GROUNDWATER ARSENIC CONTAMINATION IN SHALLOW AQUIFERS OF
THE MISSISSIPPI DELTA IN SOUTHERN LOUISIANA

AN ABSTRACT SUBMITTED ON THE FIFTEENTH DAY OF DECEMBER 2015
TO THE DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
OF THE SCHOOL OF SCIENCE AND ENGINEERING
OF TULANE UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY BY

NINGFANG YANG

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ABSTRACT

This dissertation combines field data, laboratory experiments, and mathematic models to (1) predict the probability of groundwater arsenic (As) contamination caused by geogenic sources and processes in shallow aquifers of the Mississippi Delta in southern Louisiana, (2) study the role microbes play in controlling As mobilization from sediments to groundwaters, and (3) simulate As mobilization and transport caused by changing redox conditions and groundwater geochemistry along a flow path within the southeastern Chicot aquifer in southern Louisiana. A model based on surface hydrology, soil properties, geology, and sedimentary deposition environments predicts that the Holocene shallow aquifers in southern Louisiana are at high risk of As contamination. Sediment incubation and pore-water chemistry suggest that microbes play a key role in mobilizing As from sediments by reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides. Finally, groundwater samples were collected along a 10 km flow path in the southeastern Chicot aquifer to determine groundwater geochemical parameters and to simulate reactive transport of Fe and As species along the studied flow path. The model well captures the general trends of Fe(II) and As(III) concentrations along the studied flow path and the close correspondence between Fe(II) and As(III) of the both measured and model predicted As(III) and Fe(II) concentrations support the hypothesis that microbially mediated reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides is the primary mechanism causing As mobilization from sediments to the shallow reducing groundwaters of the Mississippi Delta in southern Louisiana.
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Chapter 1

Introduction

1.1 Background of Arsenic

Arsenic (As), a ubiquitous metalloid occurs naturally in the environment, is widely distributed in the atmosphere, lithosphere (e.g., soils, sediments, and rocks), hydrosphere (e.g., surface and ground waters), and biosphere (e.g., microorganisms, plants, and animals). In air, total mean As concentrations range from 0.02 ng/m$^3$ to 4 ng/m$^3$ in remote and rural areas, from 3 mg/m$^3$ to about 200 mg/m$^3$ in urban areas, and concentrations greater than 1000 ng/m$^3$ have been measured in areas close to industrial plants (WHO, 2001). The average abundance of As is 2.5 mg/kg in the earth’s crust (Bowell et al., 2014) and 5.7 mg/kg in the upper continental crust (Hu and Gao, 2008). As of July 2014, As has been identified as a critical component for 568 known minerals (IMA, 2014), with pyrite as the largest As reservoir in crustal rocks (Nordstrom, 2000). Pyrite is usually formed in low-temperature sedimentary environments under strong reducing conditions, is present in the sediments of rivers, lakes, and aquifers, and is considered as a critical control on biogeochemical cycles of various trace elements (Bowell et al., 2014). Other minerals contain high As concentrations are metal oxides and hydrous metal oxides, for example, Fe(III) oxides/oxyhydroxides can contain As concentrations up to weight percent values (Smedley and Kinniburgh, 2002). Arsenic concentrations are usually around 1 mg/kg or less in most silicate minerals and less than 10 mg/kg in carbonate minerals (Smedley and Kinniburgh, 2002). Arsenic concentrations in rocks are generally low, less than 5 mg/kg in igneous and metamorphic rocks and 5 ~
10 mg/kg in sedimentary rocks (Smedley and Kinniburgh, 2002). Soils usually contain higher As than rocks, and As concentrations in natural soils range from 0.2 mg/kg to 40 mg/kg, with the lowest concentrations in sands and those derived from granites and the highest concentrations in muds and clays (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Smith et al., 1992) and hydrothermal ore deposits, coal, and lignite deposits (Bowell et al., 2014).

Arsenic was first isolated from orpiment (As$_2$S$_3$) by Albertus Magnus in 1250 A.D. (Mandal and Suzuki, 2002). Arsenic is toxic, colorless, odorless, tasteless, and is undetectable in food and beverages until 1845, therefore, has been used as a homicidal and suicidal agent for a long time. Toxicity of As is greatly dependent on its speciation and valence or oxidation states (Kumar and Riyazuddin, 2010). In the environment, As exists as both inorganic and organic forms at different valence and oxidation states [e.g., As(-III), As(0), As(III), As(V)]. Generally, inorganic species are more toxic than organic species and trivalent oxidation state is more toxic than pentavalent oxidation state (Kumar and Riyazuddin, 2010). Acute exposure to low levels of As can cause nausea, vomiting, diarrhea, numbness in hands and feet, etc., and chronic consumption of As-contaminated water and food can cause serious health problems, such as keratosis, skin discoloration, cancers (e.g., skin, lung, liver, kidney, and bladder) (Chen et al., 1992; Smith et al., 2002, 1992), infant mortality (Rahman et al., 2010), and decreased intellectual and motor function in children (Parvez et al., 2011). During the past 100 years, As and its compounds have been extensively used in various areas, for example, insecticides and pesticides (e.g., lead hydrogen arsenate, monosodium methyl arsenate, and disodium methyl arsenate) in agriculture and wood preservatives (e.g., chromated
copper arsenate) and feed additives in poultry and swine production (e.g., roxarsone) in industry. Although anthropogenic activities such as agricultural and industrial practices as well as past and current mining have adversely affected environments (e.g., air, water, and soil) and human health, the largest mass poisoning in human history is caused by chronic consumption of naturally occurring As-contaminated groundwaters in the deltas and floodplains in South and Southeast Asia.

1.2 Arsenic Contamination in Groundwater

Arsenic in groundwater mainly exists as inorganic forms and generally, trivalent arsenite [As(III)] is the dominant species in reducing groundwater and pentavalent arsenate [As(V)] is the dominant species in oxidizing groundwater (Campbell and Nordstrom, 2014; Nordstrom and Archer, 2003), both of which are responsible for the greatest natural mass poisoning in human history (Smith et al., 2002). As of 2009, more than 140 million people worldwide were drinking As-contaminated groundwater (Ravenscroft et al., 2009), with the most seriously affected area centralized in the deltas and floodplains in South and Southeast Asia, e.g., the Ganges-Brahmaputra-Meghna Delta in India and Bangladesh (McArthur et al., 2001; Zheng et al., 2004), the Mekong River Delta in Cambodia (Papacostas et al., 2008), and the Red River Delta in Vietnam (Berg et al., 2001). Since the symptoms of chronic As poisoning began to appear in the early 1980s, numerous studies have been conducted in the affected areas (Acharyya et al., 1999; Berg et al., 2007; Harvey et al., 2005; McArthur et al., 2001, 2004). Studies in South and Southeast Asia show that groundwaters with high As concentrations are commonly associated with young (i.e., Holocene), organic-rich, alluvial/deltaic deposits
that are under reducing conditions (Smedley & Kinniburgh 2002; Ravenscroft et al. 2005; Winkel et al. 2008). Studies also show that groundwater As contamination commonly occurs in deltas and floodplains that are characterized by flat topography and low hydraulic gradient, therefore, topography and hydraulic gradient of aquifer are other potential factors affecting groundwater As contamination (Amini et al., 2008; Winkel et al., 2008; Yang et al., 2014). Iron oxides/oxyhydroxides were the primary identified As-hosting mineral phases in the aquifer sediments in the Ganges-Brahmaputra-Meghna Delta (Harvey et al., 2005; McArthur et al., 2008) and previous studies indicated that Fe(III) oxides/oxyhydroxides played an important role in controlling As concentrations in groundwater (McArthur et al., 2001; Nickson et al., 1998, 2000). Therefore, factors that could affect reductive dissolution of Fe(III) oxides/oxyhydroxides could also have an impact on As concentrations. Metal reducing microbes (e.g., Fe reducer) living within aquifer sediments are responsible for a number of important biogeochemical processes controlling the fate and mobility of trace elements at low-temperature sedimentary environment, for example, reductive dissolution of Fe(III) oxides/oxyhydroxides and subsequent release of adsorbed and/or co-precipitated As to groundwater in reducing anoxic aquifers (Lovley et al., 2004). The availability of organic matter (e.g., dissolved organic carbon in groundwater, sedimentary organic matter in aquifer sediments) is a limiting factor for microbially mediated reductive dissolution of Fe(III) oxides/oxyhydroxides in aquifer systems (Neidhardt et al., 2014; Radloff et al., 2008).

Mechanisms controlling As mobilization from aquifer sediments to groundwaters are complicated and incompletely understood, however, four mechanisms are generally accepted: (1) oxidation of iron sulfide minerals (e.g., pyrite) containing trace amounts of
As (Das et al., 1996); (2) desorption of As from mineral surfaces via competitive exchange with other anions [e.g., phosphate and/or carbonate, (Acharyya et al., 1999)]; (3) reductive dissolution of As-bearing Fe(III) oxide/oxyhydroxides and the subsequent release of adsorbed or co-precipitated As (Bhattacharya et al., 1997; Harvey et al., 2002; McArthur et al., 2001, 2004; Nickson et al., 2000; Zheng et al., 2004); and (4) microbial-facilitated mineral (i.e., apatite) dissolution as a means of nutrient acquisition (Datta et al., 2009).

1.3 Research Objectives

The Mississippi Delta, the largest river delta in North America, shares broadly similar characteristics (e.g., geology, topography, sedimentary depositional environment) to the deltas and floodplains in South and Southeast Asia. For example, shallow aquifers of the Mississippi Delta commonly consist of young Holocene alluvial/deltaic deposits, are under reducing conditions, poorly drained, and associated with high levels of organic matter content (e.g., peat), which are all favorable conditions for developing the high As groundwaters. However, only a few cases on groundwater As contamination have been reported in the past ten years (Gobb, 2005; Mallett, 2004; Tollett et al., 2003), therefore, this research will focus on naturally occurring As contamination of the shallow aquifer groundwaters in the Mississippi Delta in southern Louisiana. The objectives of this study are to identify areas that are at risk of groundwater As contamination and to evaluate mechanisms controlling As mobilization, and specifically, how microbial mediated reductive dissolution of Fe(III) oxides/oxyhydroxides affect As mobilization from
sediments to groundwaters in shallow aquifers of the Mississippi Delta in southern Louisiana. The specific goals of this dissertation are:

(a) To build a probability model predicting geogenic As contamination in the shallow aquifer groundwaters of the Mississippi Delta in southern Louisiana.
(b) To investigate the possible roles that microbial respiration play in mobilizing As from sediments to groundwaters in southern Louisiana.
(c) To model the reactive transport of Fe and As species along a groundwater flow path in the southeastern Chicot aquifer in southern Louisiana.

To build the As prediction model in the Mississippi Delta where few As data were available, large amounts of As data, as well as data on surface hydrology, soil properties, geology, and sedimentary depositional environments compiled from Bangladesh, one of the most severely affected regions sharing similar geology and sedimentary depositional environments to the Mississippi Delta, were used. After testing and calibration, the model was applied in the Mississippi Delta in southern Louisiana to produce a risk map showing areas at high/low risk of groundwater As contamination. The risk map showed that an area of 23,881 km$^2$ in southern Louisiana were at risk of naturally occurring As contamination in shallow groundwaters and the high risk areas were generally underlain by young Holocene alluvial deposits along the Mississippi and Atchafalaya Rivers, deltaic deposits in the lower Mississippi Delta, and organic-rich marshes along the coast.

To study how microbial activity affects As mobilization from sediments to groundwaters, sediment incubation experiments were conducted under four experimental conditions: (1) sterilized control; (2) anaerobic; (3) anaerobic + acetate; and (4) anaerobic
+ acetate + AQDS (anthraquinone-2, 6-disulfonic acid). Porewater and sediments were collected from Bayou Lafourche, Napoleonville where groundwater contained elevated As concentrations and the artificial groundwater solutions were prepared based on the average groundwater chemistry in Cow Island, Vermilion Parish, Louisiana where groundwater samples had been collected and analyzed as part of this research. Sediment incubation experiments showed that As concentrations in solution were the lowest in the sterilized controls, slightly higher in the un-amended anaerobic experiments, and the greatest in the experiments amended with acetate and especially experiments amended with both acetate and AQDS. Although Fe and manganese (Mn) concentrations exhibited an initial decrease at the beginning of the experiments, they generally followed a similar trend to As after the initial decrease. Porewater analysis showed a generally positive correlation between As and Fe concentrations. Both sediment incubation and porewater chemistry suggested that microbial activity played a key role in controlling As release from sediments to groundwaters in the shallow aquifers of the Mississippi Delta in southern Louisiana.

Finally, to model the biogeochemical reactive transport of As species along a groundwater flow path in the southeastern Chicot aquifer in southern Louisiana, groundwater samples were collected and analyzed for total dissolved As (As$_T$) and As(III), along with total dissolved Fe (Fe$_T$) and Fe(II), sulfide [S(-II)], major solute, pH, alkalinity, oxidation-reduction potential (Eh), total dissolved solids (TDS), and specific conductivity. A one-directional, advective-dispersive biogeochemical reactive transport model was developed using the X1t program of the Geochemist’s Workbench® (Version 9.0) to model As mobilization and transport in groundwaters along the studied flow path.
caused by changing redox conditions and groundwater chemistry. The model well captured the general trends of the measured Fe(II), As(III), and As(V) concentrations along the flow path, and indicated that groundwaters with high Fe(II) and As(III) concentrations were consistent with the model predicted zone where microbial reductive dissolution of Fe(III) oxidex/oxyhydroxides occurred. The model generally over predicted As(V) concentrations along the flow path due to the exclusion of sulfate reduction from the model causing complete elimination of S(-II) from groundwaters. The fact that the close correlation between the measured Fe(II) and As(III) concentrations and the well correspondence between the measured and the model predicted Fe(II) and As(III) concentrations at the mid-reaches of the studied flow path suggested that reductive dissolution of Fe(III) oxides/oxyhydroxides and the subsequent release of sorbed and/or co-precipitated As was the main mechanism causing As release in the southeastern Chicot aquifer in southern Louisiana.
Chapter 2

Predicting geogenic arsenic contamination in shallow groundwater of southern Louisiana, Unites States

Abstract

Groundwater contaminated with arsenic (As) threatens the health of more than 140 million people worldwide. Previous studies indicate that geology and sedimentary depositional environments are important factors controlling groundwater As contamination. The Mississippi Delta has broadly similar geology and sedimentary depositional environments to the large deltas and floodplains in South and Southeast Asia that are severely affected by geogenic As contamination, and therefore, may be vulnerable to groundwater As contamination. In this study, logistic regression is used to develop a probability model based on surface hydrology, soil properties, geology, and sedimentary depositional environments. The model is calibrated using 3286 aggregated and binary-coded groundwater As concentration measurements from Bangladesh and verified using 78 As measurements from southern Louisiana. The model’s predictions are in good agreement with the known spatial distribution of groundwater As contamination of Bangladesh, and also indicate high risk of As contamination in shallow groundwaters from Holocene sediments of the Mississippi Delta in southern Louisiana. Furthermore, the model correctly predicted 79.5% of the existing shallow groundwater As measurements in the study region, indicating good performance of the model in predicting groundwater As contamination in shallow aquifers of the Mississippi Delta in southern Louisiana.
2.1 Introduction

Arsenic (As) is a highly toxic and carcinogenic metalloid and is among the few elements that can be mobilized at common groundwater pH values (i.e., 6.5 ≤ pH ≤ 8.5) under both oxidizing and reducing conditions (Smedley and Kinniburgh, 2002). Long-term consumption of As-contaminated groundwater can cause serious health effects, such as increased risk of various cancers (e.g., skin, lung, liver, bladder, and kidney) (Smith et al., 2002, 1992), increased infant mortality (Rahman et al., 2009), and reduced intellectual and motor function in children (Parvez et al., 2011). Ravenscroft et al. (2009) estimated that consumption of As-contaminated groundwaters (i.e., As > 10 µg/L) had affected more than 140 million people in the world, and the most severely affected region is the Ganges-Brahmaputra-Meghna Delta in Bangladesh and India, which has, therefore, been the focus of substantial investigations (Ahmed et al., 2004; Ravenscroft et al., 2005; Swartz et al., 2004; Weinman et al., 2008). Geogenic processes are the main cause for the elevated As concentrations in local groundwaters from the Ganges-Brahmaputra-Meghna Delta (Ahmed et al., 2004; Harvey et al., 2005; Ravenscroft et al., 2009, 2005; Weinman et al., 2008). Aquifers with elevated groundwater As concentrations commonly consist of Holocene riverine and deltaic sediments, under reducing conditions, that are poorly drained, and associated with high levels of organic matter content (Ahmed et al., 2004; Anawar et al., 2013; Smedley and Kinniburgh, 2002; Weinman et al., 2008). Therefore, it is reasonable to expect that other areas that share similar combinations of these geological, geochemical, and hydrological characteristics may also be at risk of groundwater As contamination.
The Mississippi Delta in southern Louisiana, United States, represents a large river and delta complex that shares broadly similar characteristics to the Ganges-Brahmaputra-Meghna Delta. For example, shallow aquifers in the Mississippi Delta are composed of relatively young (e.g., Holocene), organic-rich (e.g., peat), and alluvial/deltaic sediments (Törnqvist et al., 2008), all of which are considered important factors in controlling the spatial distribution of groundwater As contamination (Smedley and Kinniburgh, 2002; Winkel et al., 2008, 2011). Groundwater As contamination has generally not been reported in the Mississippi Delta region in southern Louisiana, which likely reflects the fact that the chief drinking water sources for local major population centers (i.e., New Orleans and Baton Rouge) are surface water from the Mississippi River and deep groundwaters. Nonetheless, a recent study reported high As concentrations in shallow groundwaters from alluvial aquifers of the Mississippi River Valley in southeastern Arkansas (Sharif et al., 2008). Our preliminary data (Table 2.1) showed that shallow groundwater As concentrations in southern Louisiana ranged from 0.04 µg/L to as high as 100 µg/L, which demonstrated the possibility that shallow groundwaters in southern Louisiana are at risk of As contamination. It is important to note that historical application of arsenical pesticides to control the bow weevil (*Anthonomus grandis*) in cotton-growing regions of the Gulf south (e.g., Arkansas, Texas, northern and eastern Louisiana) complicates the interpretation of the source of the high As groundwaters in southeastern Arkansas, and possibly southern Louisiana. Most of the region of southern Louisiana in this contribution is dominated by sugarcane, rice, and crayfish (*Procambarus clarkii*) cultivation, and consequently does not belong to the historical cotton belt. Therefore, in this contribution we are primarily interested in identifying
potential As-contaminated groundwaters caused by natural sources and processes in reducing shallow aquifers with flat topography and low hydraulic gradients in the Mississippi Delta in southern Louisiana. Specifically, logistic regression is applied to develop a risk model using surface hydrology, soil properties, geology, sedimentary depositional environments, and groundwater As concentration data from Bangladesh. The model is then applied to southern Louisiana where few As concentration data are available to predict the probability of shallow groundwater As contamination from natural sources and processes in southern Louisiana. This model can guide scientists and government agencies in targeting the high As risk areas, initiating early protection measures, and hence, preventing chronic As poisoning in local populations.

