

HYDROGEOCHEMICAL EVOLUTION OF ARSENIC ALONG GROUNDWATER  
FLOW PATHS: LINKING AQUEOUS AND SOLID PHASE ARSENIC  
SPECIATION

by

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## DEDICATION

This dissertation is dedicated to my parents, Lailun Nahar and Mahbub Haque. Without their support and encouragement, I could not have completed this journey.

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April 18, 2007

ABSTRACT

HYDROGEOCHEMICAL EVOLUTION OF ARSENIC ALONG GROUNDWATER  
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The central hypothesis of this Doctoral research work is that changes occurring along groundwater flow paths that accompany chemical weathering and oxidation-reduction reactions catalyze both arsenic (As) mobilization from, and capture by, minerals via adsorption/desorption and/or mineral dissolution/precipitation reactions. This central hypothesis is addressed by (i) quantifying concentrations and speciation of As, and ancillary geochemical parameters, including a number of redox sensitive parameters in groundwater samples collected along flow paths, and (ii) determining solid phase speciation of As in aquifer sediment samples, with specific emphasis on the

labile (i.e., surface exchangeable) and non-labile As fractions (e.g., precipitated with Fe oxides). In order to accomplish these objectives, a series of groundwater samples were collected along flow paths in three well characterized, drinking water aquifers: Carrizo Sand (Texas), Upper Floridan (Florida), and Aquia (Maryland). Results of the groundwater studies demonstrate that the Carrizo and the Upper Floridan aquifers exhibit low dissolved As concentrations ( $<1.4$  ppb or  $\sim 19$  nmol kg<sup>-1</sup>), whereas the Aquia aquifer has As concentrations in many wells that exceed the current US Environmental Protection Agency's maximum contaminant level for As in drinking waters of 10 ppb (133 nmol kg<sup>-1</sup>). The results further indicate that the type of As [As(III) vs. As(V)] released in solution is largely dependent on respiratory microbial consortia present within the aquifer [i.e., Fe(III) reducing bacteria, dissimilatory As(V) reducing prokaryotes (DARPs), and Fe(III) reducing DARPs]. In the final aspect of the project, to address the source and lability of As in sediment, samples were collected from within the Aquia and Carrizo Sand aquifers. These sediment samples were examined petrographically and by X-Ray diffraction, and subsequently subjected to a sequential extraction scheme. By combining the results of Aquia groundwater and sediment studies, it was established that dissimilatory Fe(III) reduction driven by suboxic, non-sulfidogenic Aquia groundwaters release a significant amount of As from the non-labile fraction of As, which is associated with amorphous and/or well crystallized Fe(III) oxide/oxyhydroxides that form coatings on aquifer mineral surfaces. Results of sequential extraction for the Carrizo Sand aquifer are presented in the Appendix for future consideration.

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## CHAPTER 1

### INTRODUCTION

Arsenic (As) is a toxic metalloid that is now recognized to be one of the main global groundwater quality problems, most notably in the Ganges-Brahmaputra Delta region of Bangladesh, and neighboring West Bengal in India. In these regions alone, approximately 40 million people are suffering from severe and chronic As poisoning due consumption of drinking water from contaminated groundwater sources (Smedley and Kinniburgh 2002). Groundwaters from these and other regions exhibiting high As concentrations are commonly associated with young (i.e., Quaternary) alluvial/deltaic sedimentary deposits and are characterized by reducing conditions with high dissolved iron (Fe) concentrations (Smedley, 2003; Nordstrom, 2002). However, the biogeochemistry of As in groundwaters and the mechanisms responsible for As mobility that lead to elevated concentrations are relatively poorly understood. At the time this research commenced and until now no investigators have systematically examined how As concentrations and speciation change along groundwater flow paths in response to changing pH, redox conditions, and solution compositions. Moreover, although it is generally recognized that surface exchangeable As (i.e., labile) buffers dissolved As concentrations in groundwater systems (Dixit and Hering, 2003; Hamon et al., 2004), and

