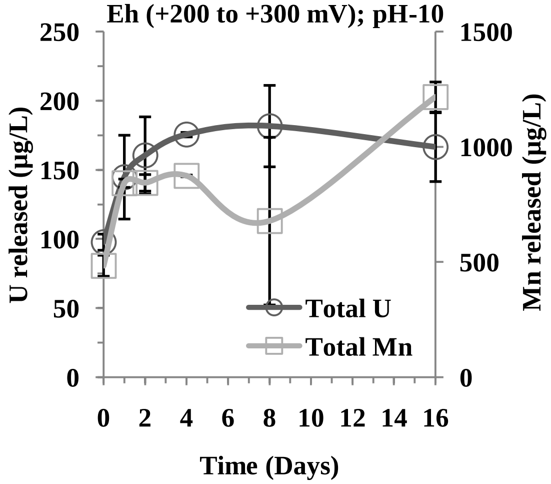


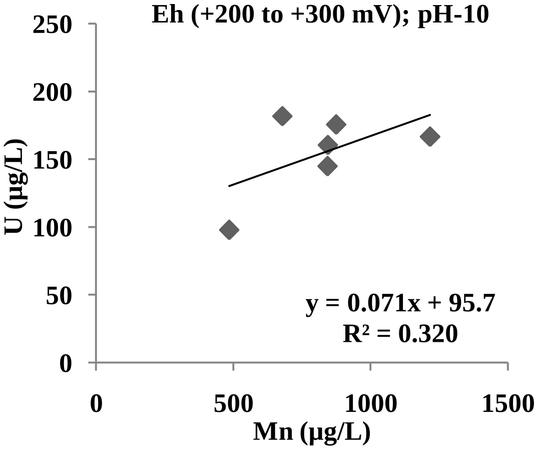
Figure 3B.4: Effects of pH on the release of U, Fe and Si with time and correlation of U with Fe and Si at pH = 10.

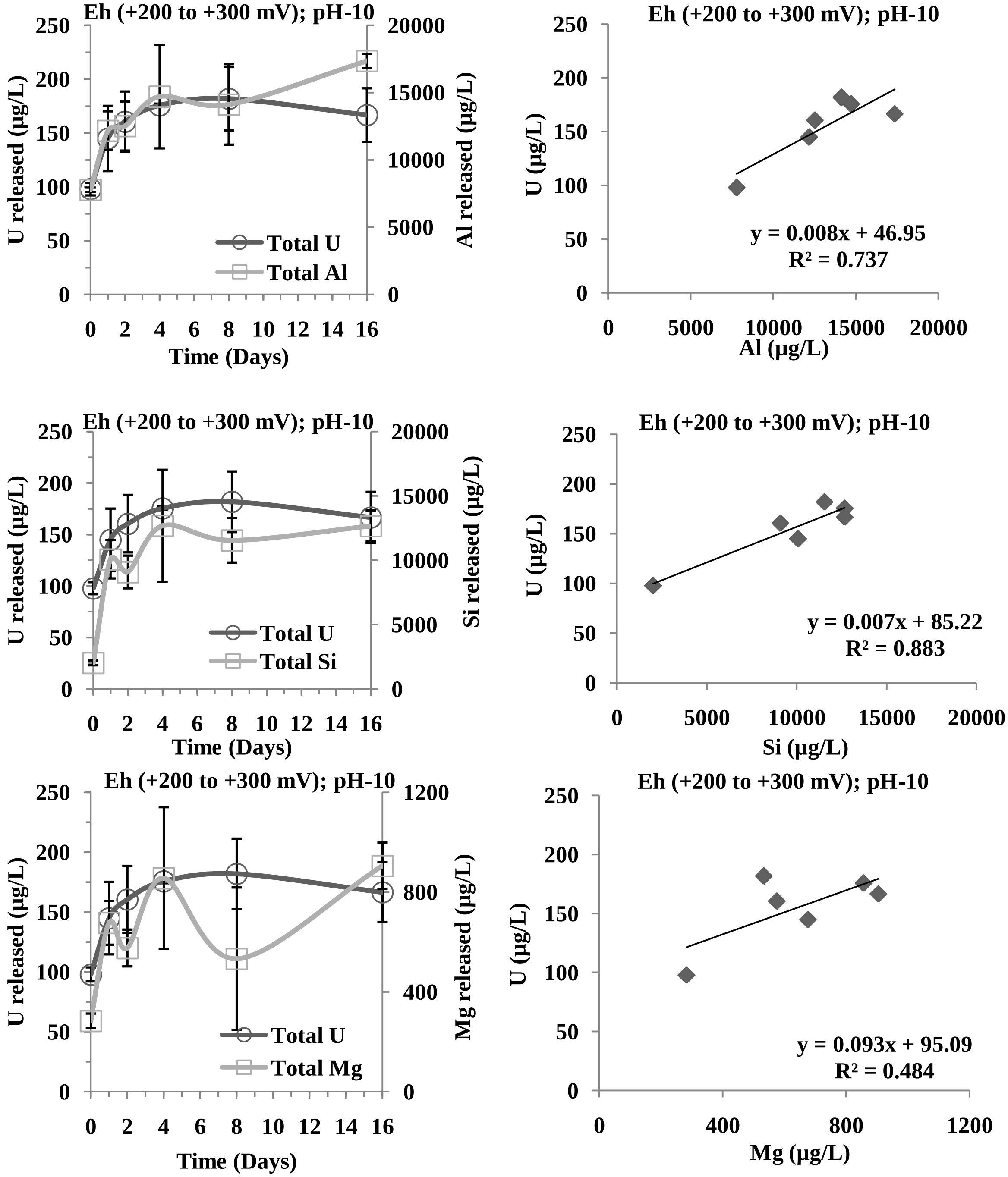
# Appendix 3C: Effects of Eh on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca.





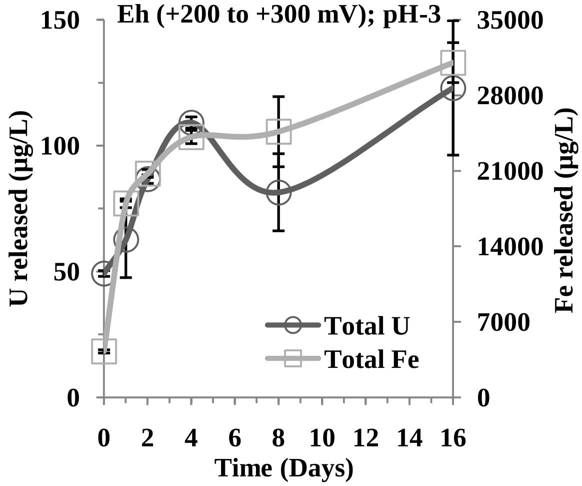


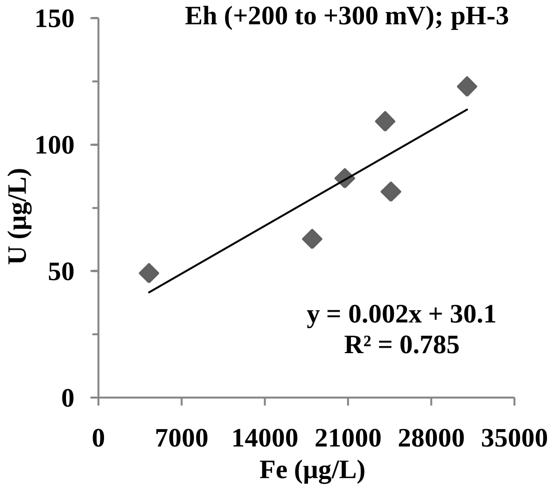


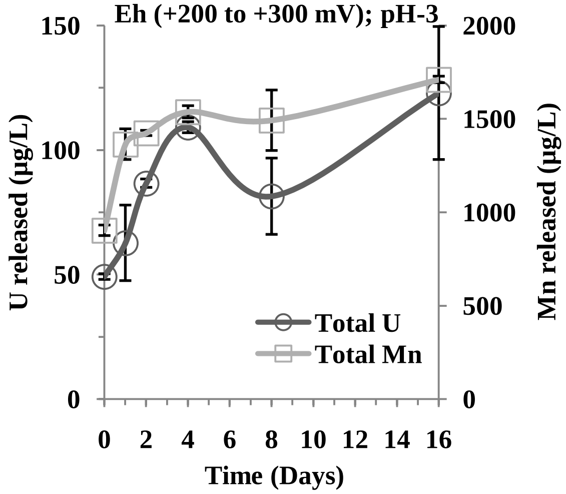


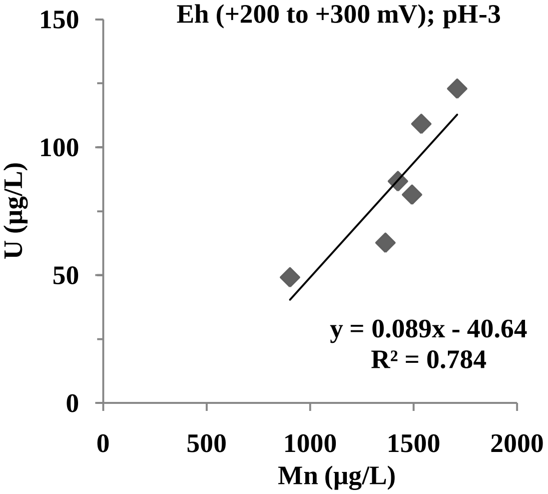
*Release of Ca was below detection limit of 126 µg $L^{-1}$ at pH 10

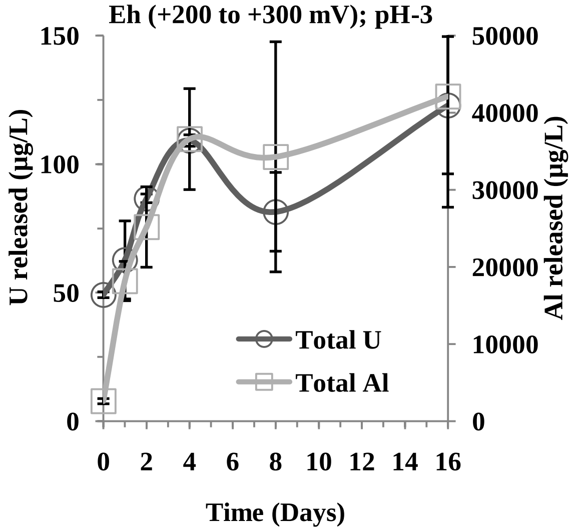
Figure 3C.1: Effects of Eh (+200 to +300 mV) on the release of U, Fe, Mn, Al, Si and Mg with time and correlation of U with Fe, Mn, Al, Si and Mg at pH = 10.