2.2 Methods and Materials

2.2.1 Groundwater As data

Because As concentration data for shallow groundwaters from southern Louisiana are sparse, we employed data from Bangladesh to build and calibrate the model. Groundwater As concentration data of Bangladesh were obtained from the British Geological Survey (BGS) and the Department of Public Health Engineering (DPHE) (BGS and DPHE, 2001), which consisted of 3448 As measurements from shallow aquifers (< 100 m). Arsenic concentration data of southern Louisiana consisted of 78 As measurements from shallow aquifers (< 50 m), of which 55 data points were compiled from the United States Geological Survey (USGS) (Focazio et al., 1999) and 23 samples were measured as part of the current study (Table 2.1). The details on groundwater sampling, preservation, As analysis and the analytical results were described in Chapter 3.
(see 3.3 Method and Materials). The As data from southern Louisiana were used to validate the model.

Table 2.1 Total dissolved As concentrations in shallow groundwaters of southern Louisiana.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Arsenic concentration (ug/L)</th>
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<td>29.9206</td>
<td>-91.0445</td>
<td>2.00</td>
</tr>
<tr>
<td>11</td>
<td>29.9247</td>
<td>-91.0154</td>
<td>26.20</td>
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<tr>
<td>12</td>
<td>29.9263</td>
<td>-91.0471</td>
<td>9.90</td>
</tr>
<tr>
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<td>29.9264</td>
<td>-91.0472</td>
<td>37.63</td>
</tr>
<tr>
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<td>29.9269</td>
<td>-90.3952</td>
<td>15.00</td>
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<td>29.9296</td>
<td>-91.0348</td>
<td>23.97</td>
</tr>
<tr>
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<td>29.9299</td>
<td>-91.0487</td>
<td>5.45</td>
</tr>
<tr>
<td>17</td>
<td>29.9330</td>
<td>-91.0259</td>
<td>36.78</td>
</tr>
<tr>
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</tr>
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<td>21</td>
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<td>-91.0175</td>
<td>0.80</td>
</tr>
<tr>
<td>22</td>
<td>29.9591</td>
<td>-92.2249</td>
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</tr>
<tr>
<td>23</td>
<td>29.9917</td>
<td>-91.0624</td>
<td>29.53</td>
</tr>
</tbody>
</table>

2.2.2 Independent Variables
Based on previous investigations (Amini et al., 2008; Ayotte et al., 2006; Lado et al., 2008; Winkel et al., 2008, 2011; Zhang et al., 2012), a total of 15 independent variables, which were considered potentially closely correlated to groundwater As contamination, were initially compiled for the logistic regression analysis from various sources (Table 2.2). Due to differences in resolution and data format, the 15 variables (Table 2.3) were uniformly converted to a raster format at 1 km resolution using ArcGIS (Version 10) and then classified into the following 4 categories.

2.2.2.1 Geology

Detailed geological maps of Bangladesh and southern Louisiana were available in digital format from the USGS and the Louisiana Geological Survey, respectively (Table 2.2). Based on geology and sedimentary depositional environments, the data provided on the geological maps were reclassified into 5 categories, including pre-Holocene deposits, deltaic deposits, organic-rich deposits, alluvial deposits, and tidal deposits (Figure 2.1 and 2.2).

2.2.2.2 Soil

Soil properties of Bangladesh and southern Louisiana were compiled from the digital soil map of the world available through the Food and Agriculture Organization of the United Nations and the soil map of Louisiana from the USGS (Table 2.2). Both maps were reclassified into 6 soil variables, including coarse, medium, and fine soil texture, as well as the average content of silt, clay, and sand in the top 1 m soil layer.
Table 2.2 Sources of GIS data compiled and used for the logistic regression analysis in Bangladesh and southern Louisiana.

<table>
<thead>
<tr>
<th>GIS data</th>
<th>Scale/Resolution</th>
<th>Publisher, source website*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geological map of Louisiana</td>
<td>1:100,000</td>
<td>Louisiana Geological Survey, <a href="http://www.lgs.lsu.edu/deploy/content/PUBLI/contentpage17.php">http://www.lgs.lsu.edu/deploy/content/PUBLI/contentpage17.php</a></td>
</tr>
<tr>
<td><strong>Soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil map of the World (version 3.5)</td>
<td>1:5,000,000</td>
<td>Food and Agriculture Organization of the United Nations</td>
</tr>
<tr>
<td><strong>Topography</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hydrology</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Website access verified on December 7th, 2013.
Table 2.3 Independent variables initially considered in building the As prediction model for Bangladesh.

<table>
<thead>
<tr>
<th>Category</th>
<th>Independent variables</th>
<th>Raster Format</th>
<th>Significance (p-value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geology and sedimentary depositional environment</td>
<td>Pre-Holocene deposits</td>
<td>Categorical</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deltaic deposits</td>
<td>Categorical</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Organic-rich deposits</td>
<td>Categorical</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Alluvial deposits</td>
<td>Categorical</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Tidal deposits</td>
<td>Categorical</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>Soil</td>
<td>Coarse-textured soil</td>
<td>Categorical</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Medium-textured soil</td>
<td>Categorical</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Fine-textured soil</td>
<td>Categorical</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Sand content</td>
<td>Continuous</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Silt content</td>
<td>Continuous</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Clay content</td>
<td>Continuous</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Topography</td>
<td>Slope</td>
<td>Continuous</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Topographic wetness index</td>
<td>Continuous</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>Hydrology</td>
<td>Density of rivers</td>
<td>Continuous</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Distance to rivers</td>
<td>Continuous</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>
Figure 2.1 Classified geological map of Bangladesh.
2.2.2.3 Topography

High-resolution digital elevation model (DEM) data of Bangladesh and southern Louisiana were obtained from the USGS, and subsequently up-scaled to 1 km resolution to calculate slope and topographic wetness index (TWI). Topographic wetness index is
commonly used as an indicator for soil moisture content and soil organic matter content.

The equation used to calculate TWI is as follows:

\[
TWI = \ln\left(\frac{A_C}{\tan\beta}\right)
\]  

(2.1)

Here, \(A_C\) is the upstream contributing area and \(\beta\) is the slope of the landscape.

2.2.2.4 Hydrology

The major rivers and their tributaries of Bangladesh (i.e., Ganges, Brahmaputra, and Meghna) and southern Louisiana (i.e., Mississippi and Atchafalaya) were digitized to calculate raster maps of the density of rivers and the distance to rivers at 1 km resolution. Density of rivers is calculated as the total length of rivers per raster cell (i.e., 1 km \(\times\) 1 km), and distance to rivers is the shortest distance from the center of each raster cell to rivers. Both variables can influence hydrological processes within aquifers, and were previously shown to be strong predictors of elevated As concentrations in shallow groundwaters (Zhang et al., 2012).

2.2.3 Development of the As Prediction Model

Groundwater As concentrations are point measurements at different well depths, whereas other independent variables are either vector or raster variables with coarser spatial resolution. Because the 15 independent variables (Table 2.3) were all converted to a raster format with a pixel size of 1 km, the point measurements of As concentrations were also aggregated using the geometric mean to a resolution of one point per pixel with a pixel size of 1 km. Data aggregation reduced the dataset of Bangladesh to 3286
individual values, which were binary-coded for later analysis using the World Health Organization drinking water standard for As (i.e., 10 µg/L) as the threshold. The aggregated data were binary-coded because our goal was to develop a model predicting the probability of groundwater As contamination, such that there were only two possibilities: (1) contaminated (As ≥ 10 µg/L, binary-coded as 1); or (2) uncontaminated (As < 10 µg/L, binary-coded as 0). These binary-coded variables are the dependent variables in this study.

Logistic regression is a probabilistic statistical method, which can be used to predict a binary outcomes from various independent variables (i.e., numerical or categorical) (Hosmer et al., 2013). Logistic regression has been widely used in environmental assessment and investigation, including predicting the probability of groundwater As contamination (Amini et al., 2008; Ayotte et al., 2006; Lado et al., 2008; Winkel et al., 2008, 2011; Zhang et al., 2012). In this contribution, logistic regression is applied to develop a risk model based on the relative importance of geology and sedimentary depositional environments, topography, hydrology, and soil properties in exerting controls on groundwater As contamination in Bangladesh. The model is subsequently applied to the Mississippi Delta in southern Louisiana, where little information exists regarding the possibility and geographic distribution of As contamination in shallow groundwaters caused by natural sources and processes. The statistical significance of each independent variable in predicting the probability of As contamination in shallow groundwaters is tested using stepwise logistic regression. It begins with the most significant independent variable, after testing the abilities of the remaining independent variables in explaining the remaining model error, the next most
significant independent variable is added. This procedure is repeated until no other independent variables left can significantly explain the remaining model error. Finally, only the statistically significant independent variables will be included in the final model. The dependent variable is the natural logarithm of the odds, \( \frac{p}{1-p} \), where \( p \) is a numerical value representing the probability of the occurring event. The log transformation converts the dependent variable constrained between 0 and 1 into a continuous variable that is linearly related to the combination of the independent variables, such that

\[
Y = \ln\left(\frac{p}{1-p}\right) = \ln\left(p_1 - p\right) = C + \sum_{i=1}^{n} \lambda_i X_i \tag{2.2}
\]

where

\[
p = \frac{\exp(C + \sum_{i=1}^{n} \lambda_i X_i)}{1 + \exp(C + \sum_{i=1}^{n} \lambda_i X_i)} \tag{2.3}
\]

Here, \( Y \) is the log transform of the dependent variables, \( \frac{p}{1-p} \), which is related to the odds of occurrence of an event, \( C \) is the intercept of the regression, and \( \lambda_i \) are the weighting coefficients of each independent variable, \( X_i \) (Hosmer et al., 2013).

Once the model is developed, its predictive performance under different probability cutoff values is evaluated using the receiver operating characteristic (ROC) analysis. The ROC curve describes the predicative performance of the logistic regression model as the probability cutoff value varies. The optimal probability cutoff value is a value at which the model obtains best predicative performance, which will be used to classify the probability map into a risk map showing areas that are predicted to be at risk of groundwater As contamination and regions that are not likely to be at risk. It is critical
to note that a good fit of the regression model does not necessarily mean a good predictive performance of the model. Consequently, the best way to validate the predictive ability of the model is to use a new data set that is not employed in developing the model (Berk, 1984). In this study, groundwater As data from Bangladesh (n = 3286) were used to build the model, whereas data obtained from southern Louisiana (n = 78) were used for validation of the model. Because the current amount of groundwater As concentration data in southern Louisiana is sparse, full validation of the predictive ability of the model for this region awaits additional planned groundwater sampling and analysis.

2.3 Results

2.3.1 Arsenic Prediction Model

Statistical significance of each independent variable was tested at a 95% confidence level using the stepwise logistic regression. The results showed that only 7 of the 15 compiled independent variables were significant in predicting As-contaminated shallow groundwaters in Bangladesh (Table 2.4), and therefore, were retained in the final model to evaluate the probability of shallow groundwater As contamination in southern Louisiana. The stepwise logistic regression indicates that pre-Holocene deposits ($\lambda = -3.42$) and distance to rivers ($\lambda = -1.86$) are negatively correlated to shallow groundwater As contamination (As $\geq 10$ µg/L), of which, pre-Holocene deposits play the most important role in the model. In contrast, Holocene sedimentary depositional environments contribute positively to the model, of which, deltaic deposits ($\lambda = 1.62$) play the most important role, followed by organic-rich deposits ($\lambda = 0.82$), and then recent alluvial
deposits (\(\lambda = 0.51\)) in terms of relative importance for predicting shallow groundwater As contamination in Bangladesh. Of the soil variables, medium-textured soil (\(\lambda = 1.16\)) and clay content (\(\lambda = 0.11\)) of the top 1 m soil layer are positively correlated to shallow groundwater As contamination, meaning that both of these parameters are important indicators of elevated As concentrations in shallow groundwaters in Bangladesh.

Table 2.4 Significant independent variables used in the final logistic regression model for Bangladesh.

<table>
<thead>
<tr>
<th>Category</th>
<th>Variables</th>
<th>(\lambda)</th>
<th>Ward-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrology</td>
<td>Distance to rivers</td>
<td>-1.86</td>
<td>124.56</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Geology and sedimentary depositional environments</td>
<td>Pre-Holocene deposits</td>
<td>-3.42</td>
<td>55.49</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Deltaic deposits</td>
<td>1.62</td>
<td>50.83</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Organic-rich deposits</td>
<td>0.82</td>
<td>12.41</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Alluvial deposits</td>
<td>0.51</td>
<td>6.25</td>
<td>0.0125</td>
</tr>
<tr>
<td>Soil</td>
<td>Medium-textured soils</td>
<td>1.16</td>
<td>45.50</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Clay content</td>
<td>0.11</td>
<td>41.26</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Intercept</td>
<td>Intercept</td>
<td>-4.11</td>
<td>44.63</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Weighting coefficients (\(\lambda\)) of the independent variables were used in the model to calculate probability of As contamination in shallow groundwaters. Large \(\lambda\) values represent greater relative importance, small values represent lower relative importance, positive values represent positive correlation, and negative values represent negative correlation. Ward values indicate the relative importance of the independent variables in predicting As contamination in shallow groundwaters, and p-values show the statistical significance of the independent variables.

2.3.2 Probability Map and Risk Map
The performance of the As prediction model was evaluated using the ROC analysis. Specifically, the area under the curve (AUC) is a measure of the model’s performance, with values typically varying between 0.5 and 1. Despite the fact that our model only considers surface parameters (i.e., 2-D datasets and not 3-D datasets that include the vertical dimension), the AUC value of 0.76 (Figure 2.3) indicates that the model does a good job at predicting groundwater As contamination for shallow aquifers.

![ROC Curve for Model](image.png)

Figure 2.3 Receiver operation characteristic curve (ROC) obtained from the As prediction model for Bangladesh.
(<100 m) in Bangladesh. Sensitivity measures the model’s ability to correctly classify groundwater samples with As concentrations greater than or equal to 10 µg/L (true positive), whereas specificity measures the model’s ability to correctly classify groundwater samples with As concentrations less than 10 µg/L (true negative). Classification results of the As prediction model under different probability cutoff values are presented in Figure 2.4, which shows that sensitivity is inversely related to specificity. To obtain a model with better predicative performance, a value of 0.5, where the model

Figure 2.4 Performance of the As prediction model at different probability cutoff. Sensitivity is the correctly classified samples in the group with As concentrations ≥ 10 µg/L. Specificity is the correctly classified samples in the group with As concentrations < 10 µg/L. The optimal probability cutoff value is obtained at the point where sensitivity and specificity intersects. has both higher sensitivity and specificity, is selected as the optimal probability cutoff value to classify the As probability map into the binary risk map (Figure 2.4).
The map showing the predicted probability of groundwater As contamination in Bangladesh is presented in Figure 2.5. Figure 2.5a shows that areas at high risk (probability ≥ 0.5) of As contamination are predicted to occur along the three major rivers (Ganges, Brahmaputra, and Meghna; 0.5 - 0.7), in the northeastern Sylhet basin (0.6 - 0.8), and in the Ganges Delta (> 0.7). Figure 5b presents the As risk map of Bangladesh, which shows areas at high risk (probabilities ≥ 0.5) and low risk (probability < 0.5) of groundwater As contamination. The model predicted high and low risk areas are in good agreement with the known spatial distribution of groundwater As contamination. Of the 3286 aggregated and binary-coded As concentration measurements, 68.4% are correctly predicted by the logistic regression model. More specifically, 72.8% of the groundwater samples with As concentrations greater than or equal to 10 µg/kg are correctly predicted (sensitivity), whereas 64.6% of the groundwater samples with As concentrations less than 10 µg/L are correctly predicted (specificity). Consequently, we apply the same model and approach to southern Louisiana to evaluate the probability that elevated As concentrations in shallow groundwaters may also characterize the region including the Mississippi Delta. Again, the existing As concentration data for shallow groundwaters in southern Louisiana are rare, making the logistic regression an appropriate approach to evaluate the possibility of naturally sourced As contamination of local groundwaters. Moreover, it is important to stress that the model does not allow us to predict shallow groundwaters in southern Louisiana that may be at risk of anthropogenic sourced As contamination.
2.3.3 Application of the As Prediction Model to Southern Louisiana

Figure 2.6 shows the results of the predicative model applied to southern Louisiana. The probability map shows the predicted probability of groundwater containing elevated As concentrations (Figure 2.6a). The regions where shallow groundwaters (i.e., < 50 m) exhibit high probability (≥ 0.5) of As contamination include areas underlain by alluvial deposits along the Mississippi and Atchafalaya Rivers (0.6 ~
0.8), deltaic deposits in the lower Mississippi Delta (> 0.8), and organic-rich marshes along the coast in southern Louisiana (> 0.8) (Figure 2.2 and 2.6a). The risk map (Figure 2.6b) indicates that an area of 23,881 km² in southern Louisiana may be at risk of shallow groundwater As contamination (probability ≥ 0.5) from natural sources and processes. To validate the performance of the model, 78 binary-coded As concentration measurements for shallow groundwaters (< 50 m) were compared to the risk map predicted values (Figure 2.6b). The comparison results showed that the model correctly predicted 79.5% of the total groundwater samples. Specifically, 87.5% of the shallow groundwater samples that contain As concentrations greater than or equal to 10 µg/L are correctly predicted by the model, whereas 77.4% with As concentrations less than 10 µg/L (specificity) are correctly predicted. Consequently, the performance of the model in southern Louisiana is comparable to its performance in Bangladesh. Nevertheless, additional sampling of shallow groundwaters in southern Louisiana is required to test the accuracy of the model for extensive regions of the study area for which shallow groundwater As concentration data do not currently exist.
Figure 2.6 Predicted probability of As contamination in shallow groundwaters of southern Louisiana: (a) continuous probability map; (b) risk map showing high and low risk areas overlain by 78 shallow groundwater As concentration data.
2.4 Discussion