that speciation of sorbed and co-precipitated As associated with aquifer minerals (i.e., solid phase speciation) are important (O'Day et al., 2004), there have been no systematic studies linking As concentrations and speciation in groundwaters along flow paths to the speciation of solid-phase As (labile vs. non-labile), and evolving groundwater biogeochemistry. The poor understanding of As geochemistry in groundwaters is demonstrated by two recent studies in eastern California (Levy et al., 1999; Ryu et al., 2002). Both investigations attributed the elevated As concentrations that characterize some groundwaters beneath Owens Dry Lake to conservative behavior of the metalloid in these alkaline waters. Using major solute data, a computer model and measured  $As_{total}$  concentrations, Levy et al. (1999) predicted that arsenate [As(V)] should predominate in the moderately reducing, alkaline groundwaters. However, measurements of As species in 30 groundwater samples demonstrate that arsenite [As(III)] dominates (Ryu et al., 2002).

Past studies, which include As speciation data, generally do not provide significant insight towards understanding the biogeochemical “evolution” of As concentrations and speciation along flow paths. For example, Cherry et al. (1979) investigated the application of the As(III)/As(V) redox couple as a means to estimate the redox state of groundwaters, whereas Chen et al. (1994) measured As speciation in three groundwater samples from the Blackfoot disease area of Taiwan in an attempt to establish links between As speciation and human disease. Smedley et al. (1996) invoked the possibility that microbial processes may affect As speciation in groundwaters suggesting that elevated As(III) in some of the groundwaters and streams studied could

reflect microbially mediated methylation and reduction reactions. They did not, however, test this hypothesis.

Although the number of studies reporting microbes and microbial metabolism from the deep subsurface has been rising (Chapelle, 2001), our understanding of As biogeochemistry in aquifers is severely limited. For example, despite the fact that a consensus is building that microbially mediated reductive dissolution of Fe(III) oxide/oxyhydroxides and subsequent release of adsorbed As is likely the chief mechanism accounting for the high As concentrations of groundwaters from the Ganges Delta (Nickson et al., 2000; McArthur et al., 2001), researchers are only just beginning to link microbial processes to As in the region (e.g., Akai et al., 2004). Akai et al. (2004) argued, based on microbial culture experiments using aquifer sediments from the Ganges delta that microbial processes mediate As (no speciation data) release from the sediments under anoxic conditions. It would seem that more systematic study of As, with emphasis on its behavior along groundwater flow paths, are necessary to sort out the important biogeochemical reactions and processes responsible for controlling As concentrations and speciation in the deep subsurface. Based on the literature review and the aforementioned discussion, the following research hypothesis was developed:

Physico-chemical changes occurring along groundwater flow paths within aquifers that accompany chemical weathering and oxidation-reduction reactions facilitated by the in situ microbial consortium (e.g., Fe reducers, SO<sub>4</sub> reducers), catalyze both As mobilization from, and capture by, mineral/amorphous phases via adsorption/desorption reactions and/or mineral dissolution. Utilization by microbes of

organic matter and electron acceptors [e.g., Fe(III), As(V), SO<sub>4</sub>] that are supplied by aquifer sediments and flowing groundwaters is inferred to alter geochemical conditions along flow paths (Champ et al., 1979), which may result in mobilization of surface sorbed As through pH induced desorption, and by redox related reductive (Fe oxide/oxyhydroxides) or oxidative (sulfides) dissolution. Thus, As concentrations and speciation in solution likely “evolve” along groundwater flow paths as a function of changing pH, redox conditions, and solution composition that may be driven directly and/or indirectly by microbial metabolism.

This central hypothesis is addressed by meeting the following research objectives:

(i) Elucidate the geochemical behavior of As along groundwater flow paths in well characterized aquifers with particular emphasis on quantifying As concentrations and speciation in groundwater samples to establish how aqueous As concentrations and speciation evolve along groundwater flow paths, and

(ii) Determine the speciation of As in solid phase aquifer sediment samples, with specific emphasis on the labile (i.e., surface exchangeable) and non-labile As fractions (e.g., coprecipitated with Fe oxides) associated with the solid aquifer substrate.