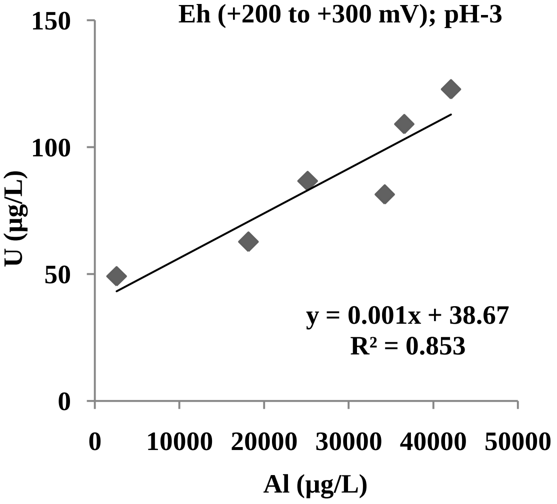

Eh (+200 to +300 mV); pH-3
U released (µg/L)
Fe released (µg/L)
Time (Days)
150
100
50
0
35000
28000
21000
14000
7000
0
0 2 4 6 8 10 12 14 16
Total U
Total Fe


Eh (+200 to +300 mV); pH-3
U (µg/L)
Fe (µg/L)
150
100
50
0
0 7000 14000 21000 28000 35000
y = 0.002x + 30.1
R² = 0.785


Eh (+200 to +300 mV); pH-3
U released (µg/L)
Mn released (µg/L)
Time (Days)
150
100
50
0
2000
1500
1000
500
0
0 2 4 6 8 10 12 14 16
Total U
Total Mn


Eh (+200 to +300 mV); pH-3
U (µg/L)
Mn (µg/L)
150
100
50
0
0 500 1000 1500 2000
y = 0.089x - 40.64
R² = 0.784


Eh (+200 to +300 mV); pH-3
U released (µg/L)
Al released (µg/L)
Time (Days)
150
100
50
0
50000
40000
30000
20000
10000
0
0 2 4 6 8 10 12 14 16
Total U
Total Al


Eh (+200 to +300 mV); pH-3
U (µg/L)
Al (µg/L)
150
100
50
0
0 10000 20000 30000 40000 50000
y = 0.001x + 38.67
R² = 0.853

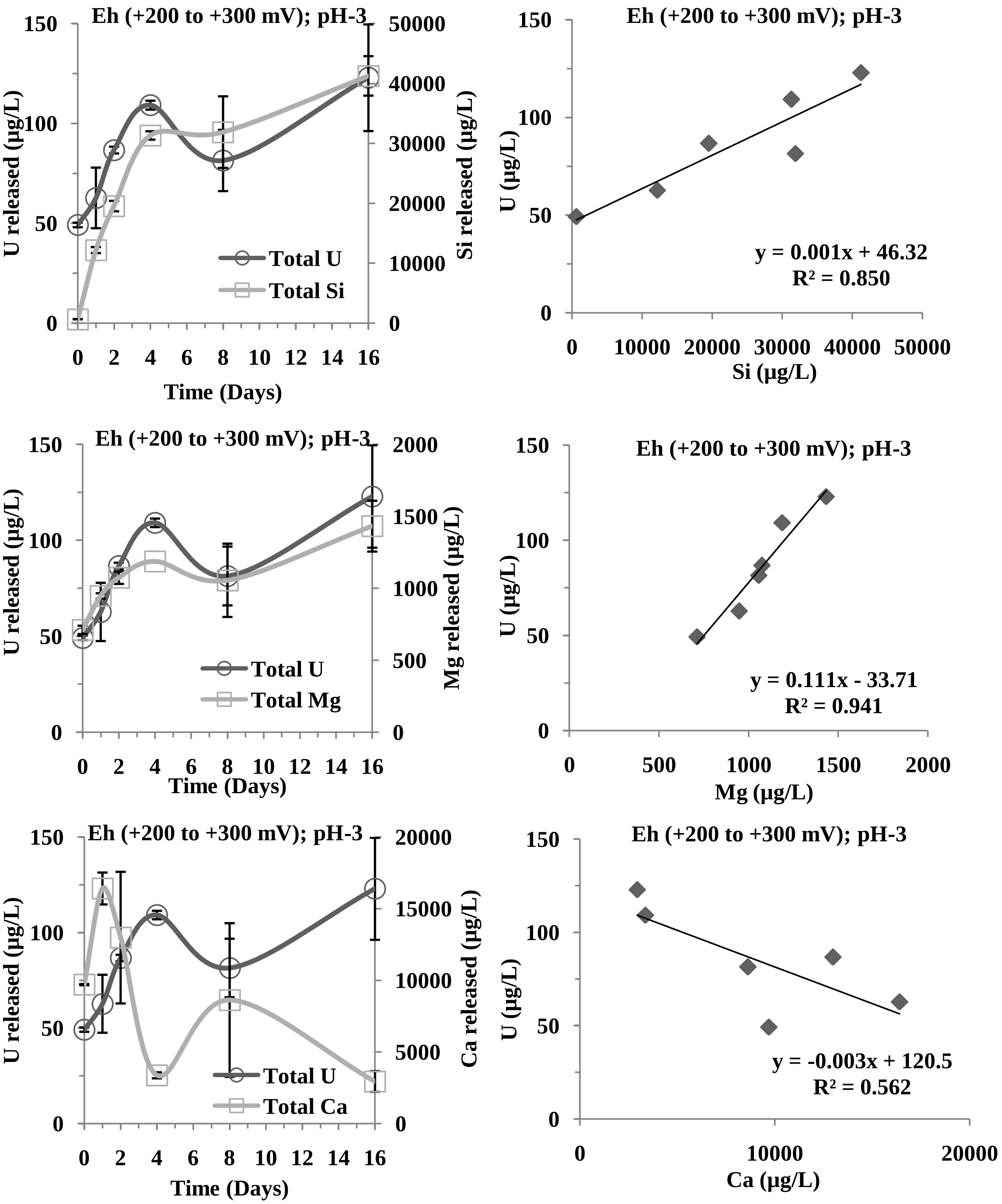
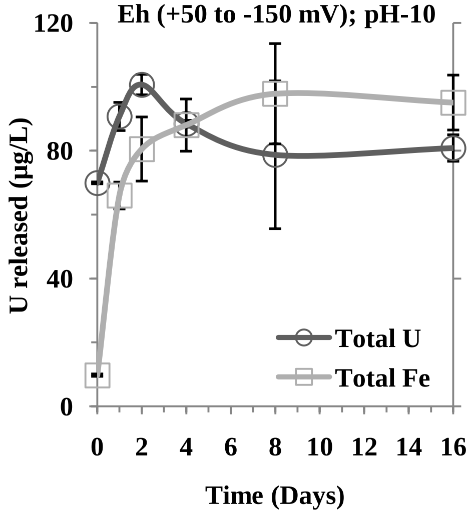
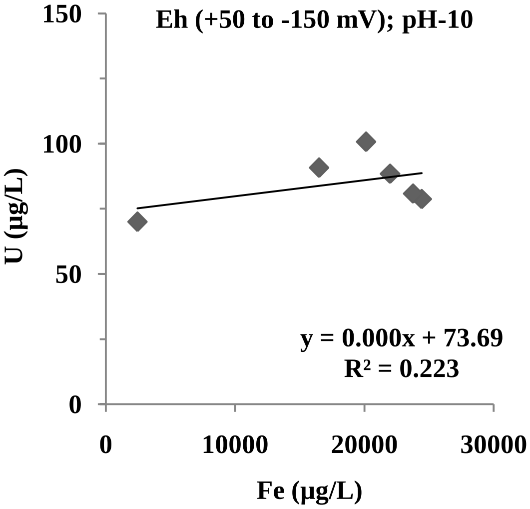
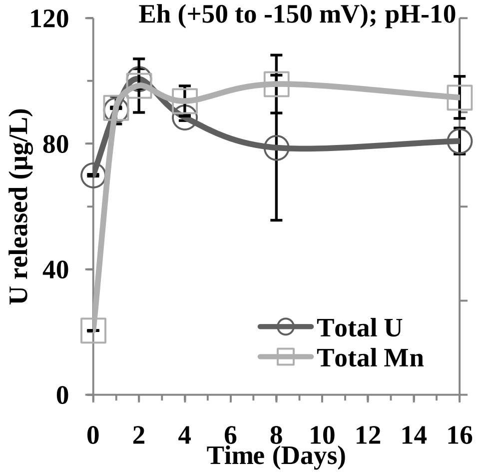
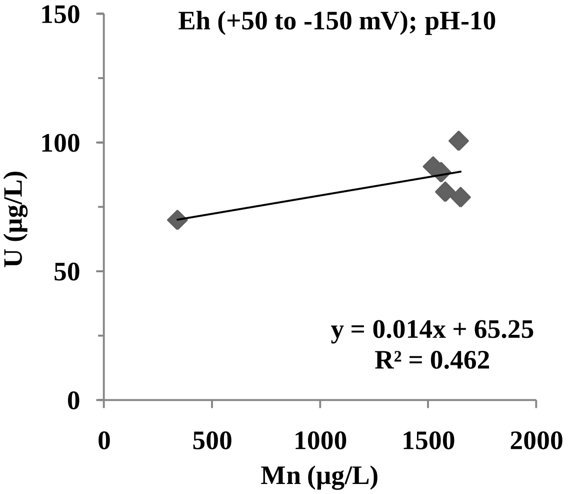