2.4.1 Parameters Contributing to the As Prediction Model

Groundwater As contamination is commonly associated with shallow aquifers consist of Holocene deposits in areas with flat topography and low hydraulic gradients (Shamsudduha et al., 2009, 2008). Specifically, the chemically reducing Holocene sedimentary depositional environments that characterize the deltas and floodplains of large rivers are thought to influence the development of As-contaminated groundwaters (McArthur et al., 2008, 2004; Shamsudduha et al., 2009, 2008). Previous studies (Winkel et al., 2008, 2011) demonstrated the statistical significance of Holocene deltaic, alluvial, and organic-rich deposits in predicting As contamination in shallow groundwaters from major river deltas of South and Southeast Asia. Our model confirmed the importance of hydrology, soil, geology, and sedimentary depositional environments in predicting groundwater As contamination in the shallow reduced aquifers of the Ganges-Brahmaputra-Meghna Delta in Bangladesh, as well as the Mississippi Delta in southern Louisiana, United States (Figure 2.5 and 2.6). The positive weighting coefficients of deltaic deposits ($\lambda = 1.62$), organic-rich deposits ($\lambda = 0.82$), and alluvial deposits ($\lambda = 0.51$) indicate that the presence of deltaic deposits in the Holocene aquifers likely exert the most important controls on the development of elevated As concentrations in the associated groundwaters, followed by organic-rich deposits, and then alluvial deposits. Deltaic deposits and alluvial deposits are formed in deltas and river floodplains, which usually developed in areas with flat topography and low hydraulic gradients. These characteristics provide favorable condition for the development of chemically reducing
environments where groundwater As contamination usually occur. In contrast, pre-
Holocene deposits are negatively ($\lambda = -3.42$) associated with groundwater As
contamination, which indicates that aquifers consist of older sedimentary deposits (e.g.,
Pleistocene) are expected to exhibit relatively low As concentrations in associated
groundwaters (McArthur et al., 2008). Soil properties and texture are indicative of current,
as well as past, drainage conditions within various depositional environments (Winkel et
al., 2008), and as such are closely related to local hydrological processes of aquifers. For
example, shallow aquifers overlain by fine-grained sediments (i.e., clay) in Bangladesh
are known to be poorly drained, and therefore, the associated groundwaters commonly
exhibit relatively high levels of As concentrations (Aziz et al., 2008). The positive
weighting coefficient of the clay content in the top 1 m soil layer ($\lambda = 0.11$) implies that
groundwaters from shallow aquifers overlain by fine-grained deposits are at relatively
high risk of developing elevated As concentrations due, in part, to the low permeability of
clay. Medium-textured soil (i.e., silt) in river basins, floodplains, and deltas is also an
indicator of the presence, transport, and/or deposition of fresh, reactive materials (e.g.,
organic matter), which favors reductive dissolution of Fe(III) oxides/oxyhydroxides
under reducing anoxic environments and subsequently release previously absorbed and/or
co-precipitated As to groundwaters (Datta et al., 2009; Dowling et al., 2002; Korte, 1991;
Nickson et al., 2000). Our model also confirmed that the presence of medium-textured
soil was indicative of elevated As concentrations in shallow groundwaters ($\lambda = 1.16$).
Distance to rivers can influence the local hydrological processes and as such can be used
as an indicator of relatively young (i.e., Holocene) sediments. Aquifers located close to
rivers commonly consist of relatively young and freshly deposited sediments, which can
provide reducing environment by driving microbial respiration and subsequently cause As enrichment in shallow groundwaters (Datta et al., 2009; Nickson et al., 2000). The negative weighting coefficient ($\lambda = -1.86$) of distance to rivers indicates that aquifers close to rivers are at high risk of As contamination, and this risk decreases with increasing distance to rivers.

The fact that the Mississippi Delta in southern Louisiana shares broadly similar geological and hydrological characteristics with the rivers and deltas of South and Southeast Asia and our model’s prediction both indicate that shallow groundwaters in southern Louisiana may also be at risk of As contamination as a result of similar natural sources and processes. Owing to the relatively low numbers of shallow groundwaters that have been sampled and analyzed for total dissolved As concentrations, the extent of naturally occurring As contamination of shallow groundwaters in southern Louisiana still remains poorly known. Nevertheless, the application of the As prediction model to southern Louisiana presented here, and its relatively accurate predictions for the existing groundwater As data, indicates that more sampling and analysis of As concentrations in shallow groundwaters are warranted. Therefore, it is not advisable to use local shallow groundwaters as an alternative drinking water source in southern Louisiana if no further assessment of groundwater As contamination is carried out.

### 2.4.2 Limitations of the As Prediction Model

The potentially important parameters controlling the distribution of naturally occurring As contamination in groundwaters inherently contain a 3-D component (i.e., depth), which defines the subsurface boundaries of aquifers formed under different
geological periods (e.g., Pleistocene or Holocene) or under different sedimentary depositional environments (e.g., alluvial, deltaic, or tidal). However, due to lack of accurate 3-D data (i.e., depth) for the extensive regions of southern Louisiana examined herein, our model is based only on 2-D surface data. Consequently, the model assumes that geology and sedimentary depositional environments expressed at the surface are the same as those at the shallow subsurface (< 50 m). Therefore, misclassifications may occur when geology and sedimentary depositional environments expressed at the surface differ from those at the shallow subsurface. Improvements on the model’s predictions are expected to thus result for cases where geology, hydrology, and/or soil properties as a function of depth can be included in the regression model (Winkel et al., 2011). Despite these and other limitations, the model generally does a good job at predicting groundwater As contamination in shallow aquifers of southern Louisiana where scarce data are currently available.

Acknowledgements

This work was supported in part by NSF grants EAR-0805332 and EAR-1014946 to K. H. J. We would like to express our gratitude to Dr. Annette Johnson, who provided critical assistance in developing the logistic regression model, and Dr. Deborah Grimm for assistance with the As analysis of the groundwater samples.
Chapter 3

High arsenic (As) concentrations in the shallow groundwaters of southern Louisiana: Evidence of microbial controls on As mobilization from sediments

Abstract

Since 2003, groundwaters in southern Louisiana have been reported to contain elevated arsenic (As) concentrations at various locations, with the highest reported value of 100 µg/L. However, few researches have been conducted regarding the mechanisms causing As release from sediments in shallow aquifers of southern Louisiana. Microbial respiration is generally considered as a major process causing As release in reducing anoxic aquifers, therefore, sediment incubation in combination with porewater samples collected from sediment cores were used to investigate the role microbes play in As release from sediments in shallow aquifers of southern Louisiana. Sediment incubations show that As concentrations in solutions were lowest in the sterilized controls, slightly higher in the un-amended experiments, and greatest in the experiments amended with acetate and especially experiments amended with both acetate and AQDS. In contrast, iron (Fe) and manganese (Mn) concentrations in solutions were the highest in the un-amended experiments. The generally low Fe and Mn concentrations and the observed production of organic flocculants in the amended solutions suggest that addition of acetate and AQDS resulted in substantial decrease in Fe and Mn concentrations in these solutions. After initial decreases in Fe and Mn concentrations in solutions, Fe and Mn both generally increase with increasing time. Arsenic in porewaters generally follows the
same trend as Fe. Our results strongly suggest that microbes play a key role in As release from sediments to groundwaters in the shallow aquifers of the Mississippi Delta in southern Louisiana.

3.1 Introduction

Naturally occurring arsenic (As) contamination in groundwaters have been reported in many regions of the world, especially the deltas and floodplains in South and Southeast Asia (Berg et al., 2001; Nickson et al., 2000; Polya et al., 2005; Shamsudduha et al., 2008; Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). As of 2009, more than 140 million people worldwide were drinking As-contaminated groundwaters (Ravenscroft et al., 2009). Due to similar geology and sedimentary depositional environments (e.g., organic-rich, fluvial/deltaic deposits) to the modern deltas and floodplains in South and Southeast Asia, shallow aquifers and the associated groundwaters in the Mississippi Delta in southern Louisiana are also possibly at risk of geogenic As contamination (Ravenscroft et al., 2009; Yang et al., 2014).

In southern Louisiana, groundwater was first reported in 2003 to contain elevated As concentrations in a study by the United States Geological Survey (USGS) concerning water quality of domestic wells (Tollett et al., 2003). Following the study by Tollett et al. (2003), the Louisiana Department of Environmental Quality (LDEQ) conducted a small scale survey focusing on As concentrations in groundwater from domestic wells in the Cow Island and Forked Island areas of Vermilion Parish in southern Louisiana and the results showed that 20% of the 25 sampled wells contained As concentrations above 10 µg/L, with the highest value reported to be 60 µg/L (Mallett, 2004). In 2011, As was
found in domestic wells in Opelousas, Louisiana, with the highest concentration reported being 54 µg/L (Bastien, 2011). More recently, Yang et al. (2014) hypothesized, based on a logistic regression probability model calibrated with geochemical, geologic, and hydrologic data that large regions of southern Louisiana may be underlain by shallow groundwaters with As concentrations exceeding 10 µg/L, the US EPA’s maximum contaminant level (MCL) for As in drinking water.

Several possible As sources exist in southern Louisiana, including As from anthropogenic activities. For example, before 1960 cattle dipping vats commonly contained aqueous solutions mixed with As-rich insecticides that were used to control ticks and other insects, and to protect cattle from a disease called “southern cattle fever” (Gresham, 2007). As such, the remnants of the now defunct cattle dip vats may represent a source of As contamination to the underlying aquifer systems. Furthermore, widespread application of arsenical pesticides to cotton fields to control the boll weevil (*Anthonomus grandis*) represents another important legacy source of As to soils and shallow groundwaters across large areas of the southern United States (Potera, 2007). Numerous industrial facilities and Superfund sites located in southern Louisiana could also represent additional possible sources of As contamination to local groundwaters (Gresham, 2007). Finally, historical cemeteries that contain As-embalmed human remains may also contribute As to local groundwaters (Duex and Gresham, 2008). For example, between 1850 to 1910, As was used as a common ingredient in embalming fluids in the United States and it is estimated that as much as 5.4 kg of As was used per body (Borstel and Niquette, 2000). As wood caskets deteriorate with age, the embalmed remains may be
directly exposed to the surrounding sediments and cause the downward movement of As into groundwaters (Gresham, 2007; Duex and Gresham, 2008).

Despite the numerous possible anthropogenic sources for As that exist in southern Louisiana, many of the shallow groundwaters that exhibit elevated As concentrations are confined beneath thick layers of clays (up to 10 m thick; Milner and Fisher, 2009) that are expected to act as effective barriers preventing the transport of anthropogenic-sourced As from the ground surface to the underlying groundwater flow systems (e.g., Duex and Gresham, 2008; Milner and Fisher, 2009). For example, in the vicinity of Cow Island and Forked Island, Louisiana, the Chicot aquifer, which can contain high groundwater As concentrations, is overlain by approximately 8 m of clay, which acts as an aquitard preventing contaminants like As from migrating from the surface to underlying groundwaters (Lovelace, 1999; Sargent, 2004; Duex and Gresham, 2008; Prakken and White, 2014). In addition, because the Mississippi Delta shares broadly similar geology, hydrology, and sedimentary depositional environments with the deltas and floodplains of South and Southeast Asia (Yang et al., 2014), we propose that high As concentrations in the southern Louisiana groundwaters reflect the same or similar, naturally occurring biogeochemical processes thought to be responsible for the elevated As concentrations in groundwaters from South and Southeast Asia, namely microbiially-driven reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides (e.g., Bhattacharya et al. 1997; Harvey et al., 2002, 2005; Mailloux et al., 2009; McArthur et al., 2001, 2004; Nickson et al., 2000; Islam et al., 2004; Polizzotto et al., 2008; Zheng et al., 2004; Yang et al., 2014). Nonetheless, although multiple examples of As contamination of shallow groundwaters have been reported in southern Louisiana, little attention has focused on the processes
that are responsible for the elevated groundwater As concentrations, which likely include anthropogenic and natural causes. For people living in rural areas of southern Louisiana who rely on private wells for drinking waters, the locally elevated groundwater As concentrations may be an unrecognized health risk.

Here, sediment incubation experiments and porewater analysis have been used to investigate the possible role that microbial respiration plays in mobilizing As from sediments to the local groundwaters in southern Louisiana. We hypothesize that reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides by the microbial consortia within the aquifer facilitates As release from sediments to groundwaters in the reducing anoxic shallow aquifers of the Mississippi Delta (e.g., Oremland and Stolz, 2005).

3.2 Study Area

The Mississippi Delta began to form about 7000 years ago when sea-level rise decelerated to less than 1 mm/yr, and currently it consists of six recognizable sub-deltas (Blum and Roberts, 2009). The study area is located in a crevasse splay at Napoleonville, Louisiana, along the west bank of Bayou Lafourche, the trunk distributary of the Lafourche sub-delta in the Mississippi Delta (Figure 3.1). Bayou Lafourche was a precursor of the modern Mississippi River. Radiocarbon and optically-stimulated luminescence measurements indicated that the Lafourche sub-delta was initiated around 1500 years ago (Törnqvist et al., 1996, 2008), and mostly abandoned by about 600 years ago (Shen et al., 2015). The distributary channel was converted into a stagnant bayou (i.e., Bayou Lafourche) after a dam was built in 1904 at Donaldsonville, where the bayou joined the present-day Mississippi River. Late Holocene stratigraphy of the Lafourche
sub-delta has been extensively studied (Fisk, 1952; Frazier, 1967; Törnqvist et al., 1996, 2008), and the results show that the near surface sediments in the study area consist of a widespread layer of woody peat overlain by up to 12 m of over-bank deposits from Bayou Lafourche. Distribution of sandy facies within the overbank deposits generally correlates to the abandoned crevasse channels. Due to relatively high sedimentary organic carbon (SOC) contents and the reducing conditions of the shallow aquifers, we expected that groundwaters in this region would contain elevated As concentrations. Indeed, our previous investigation (Yang et al., 2014) indicated that of the 13 groundwater samples collected from the Lafourche sub-delta, 60% contained As concentrations greater than 10 µg/L (i.e., the US EPA drinking water standard), and the highest value was 100 µg/L (Figure 3.1).

3.3 Methods and Materials

3.3.1 Porewater and Sediment Collection

Sediment cores were collected with a Giddings soil probe at locations A and B in June, 2013, and using a Geoprobe at location C in September, 2013. The three cores were collected along a transect perpendicular to Bayou Lafourche (Figure 3.1). When the probes reached the sampling depths, a PVC core liner (5 cm diameter, 50 cm or 150 cm long) was inserted to collect the sediment core. Right after cores were extruded from the probe, they were immediately capped with PVC caps at both ends and sealed with tape to prevent exposure to O₂.
Figure 3.1 Google Earth image of the study site showing As concentrations in shallow groundwaters (Yang et al., 2014) and the locations of where sediment cores were extracted: A (29°53′40.38″N, 91°5′13.68″W), B (29°54′53.90″N, 91°2′46.70″W), and C (29°56′N, 91°1′34.02″W) in southern Louisiana. Insert map shows the State of Louisiana and the location of the study site relative to the Red River, the Atchafalaya River, and the Mississippi River, as well as the cities of White Lake, New Orleans, and Baton Rouge, Louisiana.

Rhizon samplers (Rhizonsphere Research Products; http://www.rhizosphere.com/rhizons) were employed to extract porewaters from sediment cores. Rhizon samplers consist of: (1) a 5 cm hydrophilic porous polymer tube with an outer diameter of 4.5 mm and a pore size of 0.15 µm, supported by glass fiber; and (2) a 12 cm PVC tubing with a female luer lock, connected to a 10 mL syringe to create a vacuum (http://www.rhizosphere.com/rhizons). A small hole was created at the
surface of the sealed sediment core, into which the 5 cm porous tube of a Rhizon sampler was carefully inserted, and a 10 mL syringe was used to create a vacuum causing porewaters to flow from sediments into syringes. Consequently, porewaters extracted by Rhizon samplers were automatically filtered through a pore size of 0.15 µm. Due to limited quantities of porewaters in sediments, especially the clay-rich sediments, only a total volume of ~15 mL was collected at each depth. We note that colloids with diameters smaller than 0.15 µm could pass through the Rhizon samplers, and potentially influence the analytical results. Nonetheless, owing to the small volumes of porewater that we were able to extract from the sediment cores, additional filtration through smaller nominal pore size filters (e.g., ultrafiltration) was not undertaken in the current study. Future studies may include ultrafiltration studies of shallow groundwaters from the region.

Each porewater sample was subsequently split into three equal aliquots for measuring pH, dissolved organic carbon (DOC), and trace element (i.e., As and Fe) concentrations, respectively. Porewater pH was measured with a micro pH electrode (Fisher Scientific Orion 98633BN). Samples for DOC analysis were acidified to pH < 2 with ultrapure HCl (Seastar) and measured in triplicate using a TOC-5000 analyzer (Shimadzu) with a confidence interval of 0.02 mg/L Carbon (C) at Kansas State University. Porewaters for As and Fe analysis were acidified to pH < 2 with ultrapure HNO₃ (Seastar) and measured by high-resolution (magnetic sector) inductively coupled plasma mass spectrometer (HR-ICP-MS; Thermo Fisher Element 2) following procedures described previously (Datta et al., 2011; Haque et al., 2008; Mohajerin et al., 2014; Sankar et al., 2014).
After porewaters were collected, cores were opened and sediments were transferred into AnaeroPouchbags (Fisher Scientific, Mitsubishi™), within which a sachet of O₂ absorber (Fisher Scientific, Mitsubishi™) was included per bag to maintain the anaerobic conditions. Sediments from core A and C were analyzed for SOC using a Vario MicroCube Elemental Analyzer and loss on ignition (LOI), respectively. Sediments from the silt- and sand-rich layers in cores A and C, collected for incubation experiments, were then transferred into a glove box (Plas-Labs “Basic Glove Box” model # 818-GB) where AnaeroPouch bags were opened and sediments subsequently dried under anaerobic conditions in a N₂ atmosphere (Pearcy et al., 2011). Small roots and woody particles were manually removed before sediments were employed for the incubation experiments.

3.3.2 Sediment Incubation

3.3.2.1 Groundwater Recipe

Owing to the small volumes of porewaters extracted from the sediment cores, we were not able to analyze the major ion composition of the shallow groundwaters from the Napoleonville study site. Consequently, we used the average composition of shallow groundwaters from another study site in southern Louisiana (i.e., Cow Island) where major solute concentrations have been quantified to make the “artificial groundwater” solution used for the incubation studies described herein. Specifically, the average concentrations of the major solutes measured in 9 domestic wells were used as the basis to make the “artificial groundwater” solution, and if necessary, bicarbonate (HCO₃⁻) was used for charge balance of the averaged cations and anions and to buffer the solution pH at ~ 8.00. Reagent salts were precisely weighed and transferred to a volumetric flask to
which 1 L of de-ionized water (Milli-Q, 18.2 MΩ cm) was added to make a solution that had approximately the same composition as the average shallow groundwaters from the Cow Island site (Table 3.1). When necessary, the solution was adjusted to pH ~ 8.00 (i.e., the average pH of the Cow Island groundwaters) using 0.1 N ultrapure HCl (Seastar) or 0.1 N NaOH, and then sterilized in an autoclave for a 20 min cycle at 121 °C and 1.1 atm. After the solution cooled to room temperature (23 ± 2 °C), it was transferred to the glove box, bubbled with N₂ gas using a 25.4 cm gas dispersion tube to strip the dissolved O₂, and then capped and allowed to reach equilibrium under the O₂-free, N₂ atmosphere in the glove box (Pearcy et al., 2011).