To accomplish these objectives, an integrated field and laboratory study was implemented and three well characterized, drinking water aquifers [Carrizo Sand (Texas), Upper Floridan (Florida), and Aquia (Maryland)] were investigated (chapters 2, 3 and 4, respectively). A series of groundwater samples were collected along flow paths within each aquifer, and analyzed for inorganic As species (i.e., arsenite [As(III)] and arsenate

[As(V)], along with ancillary geochemical parameters (e.g., pH, temperature, alkalinity, Fe concentration/speciation, N species, dissolved  $S^{2-}$ , dissolved  $O_2$ , and Eh). Results of groundwater studies indicate that the Carrizo Sand and the Upper Floridan aquifers exhibit low dissolved As concentrations (below 1.4 ppb or  $19 \text{ nmol kg}^{-1}$ ), whereas the Aquia groundwaters have high As concentrations (up to 80 ppb or  $1072 \text{ nmol kg}^{-1}$ ) that in many wells exceed the US Environmental Protection Agency's current maximum contaminant level of 10 ppb ( $133 \text{ nmol kg}^{-1}$ ).

In the second part of the project to address the issue of lability (chapter 4), I chose to further investigate the Aquia and samples of the aquifer sediments using petrographic and by X-Ray diffraction (XRD) analyses, and a modified sequential extraction method specifically developed for As (Wenzel et al., 2001). By combining the results of sediment experiments and laboratory and field measurements of As and Fe speciation, dissolved  $S^{2-}$ , and ancillary geochemical parameters in groundwaters from these aquifers, it was established that changes in As concentrations and speciation in groundwaters along the flow paths result from a combination of oxidation and/or reduction of As in solution, adsorption/desorption of labile As species, or the result of release of As from the non-labile pool by mineral dissolution. The data generated in this research is expected to improve our knowledge and understanding of As speciation and mobility in aquifers and provide insight into potential microbial controls.

In the following three chapters of this dissertation, I present three manuscripts in which the biogeochemical cycling of As along groundwater flow paths are discussed. The first manuscript (chapter 2) discusses the mobilization and distribution of As along a



groundwater flow path in the relatively pristine, Carrizo Sand aquifer. In addition to concentrations and speciation of As, chapter 2 presents ancillary geochemical data for the flow path, from which biogeochemical processes that affect cycling of As are inferred. The second manuscript (chapter 3) presents dissolved As concentrations and speciation data along a flow path in the Upper Floridan aquifer and examines the cycling of As in this relatively uncontaminated aquifer. The third manuscript (Chapter 4) focuses on evaluating the natural “evolution” of As along a groundwater flow path in Aquia aquifer by combining dissolved As concentrations and speciation data with results from petrographic, XRD and sequential extraction analyses of aquifer sediments. Finally, chapter 5 is the concluding chapter that restates and ties together the major findings presented in the preceding chapters. Appendix A presents an XRD diagram and sequential extraction results of Carrizo Sand sediments.

## CHAPTER 2

### ARSENIC CONCENTRATIONS AND SPECIATION ALONG A GROUNDWATER FLOW PATH: THE CARRIZO SAND AQUIFER, TEXAS, USA

#### 2.1 Introduction

In groundwater arsenic (As) chiefly occurs as inorganic oxyanions of arsenite [As(III)] and arsenate [As(V)], although under specific conditions, methylated and other organoarsenicals species may occur (e.g., Ferguson and Gavis, 1972; Ficklin, 1983; Cullen and Reimer, 1989; Francesconi and Kuehnelt, 2002; Le, 2002). Thermodynamics predicts that the dominant species of As in surface waters is As(V), which exists, depending on the pH as either  $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ , whereas in more reducing environments, As(III) predominates and is present as  $\text{H}_3\text{AsO}_3^0$  (e.g., Ferguson and Gavis, 1972; Cherry et al., 1979; Cullen and Reimer, 1989). Deviation from such theoretical behavior, however, is commonly observed due to the sluggish redox kinetics of As (e.g., Ferguson and Gavis, 1972; Cutter, 1992). Arsenious acid ( $\text{H}_3\text{AsO}_3$ ) does not dissociate until pH of  $\sim 9.2$ , and consequently, its uncharged nature strongly affects the geochemical behavior of As(III) by increasing its mobility in groundwaters relative to As(V) (Manning and Goldberg, 1997; Goldberg, 2002; Hamon et al., 2004). Thus, the adsorption behavior of As, its mobility in groundwater, as well as its toxicity to organisms, are largely related

to chemical speciation (e.g., Manning and Goldberg, 1997; Le, 2002; Smedley and Kinniburgh, 2002; Vahter, 2002; Oremland and Stolz, 2003; Hamon et al., 2004).