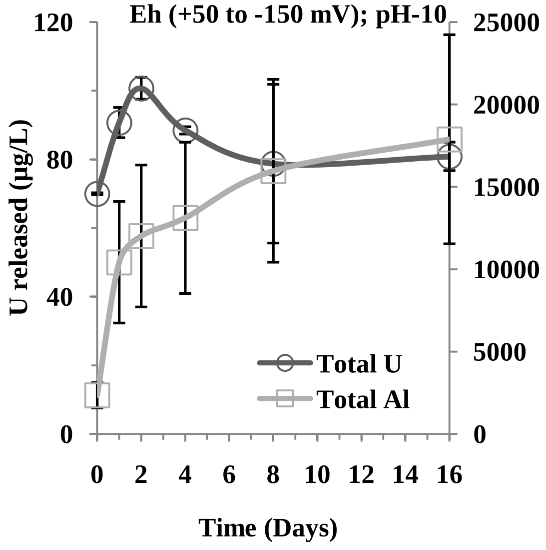
Figure 3C.2: Effects of Eh (+200 to +300 mV) on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca at pH = 3.

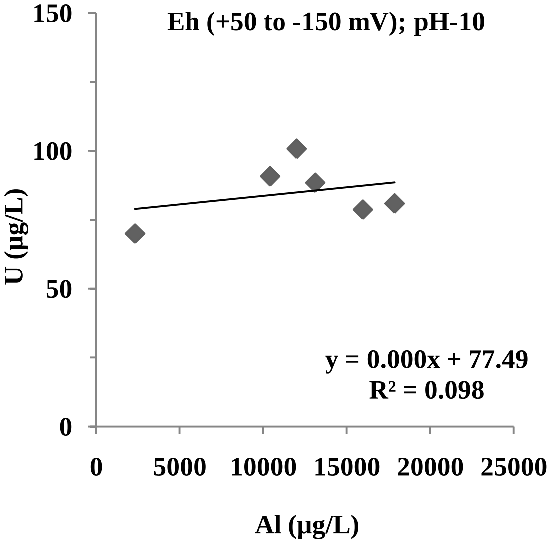

Eh (+50 to -150 mV); pH-10
U released (µg/L)
Fe released (µg/L)
Time (Days)
Total U
Total Fe
0
40
80
120
0
10000
20000
30000
0 2 4 6 8 10 12 14 16


Eh (+50 to -150 mV); pH-10
U (µg/L)
Fe (µg/L)
y = 0.000x + 73.69
R² = 0.223
0
50
100
150
0 10000 20000 30000


Eh (+50 to -150 mV); pH-10
U released (µg/L)
Mn released (µg/L)
Time (Days)
Total U
Total Mn
0
40
80
120
0
500
1000
1500
2000
0 2 4 6 8 10 12 14 16


Eh (+50 to -150 mV); pH-10
U (µg/L)
Mn (µg/L)
y = 0.014x + 65.25
R² = 0.462
0
50
100
150
0 500 1000 1500 2000


Eh (+50 to -150 mV); pH-10
U released (µg/L)
Al released (µg/L)
Time (Days)
Total U
Total Al
0
40
80
120
0
5000
10000
15000
20000
25000
0 2 4 6 8 10 12 14 16


Eh (+50 to -150 mV); pH-10
U (µg/L)
Al (µg/L)
y = 0.000x + 77.49
R² = 0.098
0
50
100
150
0 5000 10000 15000 20000 25000

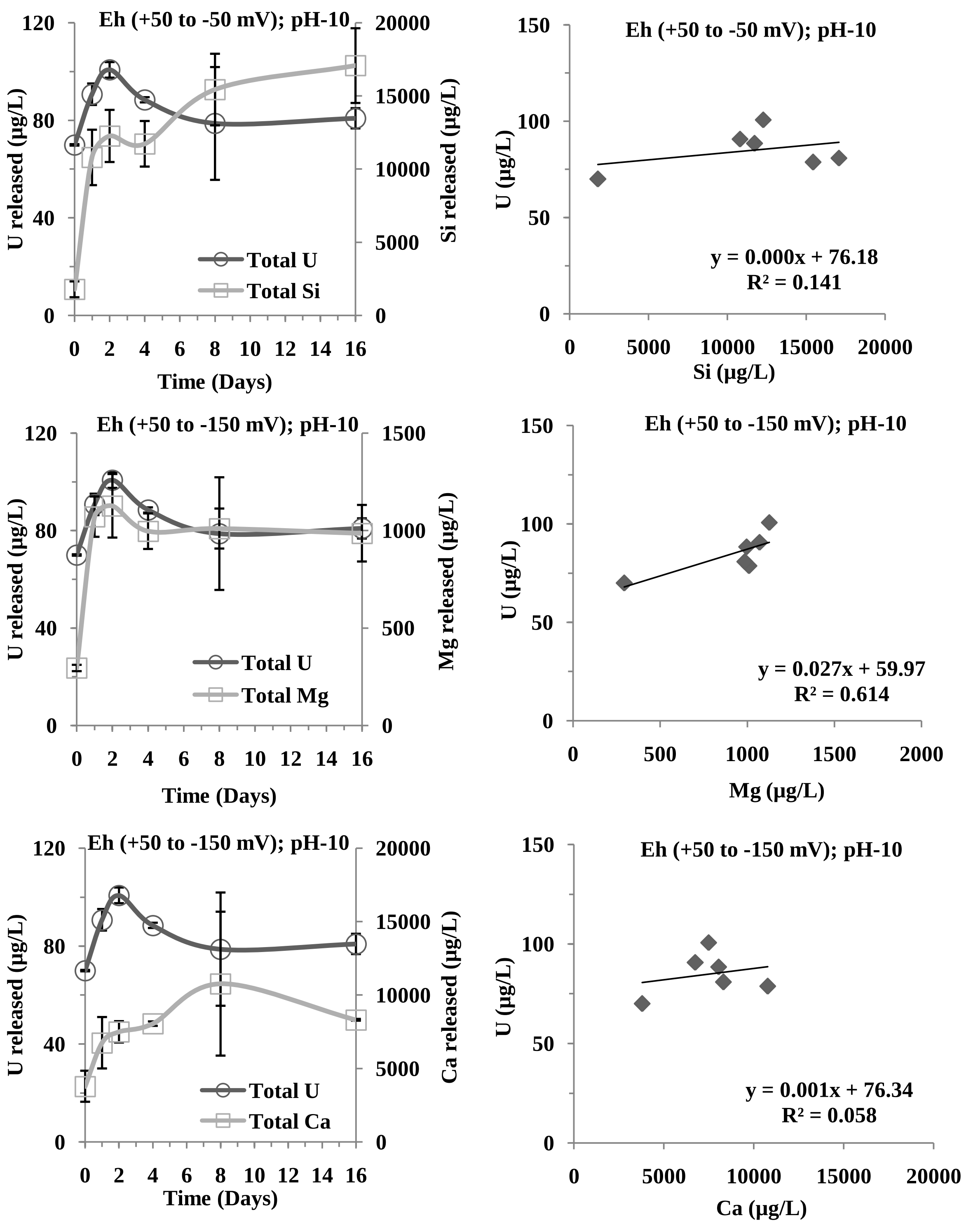
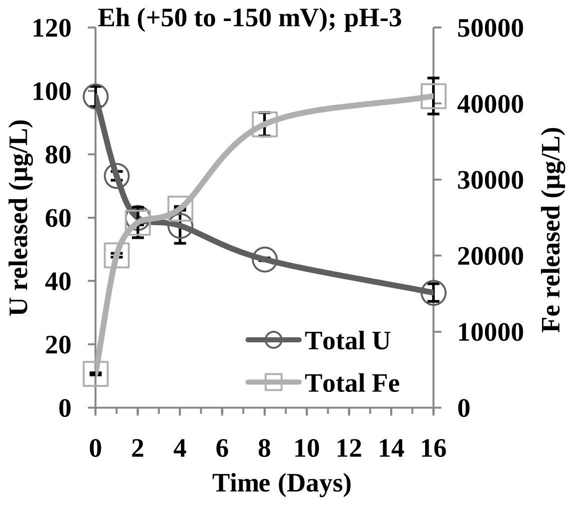
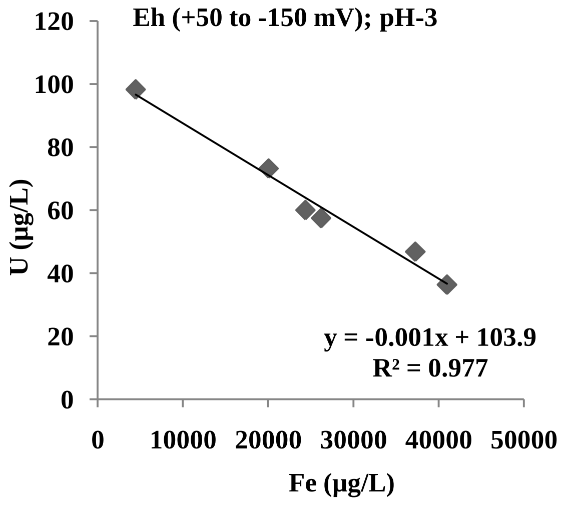
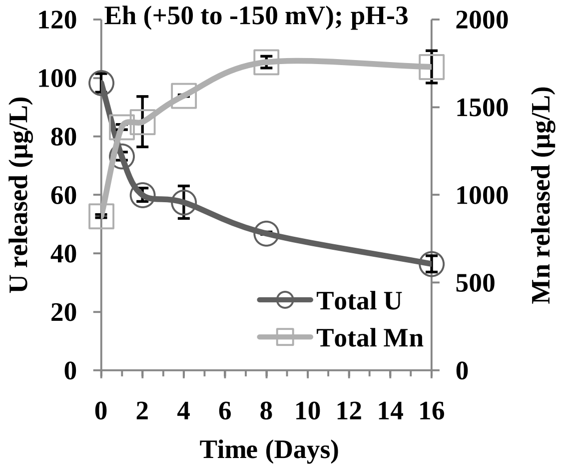
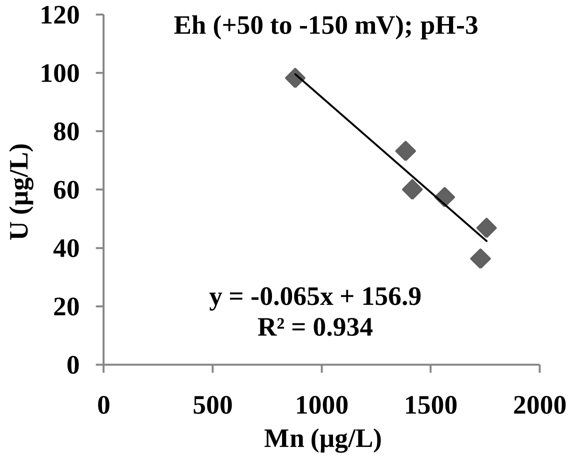