Table 3.1 Major solute concentrations in the “artificial groundwater” solution used in the incubation experiments.

<table>
<thead>
<tr>
<th>Major solutes</th>
<th>Concentration (mmol/L)</th>
<th>Reagent</th>
<th>Amount of reagent (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄³⁻</td>
<td>0.002</td>
<td>KH₂PO₄</td>
<td>0.30</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.001</td>
<td>KNO₃</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.100</td>
<td>MgCl₂*6H₂O</td>
<td>53.81</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.049</td>
<td>MgSO₄</td>
<td>5.94</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.032</td>
<td>K₂CO₃</td>
<td>2.04</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.724</td>
<td>MgCO₃</td>
<td>34.58</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.785</td>
<td>CaCl₂</td>
<td>87.12</td>
</tr>
<tr>
<td>Na⁺</td>
<td>3.567</td>
<td>NaHCO₃</td>
<td>299.59</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.412</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.2.2 Incubation Experiments

Prior to incubation experiments, all glass serum bottles (100 mL) and polyethylene centrifuge tubes (10 mL and 50 mL) were acid washed following trace element clean procedures and then sterilized in an autoclave for a 20 min cycle at 121 °C and 1.1 atm (Pearcy et al., 2011). Anaerobic sediment incubations were conducted in the
glove box under four conditions: (1) sterilized control (sterilized sediments + 50 mmol/kg 9,10-anthraquinone-2,6-disulfonic acid sodium salt [AQDS]); (2) anaerobic with no amendments; (3) anaerobic + 50 mmol/kg acetate (i.e., sodium acetate); and (4) anaerobic + 50 mmol/kg acetate + 50 mmol/kg AQDS. Acetate represents a labile form of organic carbon that is easily accessible as an electron donor for microbial respiration (e.g., reduction of metal oxides/oxyhydroxides; Crill and Martens, 1986; Islam et al., 2004; Lovley and Chapelle, 1995; Pearcy et al., 2011; Rowland et al., 2007). AQDS is a compound analogous to humic acids, which acts as an electron shuttle to overcome the need for microbes to be in direct contact with poorly soluble electron acceptors such as Fe(III) oxides/oxyhydroxides (Rowland et al., 2007). For sterilized controls, sediments were sterilized in an autoclave for 20 min at 121°C and 1.1 atm before addition of the sterilized deoxygenated “artificial groundwater” solution. For each experiment, 10 g of the well-mixed sediments from the Napoleonville site and 30 mL of the sterilized “artificial groundwater” solution were added to each bottle. The bottles were then plugged with butyl rubber stoppers and sealed with an aluminum (Al) clamp under the inert N₂ atmosphere within the glove box. Each experiment was prepared in triplicate for six specific reaction periods (i.e., 2, 7, 14, 21, 28, and 35 days).

### 3.3.2.3 Sample Collection and Analysis

After each specific reaction period, the solution-sediment slurries were transferred into a 50 mL centrifuge tube and centrifuged for 40 min at 3000 rcf (i.e., relative centrifugal force) to separate sediments from solutions. The supernatant was then filtered through a 0.45 µm syringe filter (EMD Sterivex-HV) into a 15 mL centrifuge tube and
immediately acidified with ultrapure HNO$_3$ (Seastar) to pH < 2. After storage in a refrigerator for about two weeks, light gray flocculants formed in most of the filtered and acidified solutions. To identify the flocculants, the filtered and acidified solutions were re-centrifuged for another 10 min to separate the flocculants from solutions. The supernatant was then transferred into a 15 mL centrifuge tube for analysis of As, Fe, and Mn concentrations using HR-ICP-MS following previously described procedures (Datta et al., 2011; Haque et al., 2008; Pearcy et al., 2011). The composition of the flocculants was investigated using a Hitachi S-3400 Scanning Electron Microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) and an Oxford Inca Elemental Analyzer. For the SEM-EDS analysis, two drops of the flocculants were placed on an Al stub and heated to evaporate excess water. The dried samples was observed and analyzed at 20kV. For organic carbon analysis, the flocculants were carefully transferred dropwise into a small silver foil and dried at 60 °C in an oven. The above procedures were repeated until about 10 mg of the dried flocculants were collected, and then the dried samples were analyzed using the Elemental Analyzer.

3.4 Results

3.4.1 Sediment Porewaters

Porewater pH values ranged between 7.00 and 8.12 (Table 3.2), indicating that groundwaters in the Napoleonville region were predominantly neutral to slightly alkaline. Arsenic, Fe, and DOC concentrations in porewaters varied, from 0.3 µg/L to 158 µg/L, from 0.01 mg/L to 21.5 mg/L, and from 6.0 mg/L to 31.6 mg/L, respectively (Table 3.2).
In core A, porewater As and Fe concentrations were positively associated ($r = 0.92$; Figure 3.2a). Both As and Fe concentrations decreased from 158 µg/L and 6.0 mg/L, respectively, at a depth of 100 cm (silty loam) to 9 µg/L and 0.03 mg/L, respectively, at a depth of 130 cm (silty clay loam), and then increased to 74 µg/L and 0.4 mg/L, respectively, at a depth of 160 cm (mixture of silty clay loam and silty loam; Table 3.2, Figure 3.3a). In contrast, As and DOC concentrations in porewaters showed an inverse relationship ($r = -0.74$; Figure 3.2b) and exhibited a mirror image pattern with depth (Figure 3.3a), such that DOC increased from 13.6 mg/L at 100 cm to 21.9 mg/L at 130 cm, and then decreased to 12.2 mg/L at 160 cm (Table 3.2, Figure 3.3a). Nonetheless, it is important to stress that because of the limited number of porewater samples we were able to extract from core A ($n = 3$), neither the relationships between As and Fe nor As and DOC were statistically significant. In addition to dissolved components, we also measured the SOC content of sediments from core A, which increased from 0.41% at 100 cm to 0.56% at 130 cm and finally to 0.6% at 160 cm. The SOC content was higher in the fine-grained sediments (e.g., silty clay loam) than in the overlying coarse-grained sediments (e.g., silty loam).

For core B, porewater As concentrations were positively correlated with Fe ($r = 0.96$) as well as with DOC ($r = 0.95$; Figure 3.2c-d), both of which were significant at the 99% confidence level, and consequently, all three display similar trends with depth (Figure 3.3b). Specifically, As, Fe, and DOC concentrations increased from 0.3 µg/L, 0.01 mg/L, and 10.6 mg/L, respectively, at a depth of 150 cm (silty clay loam) to 8 µg/L, 1.5 mg/L, and 31.6 mg/L, respectively, at a depth of 720 cm (sandy loam) (Table 3.2, Figure 3.3b).
Table 3.2 Porewater pH, As, Fe, and DOC concentrations, sediment texture, and sedimentary organic carbon (SOC) at various depths of the sediment cores collected in Napoleonville, southern Louisiana, United States (See Figure 3.1 and 3.2 for sediment core locations and stratigraphy).

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth (cm)</th>
<th>pH</th>
<th>As (µg/L)</th>
<th>Fe (mg/L)</th>
<th>DOC (mg/L)</th>
<th>Sediment Texture*</th>
<th>SOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>7.26</td>
<td>158</td>
<td>6.0</td>
<td>13.6</td>
<td>Silty loam</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.05</td>
<td>9</td>
<td>0.03</td>
<td>21.9</td>
<td>Silty clay loam</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>7.94</td>
<td>74</td>
<td>0.4</td>
<td>12.2</td>
<td>Silty clay loam + silty loam</td>
<td>0.61</td>
</tr>
<tr>
<td>B</td>
<td>150</td>
<td>7.35</td>
<td>0.3</td>
<td>0.01</td>
<td>10.6</td>
<td>Silty clay loam</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>7.28</td>
<td>1</td>
<td>0.01</td>
<td>6.0</td>
<td>Silty loam</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>7.45</td>
<td>4</td>
<td>0.6</td>
<td>18.2</td>
<td>Silty clay + clay</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>7.47</td>
<td>5</td>
<td>0.6</td>
<td>21.0</td>
<td>Humic clay</td>
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<tr>
<td></td>
<td>700</td>
<td>7.73</td>
<td>4</td>
<td>0.9</td>
<td>23.8</td>
<td>Sandy loam</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>7.26</td>
<td>8</td>
<td>1.5</td>
<td>31.6</td>
<td>Sandy loam</td>
<td>ND</td>
</tr>
<tr>
<td>C</td>
<td>150</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Silty clay loam</td>
<td>3.99</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Silty clay + clay</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Silty loam</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Silty clay loam</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>8.12</td>
<td>58</td>
<td>11.1</td>
<td>ND</td>
<td>Sandy loam</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>610</td>
<td>7.15</td>
<td>32</td>
<td>21.5</td>
<td>ND</td>
<td>Sandy loam</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>680</td>
<td>7.00</td>
<td>52</td>
<td>20.2</td>
<td>ND</td>
<td>Sand</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>7.10</td>
<td>38</td>
<td>20.4</td>
<td>ND</td>
<td>Sand</td>
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<td>ND</td>
<td>ND</td>
<td>Silty clay loam</td>
<td>4.75</td>
</tr>
</tbody>
</table>

* Sediment texture is classified based on USDA soil classification method. ND - data not determined.
Figure 3.2 Scatter plots showing relationships between porewater As, Fe, and DOC concentrations extracted from sediment cores A (a-b), B (c-d), and C (e). Lines represent linear regression of the data in each plot. Analytical uncertainties for many of the analyses are of the same order as the symbols.
Figure 3.3 Results of porewater analysis for pH, concentrations of As (µg/L), Fe (mg/L), and DOC (mg/L) extracted from different depths of cores A (a), B (b), and C (c). Also shown are the cores’ stratigraphy, SOC and LOI analyses. Analytical uncertainties for many of the analyses are of the same order as the symbols.
In core C, porewater As and Fe concentrations were inversely related ($r = -0.78$, not statistically significant; Figure 3.2e), and exhibited different trends as a function of depth (Figure 3.3c). Specifically, between depths 520 cm and 720 cm (i.e., interbedded silty loam and fine sand), As concentrations were relatively constant, varying between 32 µg/L and 59 µg/L, whereas Fe concentrations doubled between depths 520 cm and 610 cm, and then remained constant with depth to 720 cm (Table 3.2, Figure 3.3c). Although we were unable to quantitatively measure DOC concentrations in core C, the SOC contents were estimated by LOI. As observed in core A, the SOC contents, as reflected by the LOI measurements, in core C exhibited relatively higher values in the fine-grained sediments (i.e., silty clay loam and silty clay) than in the coarse-grained sediments (i.e., silty loam, sandy loam, and sand) (Figure 3.2 and 3.3).

### 3.4.2 Sediment Incubation

As mentioned above, upon acidification and cold storage (4 °C for ~ 2 weeks) prior to analysis, light gray flocculants formed in most of the filtered and acidified experimental solutions. Of the four experiments, the smallest amount of flocculants was produced in solutions from the sterilized control experiments, whereas the largest amount formed in the experiments amended with acetate and acetate + AQDS. Analysis of the flocculants by SEM-EDS and the Elemental Analyzer indicated that the flocculants were composed of O, Fe, S, Si, and organic carbon (Figure 3.4a-b). Aluminum and N are excluded from the analytical results because the sample stub used in SEM-EDS is made of Al and owing to the fact that the solutions were initially acidified with ultrapure HNO₃.
Arsenic, Fe, and Mn concentrations in the experimental solutions are summarized in Table 3.3, 3.4, 3.5, and presented as a function of time in Figure 3.5. Concentrations of As, Fe, and Mn were the lowest in the sterilized control experiments, where As, Fe, and Mn ranged from 30 ± 5.4 µg/L to 50 ± 4.3 µg/L, 0.1 ± 0.01 mg/L to 3.0 ± 1.8 mg/L, and 16 ± 5.4 µg/L to 113 ± 22 µg/L, respectively. More specifically, As concentrations remained relatively constant around 49 ± 1.1 µg/L during the initial 21 days of the experiments, and then slightly decreased to 35 ± 3.8 µg/L towards the end of the experiments (Table 3.3, Figure 3.5a). In contrast, Fe and Mn concentrations remained relatively constant around 0.5 ± 0.3 mg/L and 21 ± 6.4 µg/L, respectively, during the initial 14 days, and then increased to 3.0 ± 1.8 mg/L and 113 ± 22 µg/L, respectively, at the end of the experiments (Table 3.4-3.5, Figure 3.5b-c). At the end of each experiment, the pH of the solutions typically increased to 8.60 in the sterilized control experiments, 8.72 in the un-amended experiments, 8.44 in the acetate amended experiments, and 8.69 in the experiments amended with both acetate and AQDS. The relatively high HCO$_3^-$ concentration of the artificial groundwater solution used in the batch incubations (i.e., 4.4 mmol/L) acted as a relatively effective buffer against dramatic changes in pH values of the experimental solution. The slightly higher pH values of the solutions at the end of each experiment are expected to lead to slightly higher As concentrations in solutions, whereas the opposite effect is expected for Fe and Mn (e.g., Drever, 1988; Johannesson and Tang, 2009).
Figure 3.4 Results of composition analysis of flocculants by (a) the Elemental Analyzer (b) SEM-EDS. These qualitative data suggests that the flocculants are chiefly composed of Fe-rich organic matter.
Table 3.3 Summary of As released from sediments during the incubation experiments. Arsenic concentration (µg/L) data represent the mean ± standard deviation of triplicate measurements.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Control</th>
<th>Anaerobic</th>
<th>Anaerobic + acetate</th>
<th>Anaerobic + acetate + AQDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>47 ± 8.5</td>
<td>80 ± 2.6</td>
<td>53 ± 4.1</td>
<td>31 ± 1.2</td>
</tr>
<tr>
<td>7</td>
<td>50 ± 4.3</td>
<td>54 ± 12</td>
<td>70 ± 22</td>
<td>23 ± 0.7</td>
</tr>
<tr>
<td>14</td>
<td>49 ± 5.8</td>
<td>37 ± 2.0</td>
<td>129 ± 24</td>
<td>90 ± 1.9</td>
</tr>
<tr>
<td>21</td>
<td>49 ± 2.5</td>
<td>82 ± 5.8</td>
<td>148 ± 14</td>
<td>380 ± 11</td>
</tr>
<tr>
<td>28</td>
<td>30 ± 5.4</td>
<td>64 ± 9.7</td>
<td>191 ± 14</td>
<td>360 ± 27</td>
</tr>
<tr>
<td>35</td>
<td>35 ± 3.8</td>
<td>72 ± 6.7</td>
<td>197 ± 6.9</td>
<td>337 ± 21</td>
</tr>
</tbody>
</table>

Table 3.4 Summary of Fe released from sediments during the incubation experiments. Iron concentration (mg/L) data represent the mean ± standard deviation of triplicate measurements.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Control</th>
<th>Anaerobic</th>
<th>Anaerobic + acetate</th>
<th>Anaerobic + acetate + AQDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.7 ± 0.4</td>
<td>33 ± 0.1</td>
<td>24 ± 1.3</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>0.7 ± 0.7</td>
<td>22 ± 9.8</td>
<td>0.6 ± 0.1</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>14</td>
<td>0.1 ± 0.01</td>
<td>8.0 ± 1.8</td>
<td>1.2 ± 0.1</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>21</td>
<td>1.9 ± 0.9</td>
<td>39 ± 6.6</td>
<td>1.9 ± 0.2</td>
<td>7.4 ± 2.1</td>
</tr>
<tr>
<td>28</td>
<td>2.9 ± 2.2</td>
<td>40 ± 6.0</td>
<td>1.9 ± 0.3</td>
<td>10.5 ± 2.2</td>
</tr>
<tr>
<td>35</td>
<td>3.0 ± 1.8</td>
<td>60 ± 8.8</td>
<td>1.9 ± 0.1</td>
<td>10.9 ± 2.0</td>
</tr>
</tbody>
</table>

Table 3.5 Summary of Mn released from sediments during the incubation experiments. Manganese concentration (µg/L) data represent the mean ± standard deviation of triplicate measurements.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Control</th>
<th>Anaerobic</th>
<th>Anaerobic + acetate</th>
<th>Anaerobic + acetate + AQDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>17 ± 3.8</td>
<td>220 ± 17</td>
<td>164 ± 12</td>
<td>14 ± 1.8</td>
</tr>
<tr>
<td>7</td>
<td>30 ± 17</td>
<td>192 ± 80</td>
<td>46 ± 13</td>
<td>30 ± 3.0</td>
</tr>
<tr>
<td>14</td>
<td>16 ± 5.4</td>
<td>90 ± 18</td>
<td>69 ± 8.0</td>
<td>103 ± 45</td>
</tr>
<tr>
<td>21</td>
<td>61 ± 14</td>
<td>442 ± 45</td>
<td>89 ± 6.9</td>
<td>311 ± 59</td>
</tr>
<tr>
<td>28</td>
<td>101 ± 27</td>
<td>589 ± 64</td>
<td>131 ± 12</td>
<td>446 ± 59</td>
</tr>
<tr>
<td>35</td>
<td>113 ± 22</td>
<td>857 ± 154</td>
<td>135 ± 3.7</td>
<td>431 ± 63</td>
</tr>
</tbody>
</table>

For the un-amended (i.e., anaerobic, no added acetate or AQDS) experiments, As, Fe, and Mn concentrations in solutions were generally higher than for the sterilized
control experiments (Table 3.3-3.5, Figure 3.5a-c). For example, As, Fe, and Mn concentrations ranged from $37 \pm 2.0 \, \mu g/L$ to $82 \pm 5.8 \, \mu g/L$, $8.0 \pm 1.8 \, mg/L$ to $60 \pm 8.8 \, mg/L$, and $90 \pm 18 \, \mu g/L$ to $857 \pm 154 \, \mu g/L$, respectively. The concentrations of all three trace elements initially decreased in solutions over the first 14 days, and generally increased thereafter (Figure 3.5a-c). Compared to the sterilized control experiments, the relative increases in Fe and Mn concentrations were much more pronounced than for As, which remained relatively constant around $73 \pm 7.4 \, \mu g/L$ (i.e., the average $\pm \sigma$ (standard deviation) for day 21, 28, and 35) after doubling in concentrations between days 14 and 21 (Figure 3.5a-c). The un-amended experiments are the closest representation of the field conditions, and As and Fe concentrations in the un-amended experimental solutions are comparable to As (i.e., mean $\pm \sigma = 34 \pm 45 \, \mu g/L$) and Fe (i.e., mean $\pm \sigma = 6.4 \pm 8.7 \, mg/L$) in porewaters collected from the coarse-grained sediment layers within cores A and C.