Until recently, most studies reporting As in groundwaters included only concentrations and not speciation measurement, and were chiefly concerned with documenting the extent of elevated As concentrations in groundwaters (e.g., Welch et al., 1988, 2000; Nickson et al., 2000; Peters et al., 1999; McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002; Peters and Blum, 2003). However, in order to quantitatively understand As behavior and cycling in groundwater flow systems, it is not enough to only measure total dissolved concentrations inasmuch as speciation data are also critical. Many studies of As poisoning from groundwater sources, including those for the Ganges Delta, have indeed suffered in their attempts to identify As sources and the processes responsible for elevated As levels owing to: (1) a lack of speciation data and (2) because a “shot-gun” approach to sample collection was employed. The “shot-gun” approach (e.g., sampling as many wells as possible without regard to groundwater flow paths, relationships between wells, and whether collected water samples are from the same or different aquifers that may or may not be hydrogeologically connected) is useful for characterizing the areal extent of elevated As concentrations. However, such an approach reveals little about the behavior and, hence, “evolution” of As concentrations along groundwater flow paths in actual aquifers, and without speciation data, nothing quantitative can be ascertained concerning the chemical reactivity (e.g., adsorption/desorption, mobility), toxicity, and/or the bioavailability of As in these systems. Others have shown that As concentrations and speciation in marine and

lacustrine environments reflects pH, redox conditions, solution composition, and mineral substrate compositions (Andreae, 1978; Maest et al., 1988; Kuhn and Sigg, 1993; Bowell, 1994). Accordingly, because these parameters are expected to change along groundwater flow paths due to water-rock reactions and biogeochemical processes (e.g., Champ et al., 1979; Edmunds et al., 1984; Lovley and Goodwin, 1988), As concentrations, speciation, and mobility are also expected to vary along groundwater flow paths.

Furthermore, considering the differential mobility and toxicity of inorganic As species, studies of its speciation are essential to understand As behavior in groundwaters, which are a significant drinking water resource for the U.S. and the world's population (Solley et al., 1993). Here, we quantify As concentrations and speciation along a groundwater flow path in the Carrizo Sand aquifer in southeastern Texas, USA. The Carrizo Sand is an important drinking water source for the region and is used extensively for crop irrigation. In addition to As concentrations and speciation, we present ancillary geochemical data for the flow path, from which we infer biogeochemical processes that affect As concentrations and speciation along the flow path.

## 2.2 Study area

The Carrizo Sand aquifer is largely a confined aquifer, and is a major groundwater flow system in south Texas (Fig. 2.1). Groundwaters from the Carrizo Sand aquifer are used extensively for irrigation and water supply for the local population (e.g., City of Pleasanton, Texas). The aquifer is recharged where it crops out in northwest Atascosa County, where it defines the Carrizo Sand ridge. The Carrizo Sand dips southeast towards the Gulf of Mexico at a slope of  $\sim 1.09^\circ$ - $1.41^\circ$  (Pearson and White,