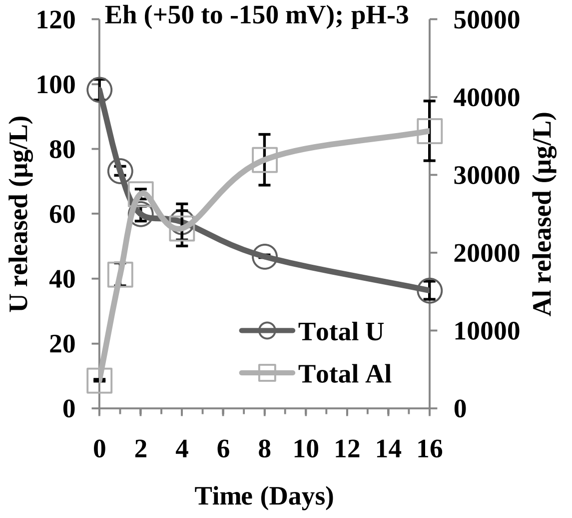
Figure 3C.3: Effects of Eh (+50 to -150 mV) on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca at pH = 10.

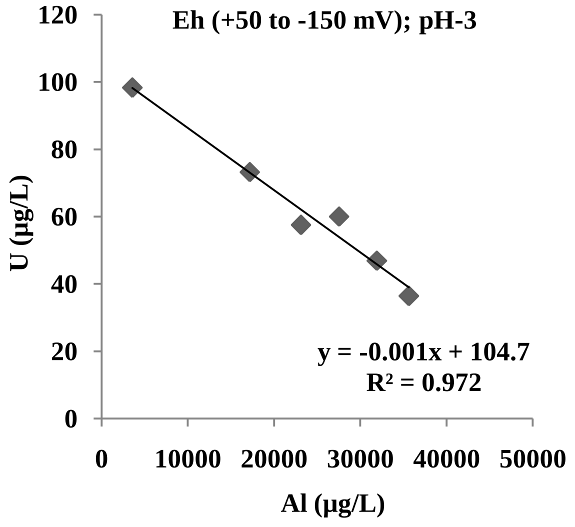

Eh (+50 to -150 mV); pH-3
U released (µg/L)
Fe released (µg/L)
Time (Days)
Total U
Total Fe
0
20
40
60
80
100
120
0
10000
20000
30000
40000
50000
0
2
4
6
8
10
12
14
16


Eh (+50 to -150 mV); pH-3
U (µg/L)
Fe (µg/L)
y = -0.001x + 103.9
R² = 0.977
0
20
40
60
80
100
120
0
10000
20000
30000
40000
50000


Eh (+50 to -150 mV); pH-3
U released (µg/L)
Mn released (µg/L)
Time (Days)
Total U
Total Mn
0
20
40
60
80
100
120
0
500
1000
1500
2000
0
2
4
6
8
10
12
14
16


Eh (+50 to -150 mV); pH-3
U (µg/L)
Mn (µg/L)
y = -0.065x + 156.9
R² = 0.934
0
20
40
60
80
100
120
0
500
1000
1500
2000


Eh (+50 to -150 mV); pH-3
U released (µg/L)
Al released (µg/L)
Time (Days)
Total U
Total Al
0
20
40
60
80
100
120
0
10000
20000
30000
40000
50000
0
2
4
6
8
10
12
14
16


Eh (+50 to -150 mV); pH-3
U (µg/L)
Al (µg/L)
y = -0.001x + 104.7
R² = 0.972
0
20
40
60
80
100
120
0
10000
20000
30000
40000
50000

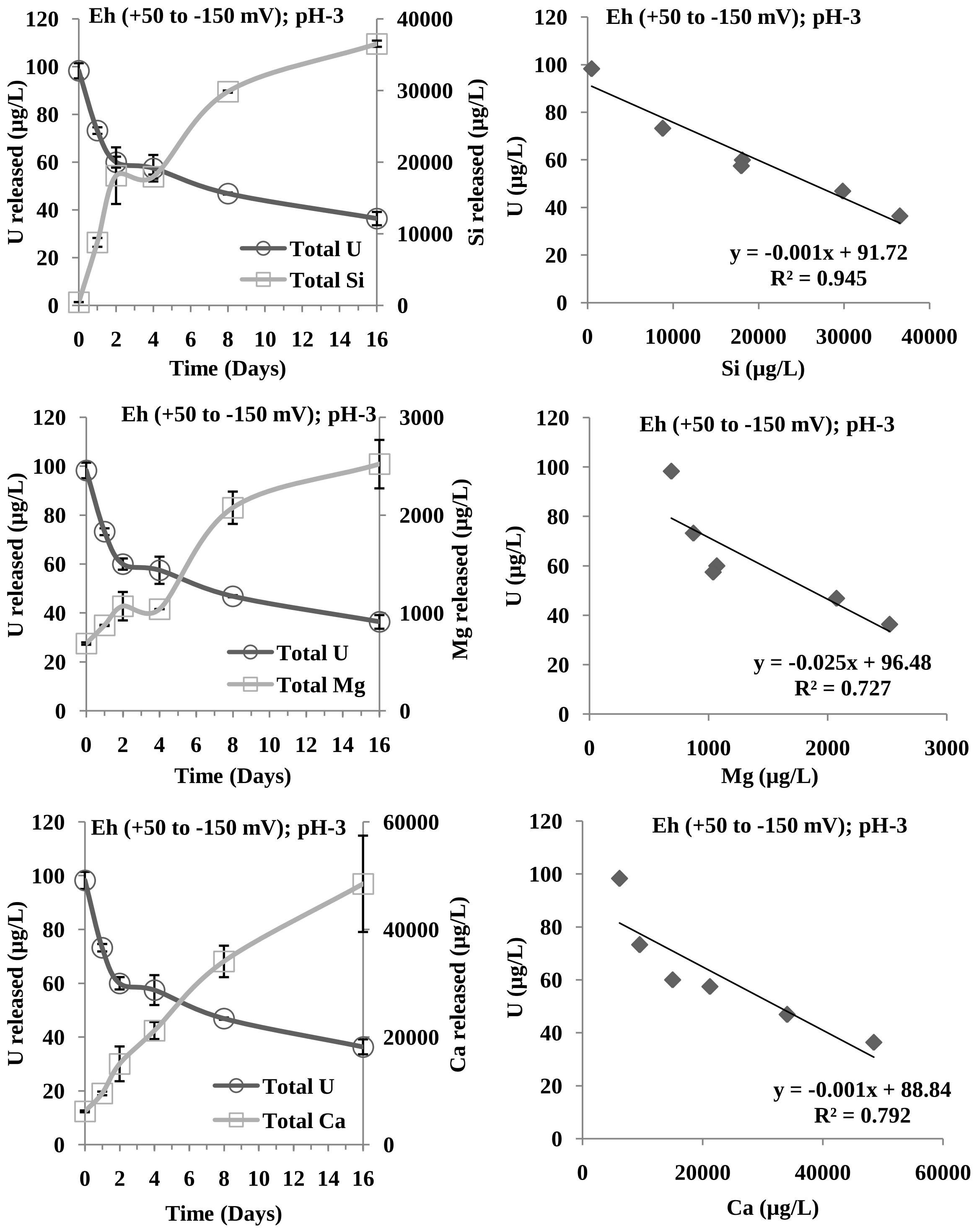
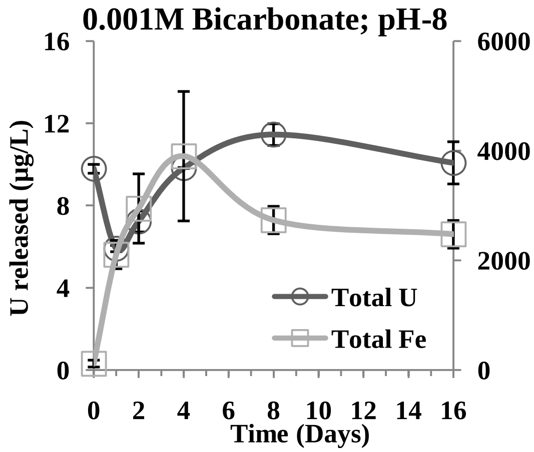
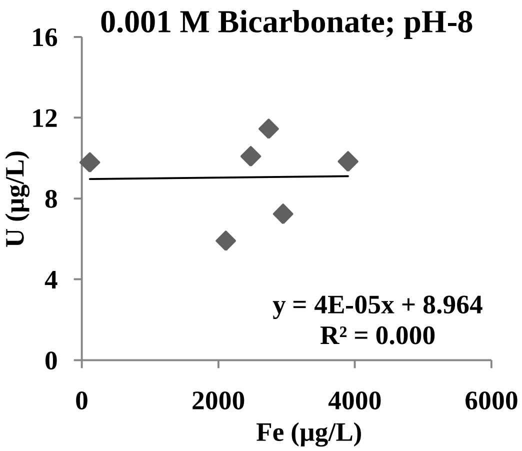
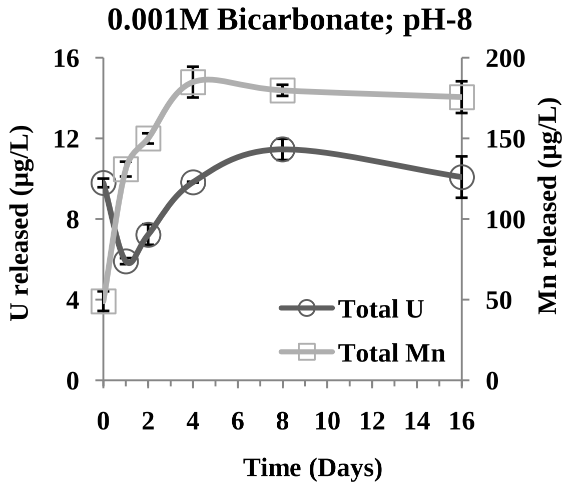