In the acetate amended experiments, As concentrations increased almost monotonically over the course of the experiments and attained higher concentrations in solutions at the end of the experiments than either the sterilized control experiments or the un-amended experiments (Figure 3.5a). For example, As concentrations increased from $53 \pm 4.1 \, \mu g/L$ at day 2 to $197 \pm 6.9 \, \mu g/L$ at day 35, or at a rate of $\sim 4.4 \, \mu g/L/\text{d}$ (i.e., $\mu g/L$ per day). In contrast, Fe and Mn concentrations in solutions decreased over the first 7 days, and then exhibited relatively constant concentrations for the remainder of the experiments (Figure 3.5b-c). Compared to the un-amended experiments, As concentration in solutions were roughly twice as high in the acetate amended experiments, whereas Fe
and Mn experienced substantial decreases, especially after the initial decreases in the acetate amended solutions.

The experiments amended with both acetate and AQDS exhibited the greatest As release as indicated by the highest As concentrations attained (i.e., 380 ± 11 µg/L) in these solutions (Table 3.3, Figure 3.5a). Arsenic, Fe, and Mn concentrations in solutions exhibited similar trends as a function of time, which followed broadly “S-shaped” curves over the 35 day course of the experiments (Figure 3.5a-c). More specifically, the release rates of As, Fe, and Mn between day 7 and day 21 were 25.5 µg/L/d, 500 µg/L/d, and 20.1 µg/L/d, respectively, whereas between day 21 and day 35, the release either stopped (e.g., As, with a release rate of -3.1 µg/L/d) or decreased (e.g., Fe, with a release rate of 250 µg/L/d, and Mn exhibited a release rate of 8.6 µg/L/d). Decreases in release rates led to a plateau in As, Fe, and Mn concentrations by the end of the experiments. For example, the mean ± σ of As, Fe, and Mn from day 28 to 35 were 348 ± 24 µg/L, 10.7 ± 2.1 mg/L, and 438 ± 61 µg/L, respectively (Table 3.3-3.5).
Figure 3.5 Concentrations of (a) As (µg/L), (b) Fe (mg/L), and (c) Mn (µg/L) in the experimental solutions from the sterilized control, the un-amended anaerobic, the anaerobic + acetate, and the anaerobic + acetate + AQDS experiments. Symbols and error bars represent the mean and standard deviations of the triplicate analyses of each experiment.
3.5 Discussion

3.5.1 Arsenic in the Napoleonville Groundwater

Reductive dissolution of Fe(III) oxides/oxyhydroxides is generally considered the primary mechanism controlling As release from sediments to groundwaters in the reducing anoxic aquifers of South and Southeast Asia (Harvey et al., 2005; Mailloux et al., 2009; McArthur et al., 2004; Nickson et al., 2000; Polizzotto et al., 2008; Zheng et al., 2004). The positive relationship between As and Fe concentrations in porewaters extracted from cores A (r = 0.92) and especially core B (r = 0.96, p < 0.01) at the Napoleonville site supports the probability that reductive dissolution of Fe(III) oxides/oxyhydroxides also plays an important role in As release from sediments to shallow groundwaters at the Napoleonville site in southern Louisiana. In contrast, DOC and particularly SOC were inversely related to As and Fe in porewaters from core A (Figure 3.3a). Closer examination of the stratigraphy of core A revealed that porewater As and Fe concentrations were the lowest within the fine-grained sediment layer (i.e., silty-clay), and substantially higher in the coarse-grained sediment layer (i.e., silt and silty loam) above and directly below the clay layer (Figure 3.3a). Furthermore, DOC concentrations in porewaters were the highest in the clay-rich layer and substantially lower in the silt-rich layer above and below the clay layer. Sedimentary organic carbon (SOC) as estimated by LOI is also generally higher in the fine-grained sediments where As was relatively low compared to the coarse-grained sediments (Figure 3.3a).

Taken together the field data from the Napoleonville site suggest that the fine-grained, clay-rich sediments act as a source of labile DOC that fuels microbial reduction
of Fe(III) oxide/oxyhydroxides by respiratory microbes, and subsequent release of sorbed and/or co-precipitated As to the shallow groundwaters. More specifically, we submit that fermentative bacteria within the fine-grained, clay-rich layers degrade SOC to produce small, labile forms of DOC such as acetate, lactate, and propionate. These labile, short-chain fatty acids subsequently diffuse from the clay-rich sediment layers into the overlying and underlying coarse-grained silt- and sand-rich layers, where they act as electron donors for Fe-reducing bacteria (e.g., Chapelle and Bradley, 1996; McMahon and Chapelle, 1991). The Fe-reducing bacteria solubilize Fe by reductive dissolution of Fe(III) oxide/oxyhydroxides, which also liberates adsorbed and/or co-precipitated As to the local shallow groundwaters.

In the case of core B, the majority of porewater samples were extracted from the clay-rich sediments, and only the deepest porewater samples (depth > 700 cm) were from the coarse-grained sediments (i.e., silt loam, sandy loam, and sand). Consequently, As and Fe concentrations in porewaters were generally low (As < 5 µg/L and Fe < 1 mg/L) for all but the deepest sample (Table 3.2, Figure 3.3b), compared to what was observed in porewaters from core A. In contrast, DOC concentrations in porewaters were generally high in core B, but similar in magnitude to DOC concentrations (≥ 20 mg/L) also measured in porewaters from the clay-rich sediments in core A. The combination of the stratigraphic data and porewater chemistry from core B are also generally consistent with the above proposed model, whereby microbial respiration that leads to As mobilization is chiefly limited to the coarse-grained sediments, where DOC, derived from fermentation of SOC in the clay-rich sediments and subsequent diffusion of labile DOC, drives microbial respiration in the coarse-grained sediments.
In the case of core C, porewater As and Fe concentrations are generally an order of magnitude higher than in core B (Figure 3.3c). A critical difference between the porewater samples from cores C and B is that all of the porewater samples from core C were extracted from the coarse-grained sediments (i.e., silt, silty loam, sandy loam, sand), as compared to the porewater samples from core B that were mainly extracted from the fine-grained sediments (i.e., silty clay, clay). Compared to core B, the 10-fold higher As and Fe concentrations in porewaters from core C suggests that microbial reduction of Fe(III) oxides/oxyhydroxides in the coarse-grained sediments is the dominant process controlling As mobilization to the porewaters. This hypothesis is further supported by the SOC data, which exhibited higher values in the fine-grained sediments as compared to the underlying coarse-grained sediments.

Overall, the data presented for the Napoleonville sediment cores and associated porewaters support the above proposed model that As release from sediments is largely confined to the coarse-grained sediments where microbial respiratory processes dominate over fermentation, and also, that the organic carbon fueling microbial Fe(III) (and possibly sulfate) reduction is sourced from the clay-rich layers within these sediments (Bethke et al., 2008; Chapelle and Bradley, 1996; McMahon and Chapelle, 1991). Future detailed field sampling at the Napoleonville site and other locations in southern Louisiana are underway to test this mechanism of As mobilization.

3.5.2 Incubation Experiments

As suggested by our field data from Napoleonville, Louisiana (Figure 3.3), and many studies in South and Southeast Asia, As mobility is strongly affected by reduction
of As-bearing Fe(III) oxides/oxyhydroxides in the reducing anoxic aquifers (Harvey et al., 2005; McArthur et al., 2004; Nickson et al., 2000; Polizzotto et al., 2008). Consequently, factors that influence Fe mobility, such as DOC (e.g., humic and fulvic acids) concentrations are also expected to affect As mobility in groundwater systems (Redman et al., 2002; Catrouillet et al., 2014). For example, Fe(II) released by reductive dissolution of Fe(III) oxides/oxyhydroxides can bind with humic acids to form Fe(II)-organic complexes (Catrouillet et al., 2014) and further facilitate reduction of Fe(III) oxides/oxyhydroxides and subsequent As release to groundwaters. Because this process can lead to decreases in Fe concentrations and increases in As concentrations in solutions, it may be another plausible explanation for the commonly observed decoupling of Fe and As concentrations in groundwaters (Horneman et al., 2004; Radloff et al., 2007; van Geen et al., 2004). The flocculants formed in the filtered and acidified solutions from the incubation experiments described herein contain Fe, O, S, and organic carbon (Figure 3.4). Thus, the composition of the flocculants and the fact that they only formed in the experimental solutions upon acidification, strongly suggests that they represent Fe- and S-rich, organic compounds like humic acid. The formation of these putative organic flocculants likely removed some Fe, Mn, and possibly even As from solutions in the incubation experiments, which may also explain the decoupling of As from Fe in some of these experiments (e.g., Figure 3.5a-c). Although we suggest that this same mechanism may explain the decoupling between As and Mn reported in some of our experiments (Figure 3.5), because the Mn contents of the flocculants were too low to be detected by the SEM-EDS, we cannot evaluate this possibility.
The sterilized control experiments exhibited the lowest As (except at day 14), Fe, and Mn concentrations of all the experimental solutions (Table 3.3-3.5; Figure 3.5). Because the sediments used in these experiments were initially sterilized, the results largely represent the effect of abiotic processes on As mobility. This “pool” of As is consistent with readily exchangeable As that is weakly adsorbed onto mineral surfaces in the sediments (Pearcy et al., 2011). Another factor that may also affect As release from the sterilized sediments is that autoclaving may have changed the sediment properties, resulting in aggregation of sediment particles and consequent reduction of sediment surface area (Lotrario et al., 1995; Trevors, 1996). Additionally, sterilization by autoclave may increase the degree of crystallinity of initially amorphous Fe(III) oxides/oxyhydroxides, which can subsequently inhibit As release from sediments (Radloff et al., 2008). Nonetheless, the release of the readily exchangeable As “pool” caused by abiotic processes is fast, and was completed within the first 2 days of the experiments, after which As concentrations remained relatively constant at 49 ± 0.6 µg/L (the average for day 7, 14, and 21) until day 21 (Figure 3.5a). The fast release of As from the sterilized Napoleonville sediments is consistent with our previous study of As release from sterilized sediments collected from the Aquia aquifer in Maryland, USA (Pearcy et al., 2011), as well as a number of other investigations of sediments from South and Southeast Asia (Islam et al., 2004; Radloff et al., 2007; Rowland et al., 2007). Arsenic concentrations in the sterilized solutions exhibited a decrease (e.g., 30%) after day 21, which may reflect re-adsorption of As onto un-reacted Fe(III) oxides/oxyhydroxides (Oremland and Stolz, 2005), clay minerals, and/or the newly formed Fe(II)-S-organic flocculants. Unfortunately, as in the case for Mn detection by SEM-EDS in the
flocculants, the As content of the flocculants was also too low to be detected by SEM-EDS. Considering the variability in the measurements by HR-ICP-MS, Fe and Mn released in the sterilized control experiments were low and remained relatively constant for the first 14 days, and then exhibited a slight increase until the end of the incubation. The gradual Fe and Mn release could be due to abiotic dissolution of newly formed secondary Fe and Mn minerals including magnetite (Fe$_3$O$_4$), siderite (FeCO$_3$), and rhodochrosite (MnCO$_3$) during the experiments (Lloyd, 2003; Coker et al., 2006).

Arsenic released in the un-amended experiments was generally higher (i.e., by up to a factor of 2) than the sterilized control experiments (Table 3.3). Because As released from the sterilized sediments only reflects abiotic processes, the higher amount of As released in the un-amended experiments must represent the amount of As mobilized by both abiotic and biotic processes in the incubation experiments. We propose that the additional As release in the un-amended experiments reflects biotic release by microbial respiration that can occur using the natural organic carbon content of the particular sediment aliquot (Figure 3.5b; Pearcy et al., 2011). Consequently, the additional As released in the un-amended experiments is consistent with microbial mediated release of As in addition to release of the readily exchangeable As “pool” by, for example, desorption and/or ion-exchange processes. The amounts of Fe and Mn released from the un-amended sediments were also substantially higher than the sterilized sediments (Table 3.4 and 3.5). The large increases in Fe and Mn concentrations in the un-amended solutions are consistent with the notion that microbial reduction of Fe(III)/Mn(III) oxide/oxyhydroxides and the subsequent releases of Fe(II) and Mn(II) have occurred in these experiments. Another possible explanation of the As concentrations increase in the
un-amended experiments is that the adsorbed or co-precipitated As(V) associated with Fe(III)/Mn(III) oxides/oxyhydroxides is being directly reduced to As(III) and subsequently mobilized into solutions (Oremland and Stolz, 2005). Future investigations that include As speciation analysis of the solutions and sediments are needed to test this hypothesis.

For the un-amended anaerobic incubation experiments, the As, Fe, and Mn concentrations follow similar trends over the course of the experiments, decreasing during the first 14 days and then increasing until the end of the experiments (Figure 3.5). The initial decreases in As, Fe, and Mn concentrations in solutions may reflect re-adsorption of the previously released readily exchangeable As (e.g., the sterilized controls) as well as loss of all three trace elements onto the newly formed organic flocculants. Nonetheless, with the increase of reaction time, microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides appear to dominate, causing increases in As, Fe, and Mn concentrations after day 14. Compared to the sterilized control experiments, the near doubling of As release in the un-amended sediments strongly suggests that microbial respiration plays an important role in mobilizing As from these sediments. As mentioned above, the un-amended incubation experiments are perhaps most similar to the situation observed in the majority of the porewater/sediment samples from the Napoleonville study site in terms of the comparable As and Fe concentrations in solution. Nevertheless, the chief exceptions are the porewaters from sediment core A, for which As concentrations attain substantially higher values (i.e., up to 158 µg/L; Table 3.2, Figure 3.3), and groundwaters from the same vicinity as core A, where we report an As concentration of 100 µg/L (Figure 3.1). Indeed, the As concentrations of these groundwaters and the
acetate amended incubation experiments described below are supportive of the notion that diffusion of labile organic carbon from the interlayered clay-rich sediments is required at the Napoleonville site to generate porewater As concentrations that can exceed ~ 100 µg/L.

Addition of acetate substantially accelerates microbial respiration (Islam et al., 2004; Pearcy et al., 2011; Radloff et al., 2007, 2008), resulting in greater As release to the experimental solutions than observed in either the sterilized control experiments or the un-amended experiments (Figure 3.5c). Addition of acetate also appeared to accelerate the formation of Fe- and S- rich organic flocculants, which led to decreases in Fe and Mn concentrations in solutions (i.e., the decrease took 14 days in the un-amended experiments, compared to only 7 days in the acetate amended experiments). However, to address such questions additional experiments will be necessary to closely monitor the timing of the formation of the organic flocculants, the corresponding solution concentrations of As, Fe, and Mn, as well as the changing concentrations of these trace elements within the flocculants as they form and precipitate. With sufficient acetate as electron donor, microbe-facilitated reduction of other electron acceptors such as sulfate and arsenate may co-occur with Fe(III)/Mn(III) reduction, causing continuous As release into solutions even at times when the hypothesized scavenging of Fe and Mn by the organic flocculants is occurring (e.g., the first 7 days). After 7 days, however, microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides appeared to dominate (Table 3.4 and 3.5), and As concentrations increased with increasing Fe and Mn concentrations until the end of the experiments (Table 3.3).
Addition of AQDS to the acetate amended experiments also appeared to accelerate the formation of Fe- and S- rich organic flocculants, which again may explain the associated decreases in Fe and Mn concentrations in solutions (i.e., finished in 7 days for Fe and 2 days for Mn). After the initial decreases in Fe and Mn concentrations, microbial reduction of Fe(II)/Mn(II) oxides/oxyhydroxides again appeared to dominate, as suggested by the increases in these metals in solutions (Table 3.4 and 3.5). Arsenic concentrations also started to increase after day 7 until day 21, and then remained relatively constant until the end of the experiments. Both Fe and Mn concentrations generally increased until day 28 and then reached a plateau at the end of the experiments. The “plateauing” of As, Fe, and Mn concentrations suggests that either the maximum amounts of available Fe, Mn, and As that can be mobilized by microbial respiration in the Napoleonville sediments have been reached by ~ days 21/28, or that the acetate added in the sediment incubations has been completely consumed, where upon microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides gradually stops after day 21. The fact that the amounts of Fe and Mn released from the sediments in the un-amended experiments were much higher than the amended experiments suggests that given a constant labile DOC source, it is possible that additional amounts of As could be mobilized from sediments due to microbial reduction of Fe(III)/Mn(III) oxides/oxyhydroxides. Thus, the addition of the electron shuttling compound (AQDS) appears to have further stimulated microbial respiration in these sediment incubations compared to the analogous experiments with only acetate added.

Compared to the un-amended experiments, the amended (i.e., acetate and acetate + AQDS) experiments attained much higher As concentrations in solutions. These results
are consistent with the addition of acetate and AQDS acting to facilitate increase in microbial respiration and hence, As mobilization by 2-fold (e.g., 197 µg/L) in the acetate amended experiments and 4-fold (i.e., 380 µg/L) in the experiments amended with both acetate and AQDS at the end of the experiments (Table 3.3). Furthermore, results of the incubation experiments support the conclusion of our field sampling and analysis, which strongly suggest that microbes play an important role in mobilizing As from sediments to shallow groundwaters at the Napoleonville site in southern Louisiana.

3.6 Conclusions

Arsenic and Fe concentrations in porewaters from Napoleonville, Louisiana, varied by an order of magnitude between the coarse-grained silt- and sand-rich sediment layers (e.g., As up to 158 µg/L) and the fine-grained clay-rich sediment layers (e.g., As < 10 µg/L). Porewater samples high in As concentrations were generally associated with high Fe and DOC concentrations. Therefore, results of porewater analysis support the hypothesis that As mobilization from sediments mainly occurs in the coarse-grained sediments where microbial reduction of Fe(III) oxides/oxyhydroxides dominates the As mobilization, and also, DOC fueling microbial Fe(III) reduction is sourced from the clay-rich layers (Bethke et al., 2008; McMahon and Chapelle, 1991). Incubation experiments using sediments from the Napoleonville site support the hypothesis that microbial reduction of Fe(III) oxides/oxyhydroxides is the chief mechanism controlling As release from sediments to shallow groundwaters at the study site in southern Louisiana. Specifically, As concentrations in the experimental solutions were low in the sterilized control experiments, slightly higher in the un-amended experiments, and the highest in
the experiments amended with acetate and acetate + AQDS. Compared to the un-amended experiments, addition of acetate and AQDS resulted in an increase in As concentrations by a factor of 2 (i.e., acetate) to 4 (i.e., acetate + AQDS). However, addition of acetate and AQDS in the amended experiments resulted in the formation of Fe- and S- rich organic flocculants in the experimental solutions, which appeared to have scavenged Fe and Mn, and perhaps even As, from solutions, leading to lower than expected concentrations of these trace elements (especially Fe and Mn) in the experimental solutions. Although As release did not exactly follow the same trend as Fe and Mn, As concentrations generally increased with increasing Fe and Mn concentrations in solutions. Results of the incubation experiments support our hypothesis that microbial reduction of As-bearing Fe(III)/Mn(III) oxides/oxyhydroxides is the primary mechanism causing As release from sediments to groundwaters at the Napoleonville site in southern Louisiana.