**DETAILS OF STUDY AREA**

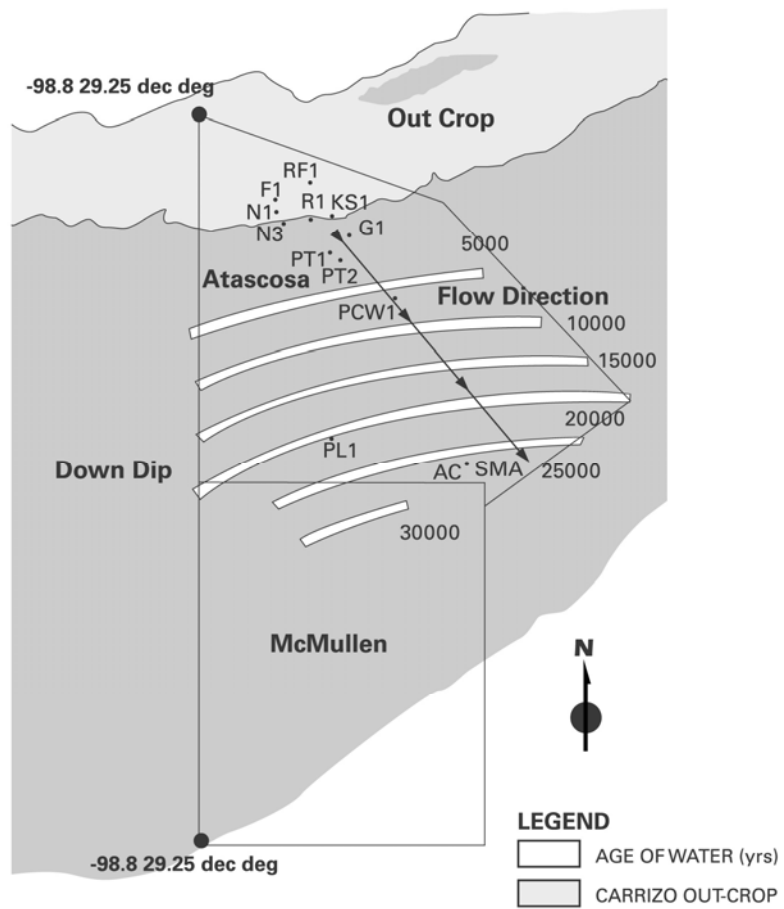


Figure 2.1: Map of the USA showing location of Texas. Inset shows location of study area, investigated flow path of groundwater, radiocarbon age of groundwater based on Pearson and White (1967) and location of sampled wells in the Carrizo Sand aquifer, South Texas, USA.

1967; Castro and Goblet, 2003). In southern Atascosa and northern McMullen Counties, wells tapping the Carrizo Sand aquifer are on the order of 1300 to 1400 m below ground surface, and produce relatively warm groundwaters (Table 2.2). Temperatures of these groundwaters are consistent with heating due to a typical, nonorogenic region geothermal gradient (i.e., 15-23°C km<sup>-1</sup>; Philpotts, 1990). In the study area, the Carrizo Sand is predominantly composed of medium-grained, unconsolidated Eocene quartz sand with minor amounts of clay, calcite, lignite and pyrite (Pearson and White, 1967). Pearson and White (1967) estimated the aquifer porosity to be ~30 to 40% and the average hydraulic conductivity to be 8.2 m day<sup>-1</sup>. Pearson and White (1967) argued that the hydraulic gradient varied along the flow path, ranging from ~1.9 m km<sup>-1</sup> in the recharge area to 0.19 m km<sup>-1</sup> ~58 km southwest from the recharge area. The thickness of the Carrizo varies substantially throughout the region. In the outcrop area in northwestern Atascosa County the estimated thickness is 100 m, whereas in southern McMullen County the thickness is estimated at 360 m (Castro et al., 2000; Castro and Goblet, 2003). Precipitation recharges the Carrizo Sand aquifer in the outcrop area in northwest Atascosa County, and the resulting groundwaters subsequently flow down-gradient towards the southeast (Pearson and White, 1967; Castro et al., 2003). High fluid pressure causes groundwater to discharge from the aquifer by cross-formational upward leakage (Castro and Goblet, 2003). In southern McMullen County, discharge is also thought to occur by upward infiltration along fractures associated with the Wilcox geothermal corridor (Castro et al., 2000; Castro and Goblet, 2003). The <sup>14</sup>C age of groundwater in the Carrizo Sand aquifer increases from ~5000 a in the vicinity of the recharge area in