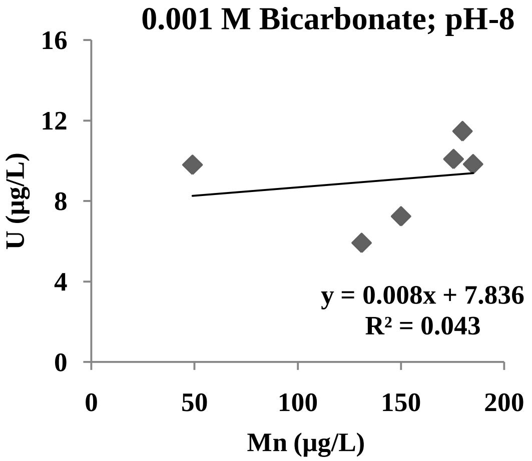
Figure 3C.4: Effects of Eh (+50 to -150 mV) on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca at pH = 3.

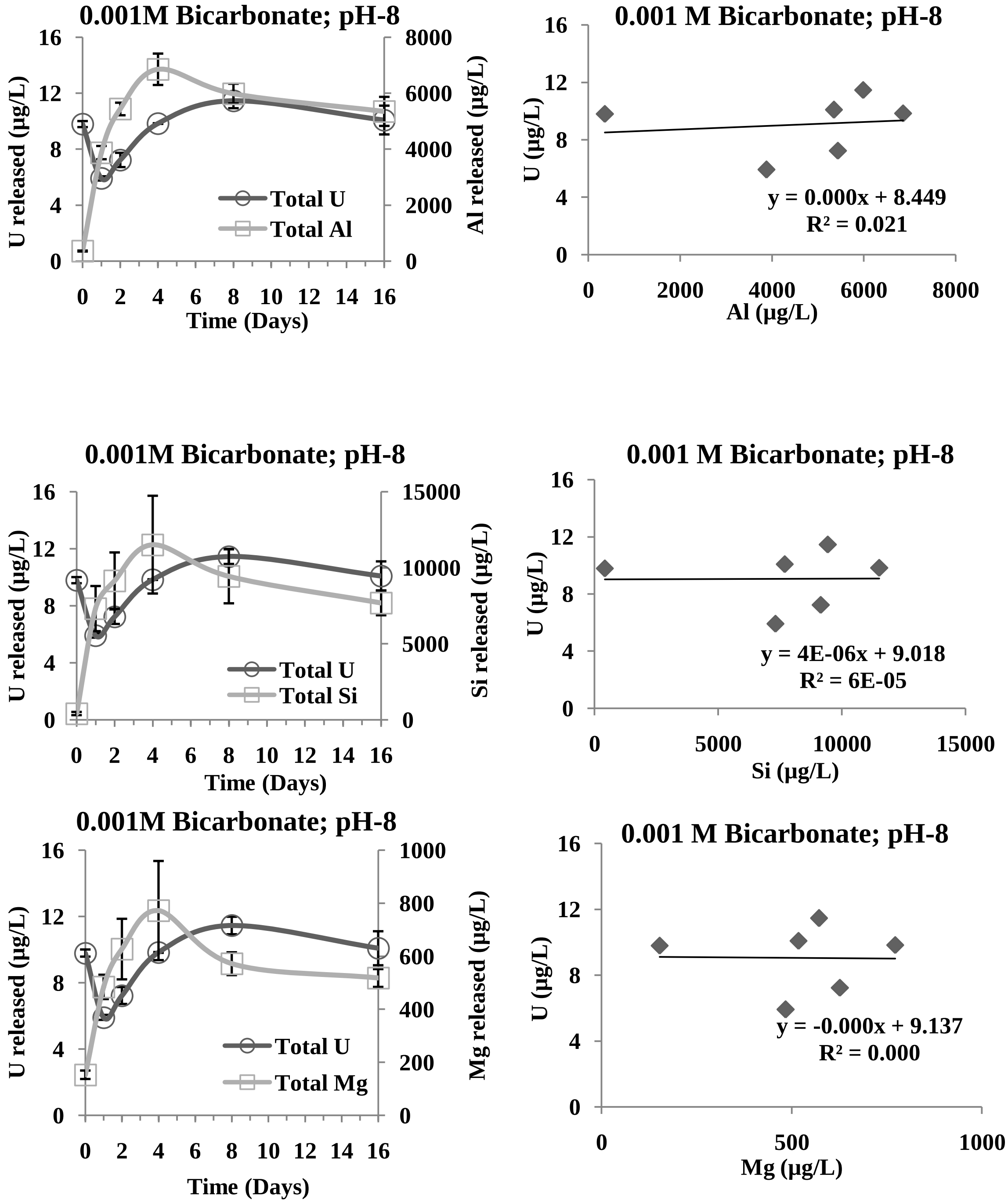
## Appendix 3D: Effects of bicarbonate on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca.





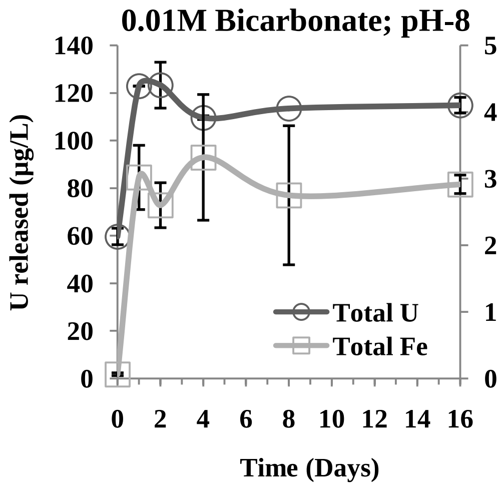


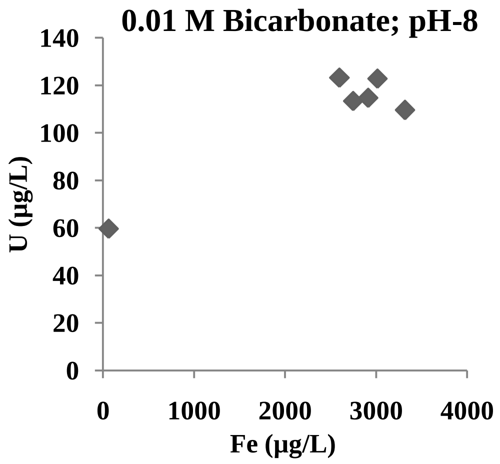


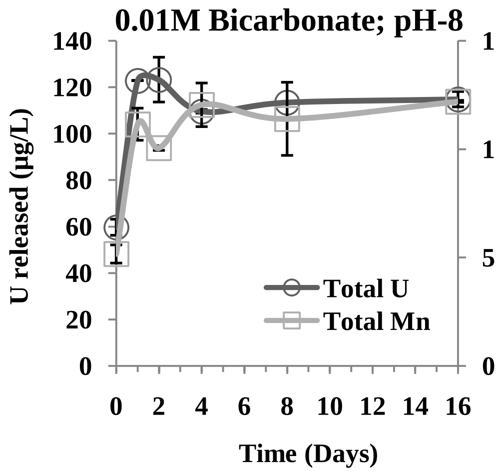


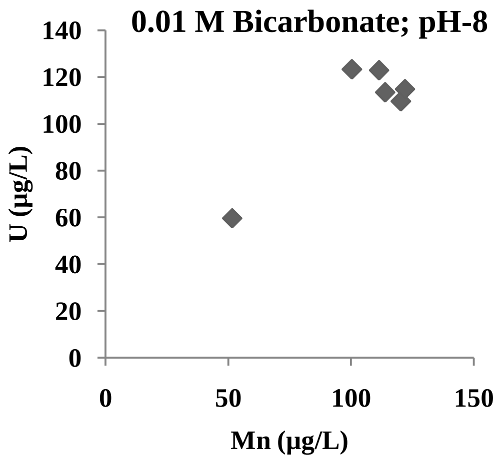
*Release of Ca was below detection limit of 134 µg $L^{-1}$ at pH 8