Published concentrations of As in groundwaters and aquifer sediments from southern Louisiana are currently limited, and the mechanisms controlling As mobilization from aquifer sediments in this region are likely complex and diverse. Therefore, future investigations should focus on: (1) determination of As concentrations and speciation in both groundwaters and aquifer sediments from the Mississippi Delta region; (2) identification of competing chemical reactions that affect As concentrations and speciation in both aqueous and the solid phases of the aquifer matrix (e.g., Oremland and Stolz, 2003); (3) ascertaining historical use and loading of anthropogenic As sources to the environment; and (4) assessing factors that can be used as parameters for predicting natural groundwater As distribution (Yang et al., 2014). Because groundwaters are
important domestic and municipal water source in southern Louisiana, a better and complete understanding of As distribution in groundwaters is essential to the health of the local population.

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Chapter 4

Geochemical cycling of arsenic (As) along a groundwater flow path in the southeastern Chicot aquifer, southern Louisiana, United States

Abstract

Total dissolved arsenic ($\text{As}_T$) and As(III) were measured in groundwaters collected along a 10 km flow path within the southeastern Chicot aquifer in southern Louisiana, United States, along with total dissolved iron ($\text{Fe}_T$) and Fe(II), and sulfide [S(-II)], major solutes, pH, alkalinity, oxidation-reduction potential (Eh), total dissolved solids (TDS), and specific conductivity. Results showed that 40% of the sampled wells contained groundwaters with $\text{As}_T > 133$ nmol/kg (i.e., 10 µg/L, WHO safe drinking water standard). Along the flow path, $\text{As}_T$ ranged from 0.5 nmol/kg (0.04 µg/L) to 644 nmol/kg (48 µg/L), with As(III) as the predominant species ranging from 0.2 nmol/kg (0.01 µg/L) to 309 nmol/kg (23 µg/L). Dissolved $\text{Fe}_T$ ranged from 32 µmol/kg (1.77 mg/L) to 53 µmol/kg (2.93 mg/L), with Fe(II) as the predominant species, which ranged from 18 µmol/kg (0.99 mg/L) to 47 µmol/kg (2.62 mg/L). Dissolved S(-II) concentrations in the southeastern Chicot aquifer groundwaters were generally below the detection limit (i.e., 0.16 µmol/kg), although concentrations did increase around the mid-reaches of the flow path. Dissolved $\text{As}_T$ and As(III) concentrations were positively correlated with $\text{Fe}_T$ ($r = 0.63$) and Fe(II) concentrations, respectively. Biogeochemical reactive transport modelling was able to capture the general trends of Fe(II), As(III), and As(V) along the studied flow path and also demonstrated that high Fe(II) and As(III) groundwaters were consistent with microbially mediated reduction of Fe(III) oxidex/oxyhydroxides that
occurred along the studied flow path. The fact that the well correspondence between the measured and the model predicted Fe(II) and As(III) concentrations at the mid-reaches of the studied flow path suggests that reductive dissolution of Fe(III) oxides/oxyhydroxides and the subsequent release of sorbed and/or co-precipitated As is the main mechanism controlling As mobilization in the southeastern Chicot aquifer.

4.1 Introduction

Arsenic (As) is one of the most toxic and carcinogenic elements naturally occurring in the environment (Haque et al., 2008; Smedley and Kinniburgh, 2002; Smith et al., 2000). Long-term consumption of groundwaters with elevated As concentrations is known to cause serious health problems, including increased risk of various cancers (e.g., skin, lung, bladder, liver, and kidney) (Chen et al., 1992; Smith et al., 2002), increased infant mortality (Rahman et al., 2010), and reduced intellectual and motor function in children (Parvez et al., 2011). As such, groundwaters contaminated with As have been recognized as a major threat to human health, especially in areas that are heavily dependent on groundwaters as the chief drinking water source. It was estimated by Ravenscroft et al. (2009) that as of 2009, at least 140 million people were drinking As-contaminated groundwaters in the world. Therefore, understanding As geochemical cycling and the mechanisms controlling As mobilization in natural groundwater systems is of great importance.

Groundwater is an important water source in southern Louisiana where industry, agriculture, and rural and domestic water use are heavily dependent on this critical resource. The Chicot aquifer in central and southern Louisiana is a major source of fresh
groundwater that is used for rice and crayfish (i.e., *Procambarus clarkii*) cultivation, is also an important drinking water source, and represents the most heavily pumped aquifer in Louisiana (Lovelace, 1999). For example, from 2005 to 2010, approximately 2461 km$^3$/d (i.e., 41% of the total withdrawals in Louisiana) of groundwater was withdrawn from the Chicot aquifer (Sargent, 2011). The extensive pumping resulted in water level decline and a substantial change of groundwater flow pattern, for example, water levels in and around the rice-growing areas (e.g., Acadia, Evangeline, and Jefferson Davis Parishes) and the Lake Charles industrial center had declined at an average rate of 30.48 cm/yr between 1900 and 1980 (Nyman et al., 1990) and groundwater flow directions had changed from the south and southeast prior to development to the north and northwest at present in southern portions of Louisiana (Lovelace, 1999; Lovelace et al., 2002; Nyman et al., 1990).

In 2003, a study by the United States Geological Survey (USGS) concerning water quality of domestic wells first reported that groundwaters in the southeastern Chicot aquifer, Louisiana contained As concentrations up to 0.7 µmol/kg (53 µg/L; Tollett et al., 2003). In 2004, the Louisiana Department of Environmental Quality (LDEQ) further surveyed As concentrations in 25 domestic wells in the Cow Island and Forked Island areas within the southeastern Chicot aquifer. This study found that 5 sampled wells contained As concentrations greater than 133 nmol/kg (10 µ/L), with the highest value reported to be 0.8 µmol/kg (60 µg/L; Mallett, 2004), and the following year Gobb (2005) reported that a domestic well in Cow Island contained As concentration as high as 10.7 µmol/kg (802 µg/L). It is not known whether these high As groundwaters reflect anthropogenic sources, or if natural processes are responsible (Duex and Gresham, 2008;
Potential anthropogenic sources could include organoarsenicals applied to cotton fields in the past to control the boll weevil (*Anthonomus grandis*), leakage of cattle dipping vats that were used to control the cattle fever ticks (*Rhipicephalus*).

Arsenic toxicity greatly depends on its chemical forms and oxidation states, and generally, inorganic species are more toxic than organic species, with trivalent As(III) being more toxic than pentavalent As(V) (Kumar and Riyazuddin, 2010). In natural groundwater systems, As species predominantly exist as inorganic forms, trivalent arsenite (i.e., $\text{H}_3\text{AsO}_3^0$) and pentavalent arsenate (i.e., $\text{H}_2\text{AsO}_4^-$), which have been implicated in the mass poisoning of tens of millions of people in South and South Asia (Ravenscroft et al., 2009; Smith et al., 2000). Studies of As in southern Louisiana are currently limited and those investigations that have been conducted have only focused on total dissolved As concentrations and not As speciation (Duex and Gresham, 2008; Gresham, 2007; Yang et al., 2014). Furthermore, the mechanisms that locally control As mobilization in groundwaters from southern Louisiana have not been addressed. Therefore, we focus here on groundwater As concentrations and speciation, and utilize groundwater geochemistry, including redox sensitive element concentrations to build a biogeochemical reactive transport model to investigate the potential mechanisms controlling As mobilization and transport in groundwaters of the southeastern Chicot aquifer in southern Louisiana.
4.2 Study Area

The study area is located in Cow Island, Vermilion Parish, Louisiana (Figure 4.1). The Cow Island area consists of low-lying flat land with an average elevation between 1.5 m and 3 m above mean sea level, is chiefly rural, and located along the southern edge of a major rice-growing area in southwestern Louisiana (Gresham 2007, Figure 4.1). Climate is warm, humid, and with frequent rains during summer. Temperatures range from highs of 38 °C in July and August to lows of -7 °C in December and January, and the average annual temperature is 20 °C (Nyman et al., 1990). The average annual rainfall is relatively constant at ~1.5 m (Nyman et al., 1990).

Cow Island is situated above the southeastern Chicot aquifer, which is located within the Atlantic and Gulf Coastal Plain physiographic province where the main landform is a flat alluvial plain, known as the Prairie Terraces (Gresham, 2007). The lithology of the Prairie formation consists primarily of a fining upward complex series of alternating beds of unconsolidated sedimentary deposits including sand, gravel, silt, and clay (Nyman, 1984; Sargent, 2004). The Chicot aquifer dips and thickens to the south from southern Vernon and Rapides Parishes, thins to the west and continues into Texas, and thickens to the east towards the axis of the Mississippi Embayment trough where it is cut by or overlain the Atchafalaya River and Mississippi River deposits (Lovelace et al., 2002; Nyman, 1984; Sargent, 2004). The underlying gravel and sand deposits form the productive Chicot aquifer units and the thick overlying silt and clay layers throughout most of the southwestern Louisiana act as the surficial confining units of the Chicot aquifer (Nyman, 1984). The surficial confining units consist of a combination of
Holocene deposits (e.g., younger overburden sediments that are near ground surface) and Pleistocene deposits (e.g., back-swamp deposits of the ancestral Mississippi River and Red River) (Gresham, 2007; Sargent, 2004). The thickness of the surficial confining units generally increase from north to south, for example, from typically less than 12 m in southern Vernon and Rapides Parishes in the north where the Chicot aquifer outcrops to 49 ~ 122 m in coastal Parishes in the south, with a maximum thickness of ~ 158 m in Vermilion and St. Mary Parishes (Sargent, 2004). The surficial confining units are thought to prevent downward migration of anthropogenic contaminants from the surface (Duex and Gresham, 2008; Gresham, 2007) and make the regions ideal for rice cultivation (Sargent, 2004).

The portion of the Chicot aquifer beneath Cow Island, Louisiana that is examined in this study belongs to the upper sand unit, which ranges from 100 m to 170 m in thickness and is chiefly composed of sand and gravel with sporadic and intermittent clay layers (Nyman, 1989). Historically, groundwater was recharged to the Chicot aquifer in the north where the aquifer outcrops (e.g., southern Vernon and Rapides, and northern Beauregard, Allen, and Evangeline Parishes; Lovelace et al., 2002; see Figure. 4.1). Beginning in the early twentieth century, and in particular intensifying in the early 1930’s to early 1940’s, groundwater pumping of the Chicot aquifer for irrigation of rice paddies and for cultivation of crayfish, led to dramatic decreases in the potentiometric head (Lovelace et al., 2002). The largest decreases in head levels are centered within a number of parishes (i.e., southern Evangeline, eastern Calcasieu, Jefferson Davis, Acadia, and western Lafayette Parishes) that are located to the north and northwest of the Cow Island study site. Consequently, groundwater flow, which was historically from the north
parishes toward the south and southeast with eventual discharge along the Gulf Coast, has shifted to the north and northwest at Cow Island, such that groundwaters now flow toward the substantial cone of depression located in the central parishes noted above (Lovelace et al. 2002, Figure 4.1).

Figure 4.1 Maps showing the Chicot aquifer in Louisiana and the study site at Cow Island, Vermilion Parish in the southeastern Chicot aquifer. The groundwater flow direction and the large cone of depression have developed since the early 20th century owing to extensive groundwater pumping for irrigation of rice paddies and cultivation of crayfish (Procambarus clarkii) (e.g., see Lovelace et al., 2002).

4.3 Methods and Materials

4.3.1 Groundwater Sampling and Analysis
Groundwater samples were collected in June 2011 from 9 domestic wells along a flow path within the southeastern Chicot aquifer, southern Louisiana (Figure 4.1). All sample bottles (HDPE), field containers (e.g., Teflon tubing), and lab-ware were thoroughly washed using trace element cleaning procedures before transport to the field site (Johannesson et al., 2004). Prior to sampling, all sample wells were purged until pH, specific conductivity, and temperature stabilized to ensure that the groundwater samples collected were representative of the aquifer and not the well bore. Groundwater temperature, pH, specific conductivity, oxidation-reduction potential (Eh), and total dissolved solids (TSD) were measured on site using a Hydrolab MiniSonde5 with a flow through cell. The flow through cell was connected to the well outflow with a polyethylene tube, allowing measurement of Eh without exposing groundwater to the atmosphere. Total dissolved iron (Fe\textsubscript{T}), Fe(II), and S(-II) were quantified in field using separate sample aliquots via a portable UV/VIS spectrophotometer (Hach DR/2400). Specifically, Fe\textsubscript{T} was determined using the FerroVer method, Fe(II) was determined using the 1, 10 Phenanthroline method, and total dissolved Fe(III) was calculated by the difference [i.e., Fe(III) = Fe\textsubscript{T} – Fe(II)] (Eaton et al., 1995). The method detection limits for Fe\textsubscript{T} and Fe(II) are both 0.36 µmol/kg (0.02 mg/L). Total dissolved S(-II) was measured using the Methylene Blue method (Eaton et al., 1995) for which the detection limit is 0.16 µmol/kg.

Groundwater was filtered through 0.45 µm in-line filter capsules (Gelman Science, polyether sulfone membrane) into pre-cleaned 125 ml amber HDPE bottles and immediately acidified to pH < 2 (ultrapure HNO\textsubscript{3}) for As\textsubscript{T} and major cations analysis, whereas samples for major anions analysis were not acidified. Arsenic species were
separated in the field using anion exchange chromatography (BioRad AG 1 x 8; 50-100 mesh, acetate form) following procedures discussed previously (Datta et al., 2011; Haque et al., 2008). Briefly, samples for As species analysis were first filtered as described above and acidified to pH ~ 3.5 (ultrapure HNO₃) before passing through the anion exchange columns. At a pH of ~3.5, As(III) exists as arsenite (H₃AsO₃⁰), which readily passes through the column and is immediately collected in pre-cleaned 30 ml amber HDPE bottles, acidified to pH < 2 with ultrapure HNO₃, and stored cold (~ 4°C) until analysis. Pentavalent As(V), however, exists as arsenate (H₂AsO₄⁻), which is strongly retained on the column (Wilkie and Hering, 1998). Dissolved As_T and As(III) were measured by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) following previously described procedures (Datta et al., 2011; Haque et al., 2008), and As(V) was determined by the difference [i.e., As(V) = As_T – As(III)] (Datta et al., 2011; Haque et al., 2008; Leybourne et al., 2014). Major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and anions (Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻) were determined by ion chromatography at Ohio State University following procedures described by Welch et al. (1996).

4.3.2 Biogeochemical Reactive Transport Modeling

To evaluate whether As is mobilized into groundwaters of the upper sand unit of the southeastern Chicot aquifer in the Cow Island area via natural biogeochemical processes, we developed a 1-D biogeochemical reactive transport model for the system that accounted for advective and dispersive flow, mineral dissolution/precipitation, and changing redox conditions caused by microbial facilitated reductive dissolution of Fe(III) oxides/oxyhydroxides. The 1-D biogeochemical reactive transport model was developed
using the X1t program of the Geochemist’s Workbench® (Version 9.0; Bethke & Yeakel 2013) and the thermo.dat database provided with the software (The Lawrence Livermore National Laboratory thermodynamic dataset; Delany & Lundeen 1989) following the procedures outlined by Bethke et al. (2008) and subsequently modified by Johannesson and Neumann (2013).

The model was applied along a hypothetical, 10 km flow path within the southeastern Chicot aquifer, extending from the vicinity of the CI-1 well to the CI-9 well (Figure 4.1). The flow domain used in the model was discretized into 100 nodal blocks distributed parallel to the modeled, 1-D flow path, and was chosen to capture the variation in groundwater chemistry in the study region by projecting the composition of the individual well along a straight line that is directed towards the center of the large cone of depression that is located north and slightly west of the Cow Island site (see Lovelace et al., 2002, Figure 4.1). Groundwaters in the aquifer were initially assumed to have a composition similar to the average composition of 48 groundwater samples collected down gradient of the historical recharge zone in the north (Prakken, 2003). We then assumed that the flow direction in the model domain shifted from south-directed (i.e., right to left) to north-directed (left to right) to corresponded to the actual intensification of pumping of the Chicot aquifer for rice and crayfish cultivation that was initiated in the early twentieth century, and in particular in the early 1930s (Lovelace et al., 2002). Consequently, our model assumed that the flow direction within the Chicot aquifer switched from south-directed to north-directed about 80 to 90 years ago, which was when model simulations begin. Hence, recharging water with the same composition of the CI-1 well enters from the left side of the flow domain (i.e., inlet) and flows toward the right,
displacing groundwater initially occupying the pore spaces that is estimated as the average of 48 groundwater samples from the vicinity of historical recharge zone, and eventually out through the right side of the domain (Bethke et al., 2008; Johannesson and Neumann, 2013).

To account for the gradual decrease in velocity along the flow path due to groundwater discharge to the surface, groundwater flow velocity in the aquifer was simulated using a diverging radial, one-dimensional flow domain (Bethke et al., 2008; Johannesson and Neumann, 2013). To match the decreasing groundwater velocity distribution along the flow path, a specific discharge of 15.24 m/y at the domain inlet and a porosity of 25%, which is typically of unconsolidated sands (Freeze and Cherry, 1979), for the entire flow path were applied in the model.

Microbial respiration is generally considered as the main mechanism controlling As mobilization in reducing anoxic aquifers (Islam et al., 2004; McArthur et al., 2001; Nickson et al., 2000; Rowland et al., 2007). Therefore, microbial respiration, which accounts for changing redox conditions along the flow path, was included in the biogeochemical reactive transport model and was modeled using kinetic rate laws of the following for:

\[ r = k_+ [X] F_D F_A F_T \]  \hspace{1cm} (4.1)

where \( k_+ \) is the forward rate constant, \([X]\) is the concentration of active biomass (mg/kg), \( F_D \) and \( F_A \) are kinetic terms for electron donation and acceptance, respectively, and \( F_T \) is
the thermodynamic potential factor (Bethke et al., 2008; Jin and Bethke, 2007, 2003, 2002).