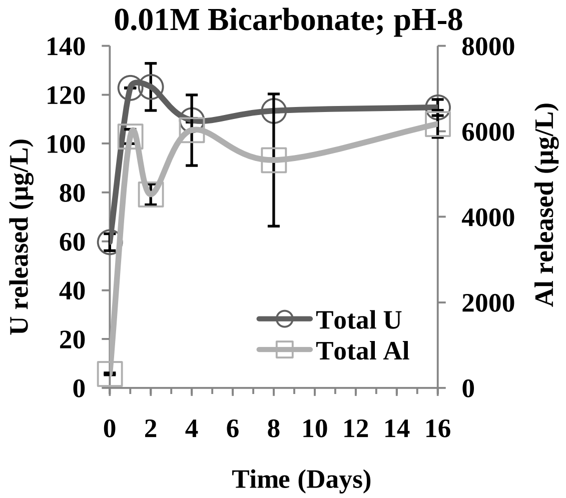
Figure 3D.1: Effects of 0.001M bicarbonate on the release of U, Fe, Mn, Al, Si and Mg with time and correlation of U with Fe, Mn, Al, Si and Mg at pH = 8.

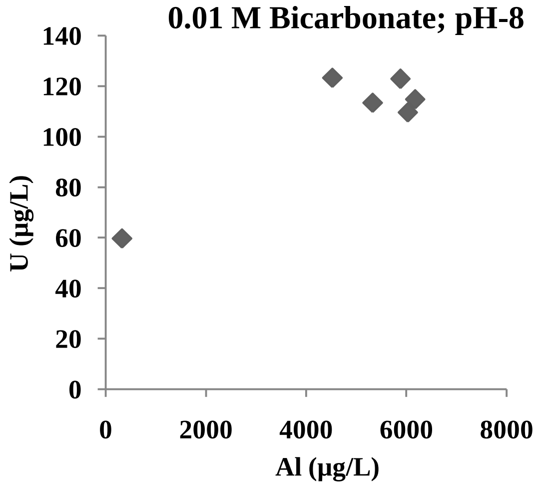

0.01M Bicarbonate; pH-8

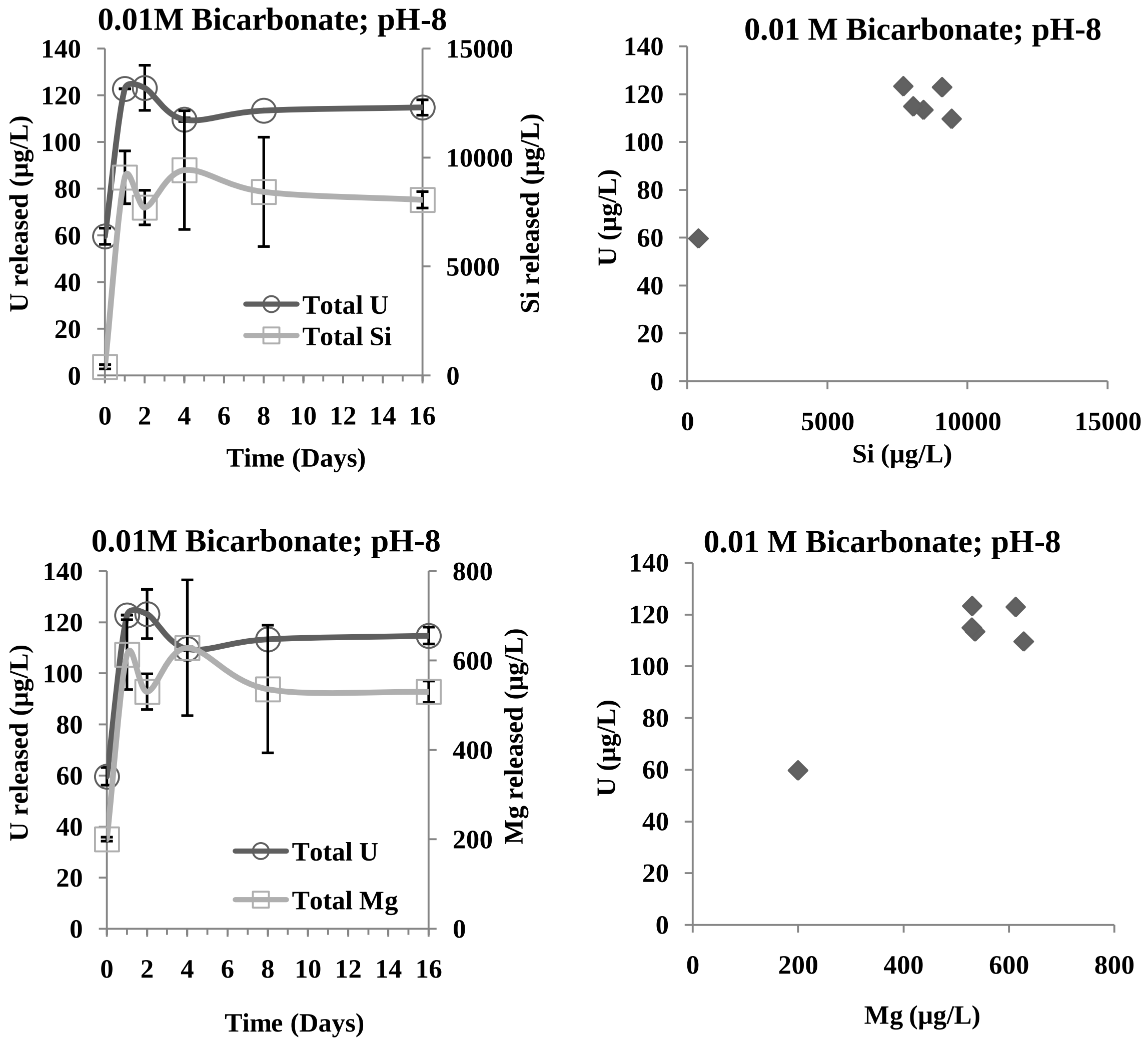

0.01 M Bicarbonate; pH-8


0.01M Bicarbonate; pH-8


0.01 M Bicarbonate; pH-8


0.01M Bicarbonate; pH-8

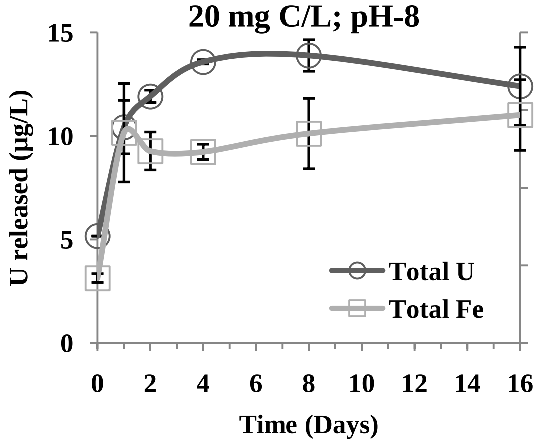

0.01 M Bicarbonate; pH-8

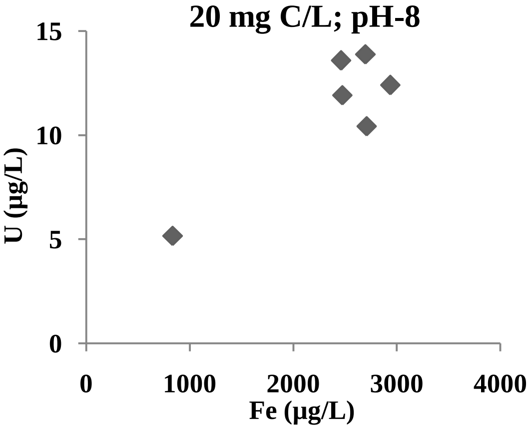


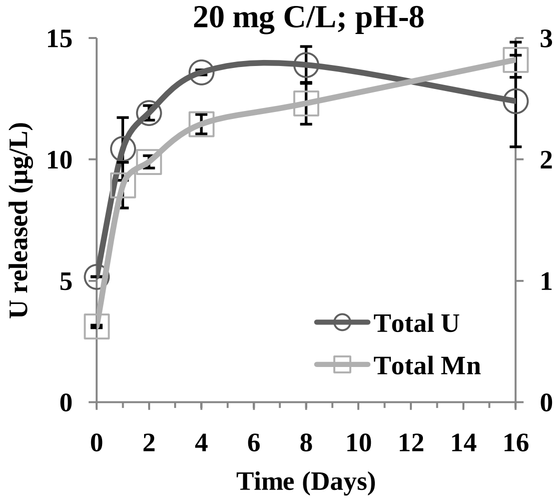
*Release of Ca was below detection limit of 134 µg $L^{-1}$ at pH 8

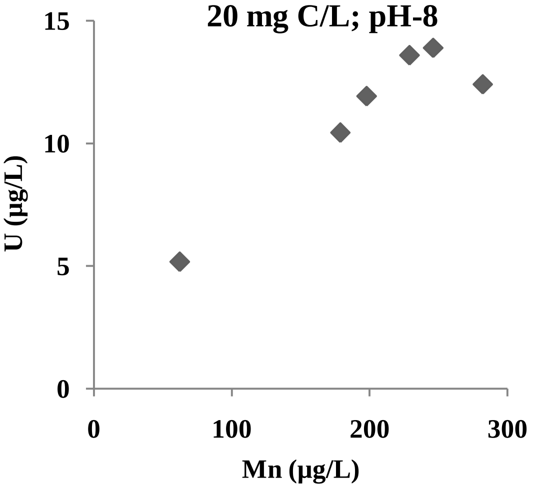
Figure 3D.2: Effects of 0.01M bicarbonate on the release of U, Fe, Mn, Al, Si and Mg with time and correlation of U with Fe, Mn, Al, Si and Mg at pH = 8.

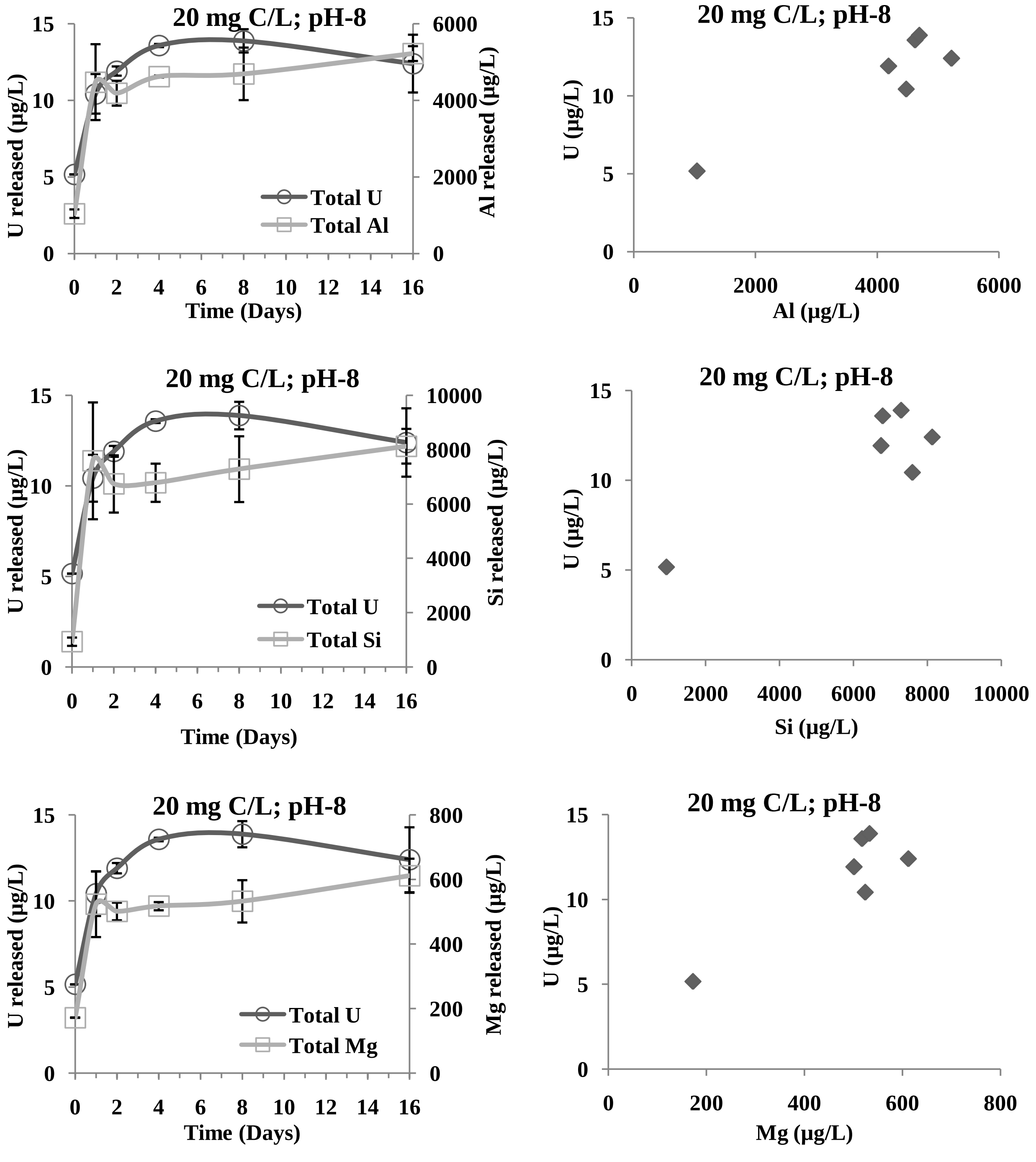
# Appendix 3E: Effects of NOM on the release of U, Fe, Mn, Al, Si, Mg and Ca with time and correlation of U with Fe, Mn, Al, Si, Mg and Ca.


20 mg C/L; pH-8


20 mg C/L; pH-8

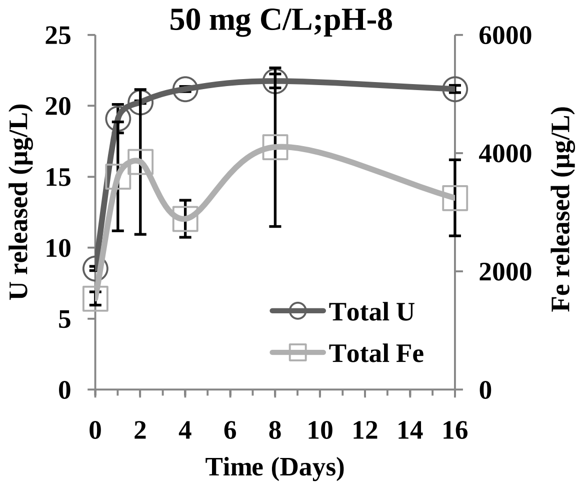

20 mg C/L; pH-8

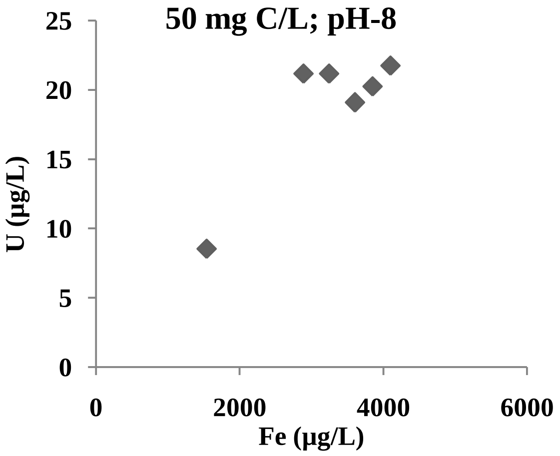

20 mg C/L; pH-8

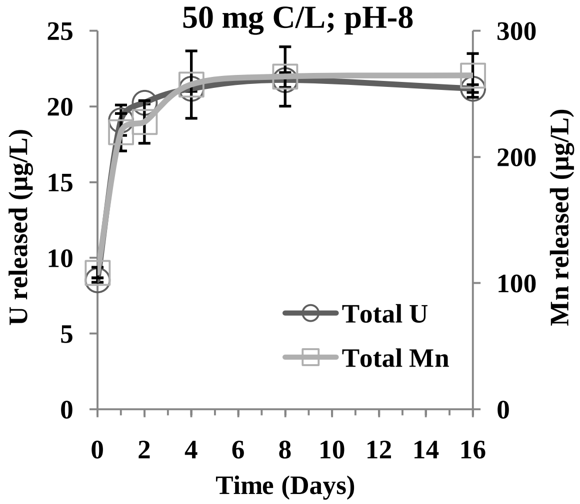


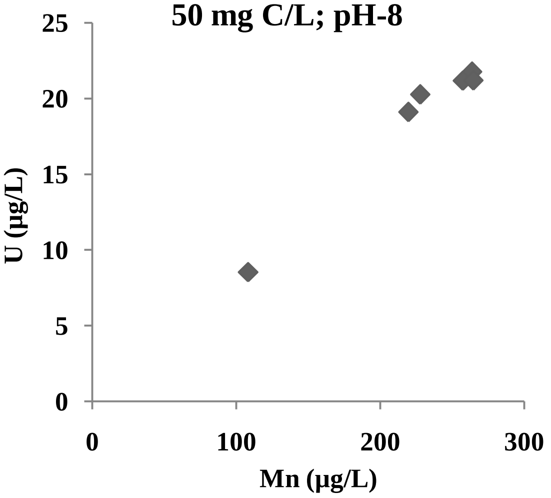
*Release of Ca was below detection limit of 134 µg L$^{-1}$ at pH 8

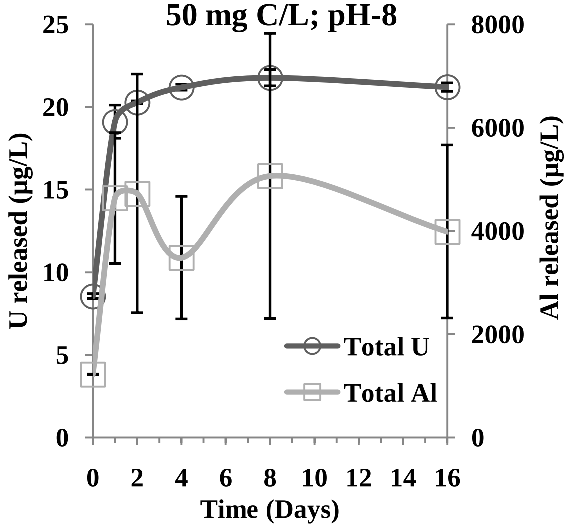
Figure 3E.1: Effects of 20 mg C/L on the release of U, Fe, Mn, Al, Si and Mg with time and correlation of U with Fe, Mn, Al, Si and Mg at pH = 8.