The thermodynamic potential factor is given by the following equation

\[ F_T = 1 - \exp\left(\frac{\Delta G_r + m_{ATP} \Delta G_p}{\chi R T}\right) \] (4.2)

where \( \Delta G_r \) is the Gibbs free energy change of the respiratory (i.e., redox) reaction, \( m_{ATP} \) is the number of adenosine triphosphate (ATP) molecules produced by the reaction, \( \Delta G_p \) is the Gibbs free energy change of the intracellular phosphorylation reaction where ATP is generated from adenosine diphosphate (ADP), \( \chi \) is the average stoichiometric number, \( R \) is the universal gas constant, and \( T \) is temperature in Kelvin (Table 4.1; Bethke et al. 2008; Johannesson & Neumann 2013). The average stoichiometric number, \( \chi \), represents the number of times the rate controlling step occurs per turnover of the respiratory reaction, which generally reflects the transfer of H\(^+\) across the microbial cell wall (Jin and Bethke, 2007, 2003, 2002). The thermodynamic potential factor can be critically important in anaerobic groundwater systems such as the southeastern Chicot aquifer where the energy microbes acquire from the environment by catalyzing redox reactions is relatively low and similar to that conserved for ATP production (Bethke et al., 2008; Johannesson and Neumann, 2013).
Table 4.1 Biogeochemical parameters used in the biogeochemical reactive transport model to simulate microbial respiration and changing redox conditions along the studied flow path within the southeastern Chicot aquifer, Louisiana. Data are from Table 3 of Johannesson and Neumann (2013) and reflect reactions involving the oxidation of one acetate molecule.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_+$</td>
<td>1.5 $\times$ $10^{-5}$ a</td>
</tr>
<tr>
<td>$K_D$</td>
<td>0.001 b</td>
</tr>
<tr>
<td>$K_A$</td>
<td>$10^6$ a</td>
</tr>
<tr>
<td>$m_{ATP}$</td>
<td>4/3</td>
</tr>
<tr>
<td>$\Delta G_P$</td>
<td>45</td>
</tr>
<tr>
<td>$\chi$</td>
<td>8</td>
</tr>
<tr>
<td>$Y$</td>
<td>9000 f</td>
</tr>
<tr>
<td>$D$</td>
<td>$10^{-9}$</td>
</tr>
</tbody>
</table>

a From study of Geobacter sulfurreducens and Shewanella putrefaciens (Roden, 2006). Units for $K_A$ are mg cells per mole of accessible Fe(III) the goethite surface based on a cell weight of $10^{-12}$ g.

b Roden and Wetzel (2003).

c Estimated from cell physiology.


e Assuming proton transfer across the cell membrane is the rate-limiting step (Jin and Bethke, 2005, 2007).

f He and Sanford (2003).

g Estimated for field conditions by Bethke (2008).

Based on previous studies (Bethke et al., 2008; Johannesson and Neumann, 2013), we assumed that acetotrophic (dissimilatory) Fe(III) reducers were initially distributed evenly throughout the modeled aquifer domain at relatively low concentrations (i.e., $10^{-6}$ mg/kg). Fermentation of sedimentary organic matter that is chiefly contained within the underlying and overlying confining clays is usually considered the primary source of labile organic carbon fueling microbial respiration in reducing anoxic aquifers (Bethke et al., 2008; Chapelle and Bradley, 1996; McMahon and Chapelle, 1991). Our previous
investigations of shallow groundwaters that exhibited high As concentrations in the vicinity of Napoleonville, Louisiana, strongly suggest that such processes are important for developing high As groundwaters in the lower Mississippi Delta regions (Yang et al., 2014, in review). Following Bethke et al. (2008) we assume that acetate (CH$_3$COO$^-$) produced by fermentation diffuses from the underlying and overlying confining clay layers into the southeastern Chicot aquifer at a rate of $\sim$4 $\mu$mol m$^{-3}$a$^{-1}$ along the flow path. In the model, acetate acts as the electron donor for Fe(III), and further assumes that Fe(III) oxides/oxyhydroxides occurs as coatings on the surface of aquifer sand grains due to high Fe(III) oxides content in sediments of the Prairie Complex in the southeast Chicot aquifer (e.g., Shen et al. 2012).

Dissimilatory microbial reduction of Fe(III) oxides/oxyhydroxides coupled to acetate oxidation is modeled using the reaction

$$CH_3COO^- + 8FeOOH(s) + 15H^+ \rightarrow 2HCO_3^- + 8Fe^{2+} + 12H_2O \quad (4.3)$$

where FeOOH$_{(s)}$ represents the mineral goethite (i.e., $\alpha$-FeOOH). The rate of microbial reduction of Fe(III) oxides/oxyhydroxides is controlled by the amount of reducible Fe(III) available on the goethite surface (Roden, 2006, 2004), which was used here as a fitting parameter to best reproduce the dissolved Fe(II) concentration of groundwaters we measured along the flow path (e.g., Johannesson and Neumann, 2013). The reaction rate is described by the following equation

$$r = k_+ m_{Fe(III)} [X]/m_{Fe(III)} + K_A m_{AC} + K_D F_T \quad (4.4)$$
where $m_{\equiv Fe(III)}$ is the concentration of sites (i.e., moles of sites per kg water) on the goethite surface where Fe(III) is available for microbes to reduce, $K_A$ is the half-saturation constant for the electron accepting half-reaction, $K_D$ is the half-saturation constant for the electron donating half-reaction (mol/kg), and $F_T$ is the thermodynamic potential factor. Due to re-adsorption of Fe(II) onto goethite surfaces (Bethke et al., 2008; Roden, 2006), the concentration of sites on goethite possessing reducible Fe(III) (i.e., $m_{\equiv Fe(III)}$) is expected to decrease as microbial reduction of Fe(III) oxides/oxyhydroxides proceeds.

4.4 Results

4.4.1 Groundwater Chemistry

Major cation and anion concentrations along with a number of other important ancillary geochemical groundwater quality parameters along the studied flow path within the southeastern Chicot aquifer, southern Louisiana were summarized in Table 4.2. Geochemical parameters measured in the field (pH, alkalinity, total dissolved solids, specific conductivity) were plotted as a function of distance along the flow path in Figure 4.2. Groundwaters along the flow path were slightly alkaline, with pH values ranged between 8.09 and 8.34 (Table 4.2, Figure 4.2a). Alkalinity, expressed as $\text{HCO}_3^-$, ranged from 4.40 mmol/kg to 7.28 mmol/kg (Table 4.2) and exhibited a general decreasing trend along the flow path (Figure 4.2b). Specific conductivity and TDS ranged from 694 $\mu$S/cm to 1423 $\mu$S/cm and 443 mg/kg to 911 mg/kg (Table 4.2), respectively, and generally followed the same trend along the flow path whereby they were the highest in the south and decreased toward the north (Figure 4.1 and 4.2c). The decreases in TDS and specific
conductivity from south to north represents a legacy signal of the historical groundwater flow where groundwater was originally recharged in the north and had a southward flow, ultimately discharged into the Gulf of Mexico (Lovelace, 1999; Nyman et al., 1990). Measured Eh values ranged between -45 mV and 1 mV, with high values near the upper reaches of the flow path and low values near the lower reaches of the flow path (Table 4.2, Figure 4.2d). Dissolved S(II) concentrations are below detection limit (i.e., 0.16 µmol/kg) for all of the Cow Island groundwaters sampled in this study (Table 4.2). Major cation concentrations were generally low and within the same order of magnitude along the flow path, whereas major anion concentrations exhibited greater variation. For example, Cl\(^-\) concentrations varied by 10-fold in the Cow Island groundwaters, ranging from 0.54 mmol/kg to 5.82 mmol/kg, and SO\(_4^{2-}\) concentrations varied by more than a factor of 45 (i.e., 0.002 mmol/kg to 0.089 mmol/kg; Table 4.2).
Table 4.2 Summaries of groundwater geochemical property and major solute composition along the studied flow path in the southeastern Chicot aquifer.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CI-1</th>
<th>CI-2</th>
<th>CI-3</th>
<th>CI-4</th>
<th>CI-5</th>
<th>CI-6</th>
<th>CI-7</th>
<th>CI-8</th>
<th>CI-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depth (m)</td>
<td>23</td>
<td>32</td>
<td>35</td>
<td>35</td>
<td>20</td>
<td>24</td>
<td>21</td>
<td>21</td>
<td>36</td>
</tr>
<tr>
<td>Distance (km)</td>
<td>2.5</td>
<td>2.7</td>
<td>3.8</td>
<td>4.0</td>
<td>6.5</td>
<td>7.2</td>
<td>7.4</td>
<td>8.5</td>
<td>12.2</td>
</tr>
<tr>
<td>T (°C)</td>
<td>22.0</td>
<td>22.0</td>
<td>25.2</td>
<td>24.5</td>
<td>22.9</td>
<td>27.4</td>
<td>21.4</td>
<td>23.3</td>
<td>22.6</td>
</tr>
<tr>
<td>pH</td>
<td>8.09</td>
<td>8.21</td>
<td>8.25</td>
<td>8.34</td>
<td>8.20</td>
<td>8.32</td>
<td>8.31</td>
<td>8.33</td>
<td>8.28</td>
</tr>
<tr>
<td>Alk (mmol/kg)</td>
<td>7.28</td>
<td>5.75</td>
<td>6.64</td>
<td>5.85</td>
<td>7.20</td>
<td>7.20</td>
<td>6.96</td>
<td>4.4</td>
<td>NA</td>
</tr>
<tr>
<td>Cond (µS/cm)</td>
<td>960</td>
<td>1423</td>
<td>1056</td>
<td>880</td>
<td>877</td>
<td>876</td>
<td>871</td>
<td>747</td>
<td>694</td>
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<tr>
<td>TDS (mg/kg)</td>
<td>614</td>
<td>911</td>
<td>676</td>
<td>563</td>
<td>560</td>
<td>560</td>
<td>558</td>
<td>478</td>
<td>443</td>
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<tr>
<td>Eh (mV)</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-38</td>
<td>-10</td>
<td>-20</td>
<td>-45</td>
<td>-19</td>
<td>-18</td>
</tr>
<tr>
<td>S(-II) (nmol/kg)</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>94</td>
<td>78</td>
<td>156</td>
<td>31</td>
<td>62</td>
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<tr>
<td>Ca²⁺ (mmol/kg)</td>
<td>0.59</td>
<td>1.28</td>
<td>0.75</td>
<td>0.79</td>
<td>0.92</td>
<td>0.93</td>
<td>0.96</td>
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<td>Mg²⁺ (mmol/kg)</td>
<td>1.03</td>
<td>1.16</td>
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<td>0.71</td>
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<tr>
<td>Na⁺ (mmol/kg)</td>
<td>3.97</td>
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<td>3.93</td>
<td>3.58</td>
<td>3.98</td>
<td>4.01</td>
<td>4.09</td>
<td>3.85</td>
<td>3.16</td>
</tr>
<tr>
<td>K⁺ (µmol/kg)</td>
<td>41</td>
<td>55</td>
<td>47</td>
<td>46</td>
<td>35</td>
<td>22</td>
<td>22</td>
<td>34</td>
<td>45</td>
</tr>
<tr>
<td>Cl⁻ (mmol/kg)</td>
<td>3.04</td>
<td>5.82</td>
<td>3.01</td>
<td>2.34</td>
<td>1.80</td>
<td>1.48</td>
<td>1.51</td>
<td>1.51</td>
<td>0.54</td>
</tr>
<tr>
<td>SO₄²⁻ (µmol/kg)</td>
<td>2</td>
<td>14</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>84</td>
<td>89</td>
<td>167</td>
<td>2</td>
</tr>
<tr>
<td>NO₃⁻ (µmol/kg)</td>
<td>BDL</td>
<td>BDL</td>
<td>1</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>PO₄³⁻ (µmol/kg)</td>
<td>1</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>2</td>
<td>BDL</td>
<td>1</td>
<td>6</td>
<td>BDL</td>
</tr>
</tbody>
</table>

Temperature (T), alkalinity as HCO₃ (Alk), specific conductivity (Cond), and total dissolved solids (TDS), oxidation-reduction potential (Eh), and S(-II). BDL=Below Detection Limit, NA=Not Available
Figure 4.2 Field parameter data including pH, alkalinity, total dissolved solids (TDS), specific conductivity, and oxidation-reduction potential (Eh) of the southeastern Chicot aquifer groundwaters plotted as a function of distance along the flow studied path.
4.4.2 Arsenic and Fe Concentrations and Speciation in Groundwaters

Concentrations and speciation of As and Fe along the studied flow path in the southeastern Chicot aquifer were presented in Table 4.3 and Figure 4.3. Along the studied flow path, \( Fe_T \) concentrations ranged from 32 µmol/kg (1.77 mg/L) to 53 µmol/kg (2.93 mg/L), Fe(II) concentrations ranged from 18 µmol/kg (0.99 mg/L) to 47 µmol/kg (2.62 mg/L), and Fe(III) concentrations varied from 2 µmol/kg (0.1 mg/L) to 20 µmol/kg (1.12 mg/L) (Table 4.3). The \( As_T \) concentrations ranged from 0.5 nmol/kg (0.04 µg/L) to 644 nmol/kg (48 µg/L), the As(III) concentrations varied between 0.2 nmol/kg (0.01 µg/L) and 309 nmol/kg (23 µg/L), and the As(V) concentrations ranged from 0.3 nmol/kg (0.03 µg/L) to 335 nmol/kg (25 µg/L) in the Cow Island groundwaters (Table 4.3). Of the 9 wells sampled from Cow Island, 4 wells contained As concentrations exceeding 133 nmol/kg (10 µg/L; the WHO safe drinking water standard). Dissolved Fe(II) and As(III) were the predominant forms in groundwaters of the sampled wells except for the CI-3 [i.e., predominated with Fe(III)] and the CI-2 and CI-7 wells [i.e., predominated with As(V)]. As shown in Figure 4.3a, \( Fe_T \) and Fe(II) followed a similar trend along the flow path, especially at the mid-reaches of the flow where both reached the highest concentrations, while Fe(III) concentrations remained relatively constant along the flow path except for the CI-3 well. Dissolved \( As_T \), As(III), and As(V) generally followed the same trend along the flow path, increasing at the upper reaches of the flow, reaching the highest concentrations at the mid-reaches of the flow, and then decreasing at the lower reaches of the flow (Figure 4.3b). Dissolved As(III) and Fe(II) concentrations followed a similar trend at the mid-reaches of the flow path where As(III) and Fe(II) both reached the highest concentrations (i.e., the CI-7 well located at 7.4 km along the flow path;
Figure 4.3). Dissolved As$_T$ was positively correlated with Fe$_T$ (r = 0.64) at the 95% confidence level, and As(III) was also positively associated with Fe(II) (r = 0.49), however, at the 80% confidence level (Figure 4.4).

Table 4.3 Concentrations and speciation of As and Fe along the studied flow path in the southeastern Chicot aquifer groundwaters.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Distance (km)</th>
<th>Fe$_T$ (µmol/kg)</th>
<th>Fe (II)</th>
<th>Fe (III)</th>
<th>As$_T$ (nmol/kg)</th>
<th>As (III) (nmol/kg)</th>
<th>As (V) (nmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI-1</td>
<td>2.5</td>
<td>37</td>
<td>30</td>
<td>7</td>
<td>83</td>
<td>51</td>
<td>32</td>
</tr>
<tr>
<td>CI-2</td>
<td>2.7</td>
<td>46</td>
<td>37</td>
<td>9</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>CI-3</td>
<td>3.8</td>
<td>38</td>
<td>18</td>
<td>20</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>CI-4</td>
<td>4</td>
<td>35</td>
<td>33</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CI-5</td>
<td>6.5</td>
<td>37</td>
<td>25</td>
<td>12</td>
<td>243</td>
<td>164</td>
<td>79</td>
</tr>
<tr>
<td>CI-6</td>
<td>7.2</td>
<td>48</td>
<td>39</td>
<td>9</td>
<td>389</td>
<td>309</td>
<td>80</td>
</tr>
<tr>
<td>CI-7</td>
<td>7.4</td>
<td>53</td>
<td>47</td>
<td>6</td>
<td>644</td>
<td>309</td>
<td>335</td>
</tr>
<tr>
<td>CI-8</td>
<td>8.5</td>
<td>32</td>
<td>20</td>
<td>12</td>
<td>194</td>
<td>155</td>
<td>39</td>
</tr>
<tr>
<td>CI-9</td>
<td>12.2</td>
<td>34</td>
<td>30</td>
<td>4</td>
<td>15</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>
Figure 4.3 Geochemical data for the southeastern Chicot aquifer groundwaters plotted as a function of distance along the studied flow path. Shown are: (a) dissolved Fe(II), Fe(III), and Fe$_T$ concentrations and (b) dissolved As(III), As(V), and As$_T$ concentrations.
Figure 4.4 Scatter plots showing relationships between (a) As$_T$ and Fe$_T$, (b) As(III) and Fe(II). Linear regression lines and correlation coefficient ($r$) are shown in each plot.

4.4.3 Biogeochemical Reactive Transport Model

The model was employed to reproduce the general trends of Fe(II) concentrations in the Cow Island groundwaters. Specifically, the goal was to examine whether microbial respiration of Fe(III) oxide/oxyhydroxides within the aquifer sediments could explain the variation of Fe(II) concentrations measured along the studied flow path, and further, by including As sorbed to these modeled Fe(III) oxides/oxyhydroxides, could reductive dissolution of Fe(III) oxides/oxyhydroxides and release of the sorbed As capture the observed trends of As concentrations in groundwaters at Cow Island? We assumed that goethite was the chief Fe(III) oxide/oxyhydroxide in the southeastern Chicot aquifer sands beneath Cow Island, and that goethite only occurred in these sediments along the first half of the modeled flow path. We also assumed that the start of the simulation runs (i.e., 75 ~ 95 years ago) coincided with the initiation of major pumping of the Chicot aquifer further north in the central parishes described above. Based on the estimated
model parameters (Table 4.1), the model captured the general trends of the measured Fe(II), As(III), and As(V) concentrations along the studied flow path at Cow Island (Figure 4.5). The model predicted a peak in Fe(II) concentrations at a distance of 5 to 6 km from the CI-1 well (i.e., the mid-reaches of the flow path) that could have formed and migrated this distance in approximately 80 years, or since the initiation of major pumping of the Chicot aquifer in the early to mid-1930s (Figure 4.5a). Along the upper reaches of the flow path (e.g., 2 ~ 4 km) where the aquifer was less reducing Fe(II) concentrations were under predicted by the model, whereas along the lower reaches of the flow path (e.g., > 8 km) Fe(II) concentrations were first over predicted and then under predicted slightly by the model (Figure 4.5a). Assuming major pumping of the Chicot aquifer intensified ~ 80 years ago, the model also capture the peak in As(III) and As(V) observed along the mid-reaches of the flow at the mid-reaches of the flow path (i.e., 6 ~ 8 km) despite slightly under predict the amount of As(III) and As(V) in groundwaters from this region. The model did a better job capturing the spread in elevated As(III) concentrations along the mid-reaches of the flow path (Figure 4.5b). More specifically, As(III) concentrations at the upper reaches of the flow path (i.e., 2 ~ 4 km) are over predicted by the model. We note that surface complexation was not included in these initial model simulations, which may account for the over predicted groundwater As(III) concentrations returned by the model for the upper reaches of the flow path. Nonetheless, further down gradient along the lower reaches of the flow path (i.e., > 8 km) the model did a good job predicting the observed decrease in As(III) concentrations. Consequently, when considering the assumption inherent in the biogeochemical reactive transport model, the simulated results did a remarkably good job reproducing the trends in the measured
As(III) concentrations (Figure 4.5b). In contrast, the model typically over predicted As(V) concentrations in the Cow Island groundwaters except for the CI-7 well (i.e., located 7.4 km along the flow path), which exhibited the highest As(V) concentration determined for the Cow Island groundwaters (Figure 4.5b). The fact that the model captures the general trends of Fe(II), As(III), and As(V) along the studied flow path suggests that microbially mediated reductive dissolution of Fe(III) oxide/oxyhydroxides in the Chicot aquifer sediments play an important role in controlling As concentrations and speciation along the flow path, especially near the mid-reaches of the flow path.
Figure 4.5 The model predicted and the measured (a) Fe(II), (b) As(III), and (c) As(V) concentrations in groundwaters along the studied flow path within the southeastern Chicot aquifer.
4.5 Discussion

4.5.1 Iron Biogeochemistry along the Flow Path

Dissolved Fe(II) concentrations in groundwaters varied along the studied flow path, indicating localized changes of redox conditions within the southeastern Chicot aquifer (Figure 4.3a). However, the average Fe(II) concentrations increased from 29.5 ± 7.8 µmol/kg (1.65 ± 0.4 mg/L, i.e., the average of the CI-1, CI-2, CI-3, and CI-4 wells) along the upper reaches of the flow to 37 ± 9.1 µmol/kg (2.07 ± 0.5 mg/L, i.e., the average of the CI-5, CI-6, and CI-7 wells) along the mid-reaches of the flow, and then decreased to 25 ± 5 µmol/kg (1.40 ± 0.3 mg/L, i.e., the average of the CI-8 and CI-9 wells) for flow beyond 8 km. The generally high Fe(II) concentrations that characterize the Cow Island groundwaters strongly suggests that Fe(III) reduction is an important biogeochemical process within the aquifer. Moreover, the increase in dissolved Fe(II) concentrations along the mid-reaches of the studied flow path suggests that either Fe(III) reduction is enhanced along this portion of the aquifer or that Fe(II) produced by reductive dissolution in the upper reaches of the flow path has moved down gradient and further enhanced Fe(III) reduction. Alternatively, it is possible that the aquifer sediments at the mid-reaches of the flow path contain more Fe(III) than elsewhere in the study region, or the Fe(III) in these sediments is more accessible to the local Fe(III) reducing microbial consortium. Samples of the upper sands from the Chicot aquifer from beneath Cow Island are required, however, to answer many of these questions.