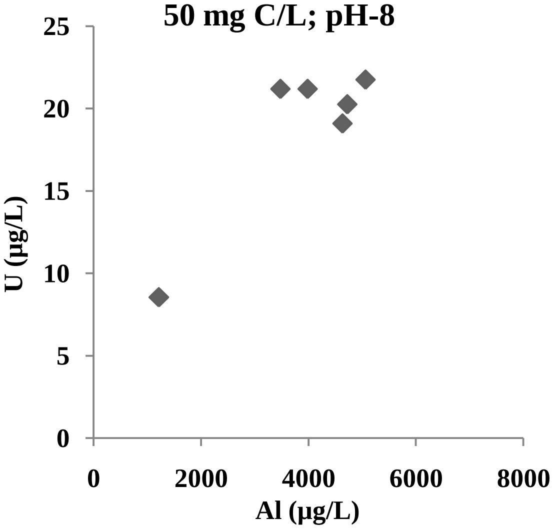

50 mg C/L;pH-8
U released (µg/L)
0
5
10
15
20
25
Fe released (µg/L)
0
2000
4000
6000
0 2 4 6 8 10 12 14 16
Time (Days)
Total U
Total Fe

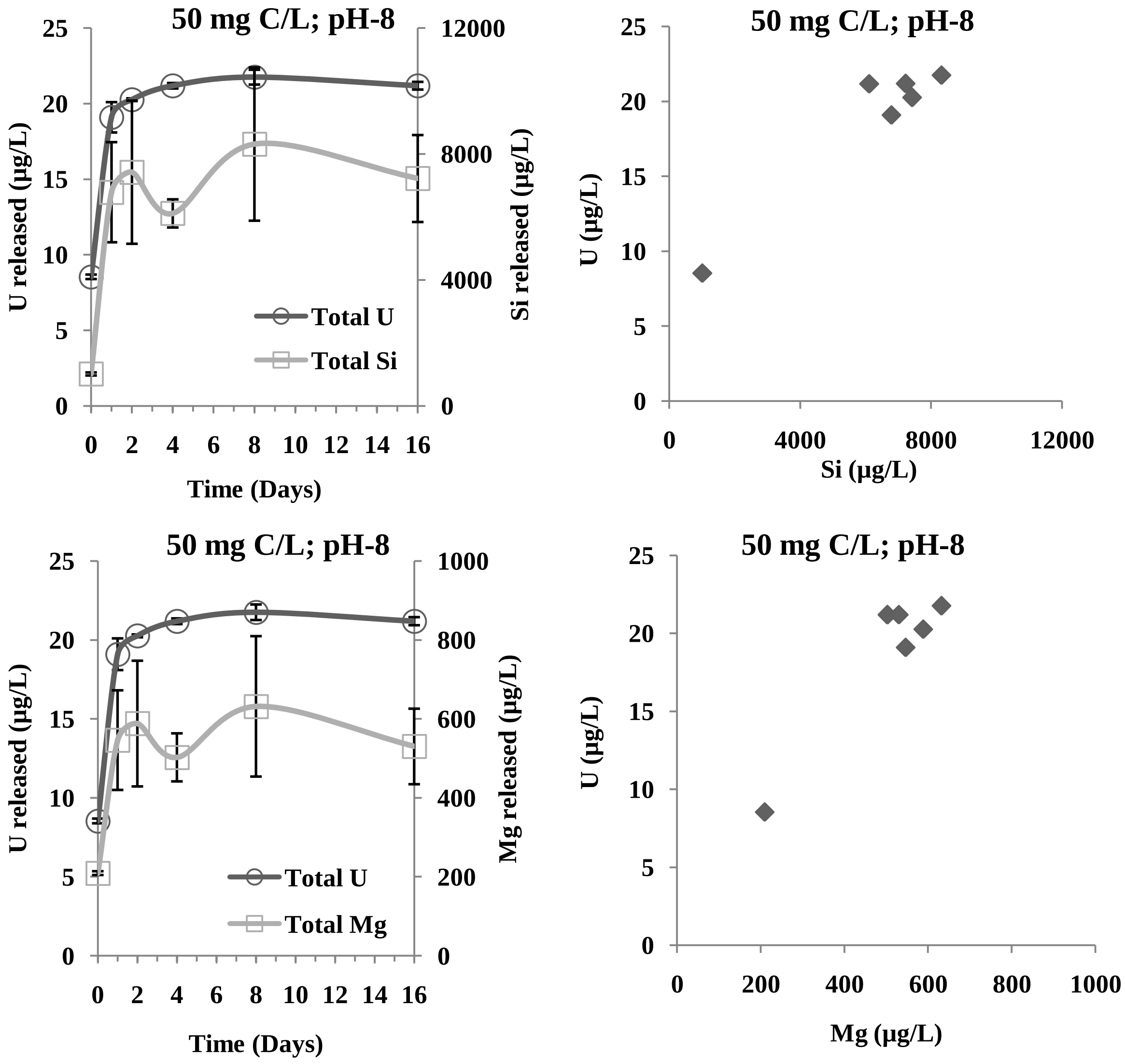

50 mg C/L; pH-8
U (µg/L)
0
5
10
15
20
25
0
2000
4000
6000
Fe (µg/L)


50 mg C/L; pH-8
U released (µg/L)
0
5
10
15
20
25
Mn released (µg/L)
0
100
200
300
0 2 4 6 8 10 12 14 16
Time (Days)
Total U
Total Mn


50 mg C/L; pH-8
U (µg/L)
0
5
10
15
20
25
0
100
200
300
Mn (µg/L)


50 mg C/L; pH-8
U released (µg/L)
0
5
10
15
20
25
Al released (µg/L)
0
2000
4000
6000
8000
0 2 4 6 8 10 12 14 16
Time (Days)
Total U
Total Al


50 mg C/L; pH-8
U (µg/L)
0
5
10
15
20
25
0
2000
4000
6000
8000
Al (µg/L)



*Release of Ca was below detection limit of 134 µg $L^{-1}$ at pH 8

Figure 3E.2: Effects of 50 mg C/L on the release of U, Fe, Mn, Al, Si and Mg with time and correlation of U with Fe, Mn, Al, Si and Mg at pH = 8.

## Appendix 3F: Eh (mV) resulted in NOM experiments.

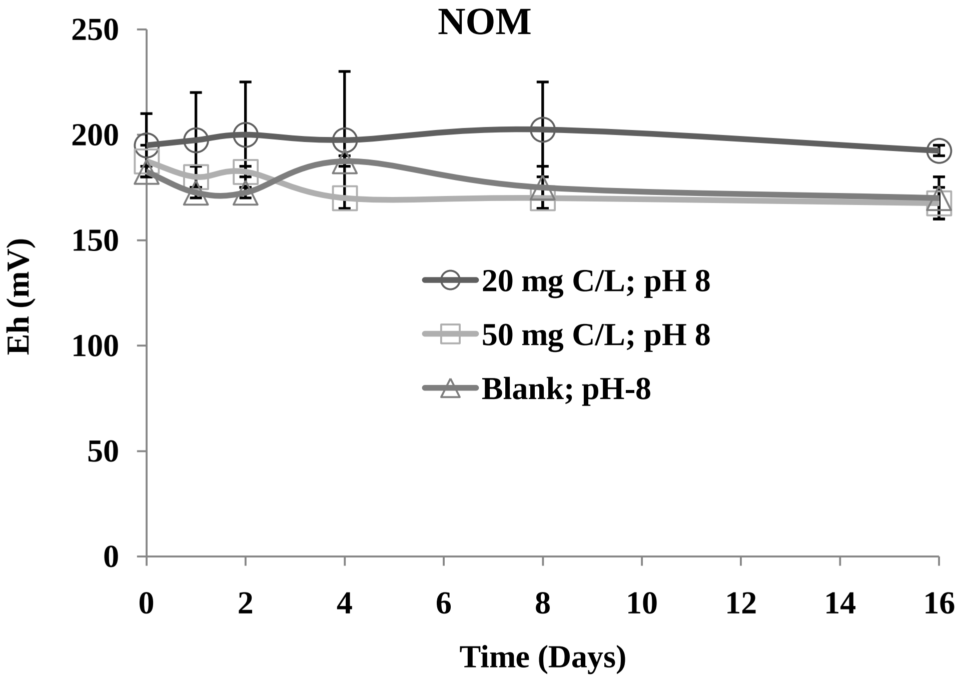


Figure 3F.1: Effects of NOM on resulting Eh (mV) with time.