4.5.2 Controls on As Concentrations and Speciation along the Flow Path
Dissolved As(III) and As(V) concentrations in the southeastern Chicot aquifer groundwaters varied along the flow path according to changes in groundwater chemistry including pH and redox condition. The studied flow path in the Chicot aquifer was generally under reducing condition (i.e., Eh < 0 mV) and largely appeared to be buffered by Fe(III) reduction (Figure 4.3). Closer examination of Figure 4.3 further showed that As(III) closely corresponded to Fe(II) changes along the flow path, such that regions of the aquifer where Fe(II) concentrations were the highest also had the highest As(III) concentrations. For example, both Fe(II) and As(III) concentrations in groundwaters increased at the mid-reaches of the flow path (i.e., 6 ~ 8 km) and reached their maximums, 47 µmol/kg (2.62 mg/L) and 309 nmol/kg (23 µg/L), respectively, at ~ 7.5 km along the flow path. With flow beyond 8 km, Fe(II) and As(III) concentrations both started to decrease along the remainder of the flow path (Figure 4.5). The model predicted Fe(II) and As(III) concentrations along the flow path also showed the same trends as the measured results, with the region of aquifer where As(III) concentrations increased and reached maximum corresponding to the region where the model predicted that Fe(III) reduction was the chief redox buffering reaction (i.e., 6 ~ 8 km, Figure 4.5).

The model mostly over predicted As(V) concentrations along the studied flow path, which may due to the exclusion of sulfate reduction from the model. Because the measured S(-II) concentrations in groundwaters were below the detection limit (i.e., 0.16 µmol/kg), we assumed that sulfate reduction was not the dominant process along the studied flow path and therefore, excluded sulfate reduction from the model. Exclusion of sulfate reduction from the model resulted in complete elimination of dissolved S(-II) from groundwaters. Under reducing conditions, dissolved S(-II) can either form pyrite
(FeS₂), arsenopyrite (FeAsS), or other sulfide minerals such as orpiment (As₂S₃) when Fe and As exist, resulting in removal of Fe(II), As(III), and As(V) from groundwaters (O’Day et al., 2004). Therefore, exclusion of sulfate reduction from the model may cause higher than expected As(V) concentrations in groundwaters and therefore, over prediction of As(V) by the model along the studied flow path.

Generally, the model did a good job capturing the general trend of Fe(II), As(III), and As(V) concentrations along the studied flow path, particularly along the mid-reaches of the flow path where reductive dissolution of Fe(III) oxides/oxyhydroxides occurred as the main mechanism controlling As concentrations and speciation in groundwaters (Figure 4.5). Beyond the mid-reaches of the flow path the measured As(III) and As(V) concentrations started to decrease, which may due to a number of processes including re-adsorption of mobilized As onto As-adsorbing materials such as Fe(III) oxides/oxyhydroxides, clay minerals, organic matter (Gresham, 2007; Haque et al., 2008), and/or co-precipitation with Fe sulfide minerals (Nickson et al., 2000; Reza et al., 2010). Decreases in As(III) and As(V) concentrations at the lower reaches of the flow path was also relatively well predicted by the model, suggesting that the model may also account for these adsorption processes along the lower reaches of the flow path.

The close correspondence between As(III) and Fe(II) concentrations along the flow path and the fact that the biogeochemical reactive transport model demonstrated that Fe(III) reduction and the consequential release of sorbed and/or coprecipitated As can explain the changes in Fe(II) and As(III) concentrations along the studied flow path further supports that reductive dissolution of Fe(III) oxides/oxyhydroxides is the main
mechanism controlling As release to groundwaters beneath Cow Island, Louisiana. Our findings are broadly similar to other investigations of reducing aquifers from the large rivers and delta plains of South and Southeast Asia where ferric iron reduction followed by release of sorbed/co-precipitated As is hypothesized to be the mechanism of As mobilization to shallow groundwaters (e.g., (Berg et al., 2001; Mukherjee and Bhattacharya, 2001; Nickson et al., 2000; Polya et al., 2005; Ravenscroft et al., 2009; Shamsudduha et al., 2008; Smedley and Kinniburgh, 2002).

4.5.3 Anthropogenic vs. Natural Sources of As at Cow Island

Historical cemeteries are potential anthropogenic sources of As due to the application of high As embalming fluid between 1859 and 1910, and it was estimated that up to 5.4 kg non-degradable As was used per body (Bloudoff-Indelicato, 2015; Borstel and Niquette, 2000). A historical cemetery, St. Ann Cemetery (SAC), is located at the mid-reaches of the studied flow path where the 4 wells (i.e., CI-5, CI-6, CI-7, CI-8) with high As concentrations are located as well. Gresham (2007) examined the date of the headstones and estimated that at least 25 graves were dated prior 1910, therefore, SAC potentially harbored 136 kg of As. As wood caskets deteriorate, the As embalmed remains are directly exposed to the surrounding sediments adding As to surrounding sediments, and from there, As can be transported by rainwater and flooding downward into groundwaters. As shown in Figure 4.1, the CI-5 well is located 0.7 km up-gradient of SAC (i.e., the CI-6 well), and the CI-7 and CI-8 wells are located 0.2 km and 1.3 km, respectively, down-gradient of SAC. Two wells (i.e., CI-8 and CI-9) down-gradient of SAC and the well at SAC (i.e., CI-6) contain groundwaters with elevated As
concentrations, therefore, SAC is a possible anthropogenic As source to groundwaters of wells that are proximal to and hydraulically down-gradient from the cemetery. However, the fact that the measured $\text{As}_T$ concentration (i.e., 644 nmol/kg, 48 µg/L) from the CI-7 well is 1.7 times higher than $\text{As}_T$ concentration (i.e., 389 nmol/kg, 29 µg/L) from the CI-6 well (i.e., As source at SAC) and the CI-5 well (i.e., 0.7 km upgradient of SAC) also contained elevated As concentration (i.e., 243 nmol/kg, 18 µg/L) suggest that other sources and processes may be responsible for elevated As concentrations in groundwater as well.

Geological and sedimentary depositional environments of the Mississippi Delta in southern Louisiana have reported to provide favorable conditions for producing the high As groundwaters (Gresham, 2007; Ravenscroft et al., 2009; Yang et al., 2014). Also, the Chicot aquifer is generally covered by thick layers of clay (i.e., range from 12 m in the north to 49-122 m in the south), which act as surficial confining units preventing downward migration of contaminants from surface (Duex and Gresham, 2008; Gresham, 2007). The facts that the measured Fe(II) and As(III) concentrations are positively correlated ($r = 0.49$) at greater than 80% significance level and our model predicted results are closely correlated with the measured results strongly support that reductive dissolution of Fe(III) oxides/oxyhydroxides may be an important mechanism controlling As release from sediments along the studied flow path. Therefore, reductive dissolution of As-bearing Fe(III) oxides/oxyhydroxides may be another contributing source for elevated As concentrations in the southeastern Chicot aquifer groundwaters.
These high As groundwaters in Cow Island may reflect both anthropogenic and natural As sources, and to better understand whether anthropogenic or natural sources are the main cause for elevated As concentrations in groundwaters, a detailed investigation of both waters and sediments of the study sites close to and far away from the anthropogenic As sources should be conducted.

4.6 Conclusions

Arsenic concentrations and speciation in groundwater were measured along the studied flow path within the southeastern Chicot aquifer in southern Louisiana, United States. Dissolved As$_T$ concentrations ranged from 0.5 nmol/kg (0.04 µg/L) to 644 nmol/kg (48 µg/L), with As(III) as the predominant species ranging from 0.2 nmol/kg (0.01 µg/L) to 309 nmol/kg (23 µg/L). Dissolved Fe$_T$ concentrations ranged from 32 µmol/kg (1.77 mg/L) to 53 µmol/kg (2.93 mg/L), with Fe(II) as the predominant species ranging from 18 µmol/kg (0.99 mg/L) to 47 µmol/kg (2.62 mg/L). Dissolved As$_T$ and As(III) were positively correlated with Fe$_T$ ($r = 0.63$) and Fe(II) ($r = 0.49$), respectively. A biogeochemical reactive transport model was applied to simulate the reactive transport of Fe(II), As(III), and As(V) along the studied flow path, and Fe(II), As(III), and As(V) concentrations predicted by the model generally followed similar trends as the measured Fe(II), As(III), and As(V) concentrations along the studied flow in the southeastern Chicot aquifer groundwaters. The close correlation between Fe(II) and As(III) concentrations of both the measured and the model predicted results along the studied flow path suggests that reductive dissolution of Fe(III) oxides/oxyhydroxides and subsequent release of sorbed and/or co-precipitated As is an important mechanism.
controlling As mobilization to the southeastern Chicot aquifer groundwaters. The fact that the 4 As contaminated wells are all located close to SAC, a potential anthropogenic As source, also suggests that SAC may be another important As source to groundwaters. To better understand the sources and the biogeochemical cycle of As in the southeastern Chicot aquifer groundwaters, studies on chemical composition of the southeastern Chicot aquifer sediments are needed and should be the future focus.

Acknowledgements

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Chapter 5

Summary

This work focused on identifying shallow aquifers of the Mississippi Delta in southern Louisiana that were potentially at risk of As contamination caused by natural sources and processes, which provided us a natural laboratory to better study and understand the factors that affecting As concentrations and the mechanisms that control As mobilization in shallow groundwaters of the Mississippi Delta in southern Louisiana.

This work started with developing a mathematical model to predict the probability of groundwater As contamination in shallow aquifers and further to identify shallow aquifers of the Mississippi Delta that were at risk of As contamination. Due to limited groundwater As concentrations data in southern Louisiana, 3448 As data and 15 independent variables (e.g., geology, soil property, topography, and hydrology) associated with each As measurement were compiled from Bangladesh and used to build and calibrate the model. Logistic regression was applied to develop the risk model based on the relative importance of geology and sedimentary depositional environments, topography, hydrology, and soil properties in controlling groundwater As concentrations in Bangladesh. The model was subsequently applied in southern Louisiana to predict the probability of groundwater As contamination in shallow aquifers and to produce a risk map showing areas at high- and low-risk of As contamination. The risk map indicated that an area of 23,881 km$^2$ in southern Louisiana was at risk of As contamination in shallow groundwaters caused by naturally occurring processes. The model’s predictions were verified using 78 As measurements in southern Louisiana and the results showed that the model correctly predicted 79.5% of the existing shallow groundwater As
measurements, indicating good performance of the model in predicting groundwater As contamination in shallow aquifers of the Mississippi Delta in southern Louisiana.

Based on the risk map, shallow aquifers of the Mississippi delta in southern Louisiana that are at high risk of As contamination normally consist of relatively young (e.g., Holocene), organic-rich, alluvial/deltaic deposits, and are generally under reducing condition. Microbes living within aquifer sediments have been widely recognized as an important factor affecting As mobilization from sediments to groundwaters in reducing anoxic aquifers (Islam et al., 2004; Oremland and Stolz, 2005, 2003; Pearcy et al., 2011; Radloff et al., 2007). Therefore, the second part of this work was focused on studying the role microbes play in mobilizing As from aquifer sediments to groundwaters. Three sediment cores were collected from Bayou Lafourche, Napoleonville, where it was predicted to be at high risk of As contamination by the model. Porewaters were extracted at different depths of sediment cores for analysis of total dissolved As and Fe concentrations and sediments were collected for laboratory incubation experiments. Sediment incubations were conducted under four experimental conditions: (1) sterilized controls [sterilized sediments + 50 mmol/kg anthraquinone-2,6-disulfonic acid (AQDS)]; (2) anaerobic with no amendments; (3) anaerobic + 50 mmol/kg acetate (i.e., sodium acetate); and (4) anaerobic + 50 mmol/kg acetate + 50 mmol/kg AQDS. The experimental solutions were collected and acidified after each specific reaction period and analyzed for total dissolved As, Fe, and Mn concentrations. Porewater analysis showed a positive relationship between As and Fe concentrations in core A ($r = 0.92$) and B ($r = 0.96$, $p < 0.01$), suggesting that reductive dissolution of Fe(III) oxides/oxyhydroxides may play an important role in As mobilization from sediments to
groundwaters at the Napoleonville site. Although As and Fe concentrations in core C did not show a positive relationship, they were both generally an order of magnitude higher than in core B. Closer examination of the stratigraphy of sediment cores indicated that higher As and Fe concentrations were generally from porewaters extracted from the coarse-grained sediments (i.e., silt, silty loam, sandy loam, sand), while higher DOC and SOC were generally obtained from the fine-grained sediments (i.e., silty clay, clay). Based on porewater analysis and examination of sediment stratigraphy we propose that As mobilization from sediments was largely confined to the coarse-grained sediments where microbial respiratory processes dominate over fermentation, and also, that the organic carbon fueling microbial reductive dissolution of Fe(III) oxides/oxyhydroxides is sourced from the clay-rich layers within these sediments. Incubation experiments showed that As concentrations were the lowest in the sterilized controls, slightly higher in the un-amended experiments, and the greatest in incubation experiments amended with acetate, and especially those amended with both acetate and AQDS. In contrast, Fe and Mn concentrations were generally lower in the amended solution, which may be due to the observed production of organic flocculants in the amended solutions, suggesting that addition of acetate and AQDS resulted in decreases in Fe and Mn concentrations in these solutions. Although As concentrations were not always positively related to Fe and Mn concentrations in solutions, it followed a similar trend as Fe and Mn. Results from porewater analysis and sediment incubations both suggest that microbes play a key role in As mobilization from sediments in the shallow aquifers of the Mississippi Delta in southern Louisiana.
Finally, the mechanisms controlling As mobilization and transport were investigated using groundwater data collected along a flow path within the southeastern Chicot aquifer and As mobilization affected by changing redox conditions and groundwater chemistry were simulated using a biogeochemical reactive transport model along the studied flow path. The model accounts for advection and dispersion of As and other solutes in the flowing groundwaters, mineral dissolution and/or precipitation along the flow path, and changing redox conditions caused by microbial activities. Along the studied flow path, total dissolved As (As\textsubscript{T}) ranged from 0.5 nmol/kg (0.04 µg/L) to 644 nmol/kg (48 µg/L), with As(III) as the predominant species ranging from 0.2 nmol/kg (0.01 µg/L) to 309 nmol/kg (23 µg/L), total dissolved Fe (Fe\textsubscript{T}) ranged from 32 µmol/kg (1.77 mg/L) to 53 µmol/kg (2.83 mg/L), with Fe(II) as the predominant species ranging from 18 µmol/kg (0.99 mg/L) to 47 µmol/kg (2.62 mg/L). Generally, As(III) and Fe(II) followed a similar trend, with increase in Fe(II) concentrations, As(III) concentrations increased as well, with the highest concentrations occurring at the mid-reaches of the flow path. The biogeochemical model well captured the general trend of As(III) and Fe(II) with the highest predicted As(III) and Fe(II) concentrations at the mid-reaches of the studied flow path, which was consistent with the measured results. The measured and model predicted As(III) and Fe(II) concentrations both support our hypothesis that reductive dissolution of Fe(III) oxides/oxyhydroxides and the subsequent release of sorbed and/or co-precipitated As to groundwaters is the primary mechanism controlling As mobilization and transport in the southeastern Chicot aquifer groundwaters.

Predictions from Chapter 2 indicate that the Holocene shallow aquifers of the Mississippi Delta in southern Louisiana that are under reducing anoxic conditions are
potentially at high risk of As contamination. Porewater analysis and laboratory
experiments from Chapter 3 suggest that microbes play an important role in As
mobilization from aquifer sediments to groundwaters under anoxic reducing conditions.
Observations and model predicted results from Chapter 4 further support the reductive
dissolution of Fe(III) oxides/oxyhydroxides as the main mechanism controlling As
mobilization and transport along the flow path within reducing anoxic aquifers.
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BIOGRAPHY

Ningfang Yang was born in the People’s Republic of China. She received her B.S. in Environmental Science from Xi’an University of Architecture and Technology in 2004 and M.S. in Cold Region Environment from Chinese Academy of Sciences in 2007. She came to the United States in 2007 and received her second Master degree in Soil Science from University of Tennessee-Knoxville in 2009. She came to the Department of Earth and Environmental Sciences at Tulane in 2009 to pursue her PhD in Earth and Environmental Sciences/Geochemistry under advisory of Dr. Karen Johannesson. She will graduate and obtain her PhD degree in December. 2015.