northern Atascosa County to approximately 30,000 a in southern McMullen County (Fig. 2.1; Pearson and White, 1967; Stute et al., 1992). Based on the  $^{14}\text{C}$  age of the Carrizo groundwater, Pearson and White (1967) estimated the flow velocity of Carrizo groundwaters to be  $2.4 \text{ m yr}^{-1}$  at roughly 16 km along the flow path, and  $1.6 \text{ m yr}^{-1}$  at approximately 50 km down-gradient. Along the same flow path, Stute et al. (1992) determined a similar, average groundwater flow velocity of  $\sim 2 \text{ m yr}^{-1}$ . Carrizo groundwaters are predominantly fresh and potable, except towards the southeast in southern McMullen County where salinity increases reaching values up to  $10 \text{ g kg}^{-1}$  (Castro et al., 2000; Castro and Goblet, 2003). The current study is limited to the portion of the aquifer in Atascosa and McMullen Counties containing potable water.

## 2.3 Methods

### *2.3.1 Field Sampling*

Prior to transport to the field, all sample bottles (HDPE), Poly-Prep chromatography columns, and Teflon® tubes used during sample filtration were meticulously cleaned using trace element clean procedures (Johannesson and Hendry, 2000). Groundwater samples were collected in June 2004 from 10 wells in the Carrizo Sand aquifer located along a previously studied flow path within Atascosa and McMullen Counties, Texas (Fig. 2.1). Measurements of pH, specific conductance, temperature, alkalinity, dissolved oxygen (DO), oxidation-reduction potential (Eh), iron speciation, and  $\text{H}_2\text{S}$  concentrations were conducted on site during the field sampling campaign. All of the wells sampled within the Carrizo Sand aquifer are production wells, and were consequently purged with high capacity pumps for at least 30 minutes prior to sample

collection. In order to ensure that all samples represented groundwaters from the Carrizo Sand aquifer and not from the well bore, water temperature, specific conductance, and pH were continuously monitored during the purging, and sample collection did not commence until these parameters were stable.

Iron speciation [Fe(II) and Fe(III)] in Carrizo groundwater was determined in the field on separate sample aliquots via UV/VIS spectrophotometry using a portable spectrophotometer (Hach DR/890). Specifically, Fe(II) was determined using the 1,10 Phenanthroline method (Eaton et al., 1995a), total Fe [Fe<sub>T</sub>] was determined by the FerroVer method (Eaton et al., 1995a), and Fe(III) was subsequently calculated by difference. The method detection limit for Fe<sub>T</sub> and Fe(II) is 0.54 μmol kg<sup>-1</sup> (Eaton et al., 1995a). Hydrogen sulfide was measured on separate aliquots using the same portable spectrophotometer and the Methylene Blue method (Eaton et al., 1995b). The method detection limit for H<sub>2</sub>S is 0.29 μmol kg<sup>-1</sup> (Eaton et al., 1995b).

Dissolved oxygen, oxidation-reduction potential (i.e., Eh in mV), pH, specific conductance, total dissolved solids (TDS) and temperature were quantified on site using a Hydrolab MiniSonde4 with a flow through cell. The MiniSonde4 was attached to each well by connecting the flow through cell to the well outflow with a polyethylene tube, which allowed dissolved oxygen and oxidation-reduction potential for each groundwater sample to be measured without exposing the groundwater to the atmosphere.

### *2.3.2 Sampling for arsenic concentrations and speciation*

Arsenic species were separated in the field using an anion exchange chromatography method developed by Ficklin (1983) and described more recently by



Wilkie and Hering (1998). The anion exchange method employed Poly-Prep 0.8x4 cm chromatography columns packed with Bio-Rad AG<sup>®</sup> 1x8, 50-100 mesh, anion exchange resin converted to the acetate form (see Wilkie and Hering, 1998 for details).

Groundwater samples were first collected from the well head into collapsible pre-cleaned LDPE cubitainers<sup>®</sup> and were then immediately filtered through 0.45 µm in-line filter-capsules (Gelman Sciences, polyether sulfone membrane) by drawing water from the cubitainers<sup>®</sup> through pre-cleaned Teflon<sup>®</sup> tubing using a peristaltic pump. The filtered samples were then acidified to pH ~3.5 by addition of ultra-pure HNO<sub>3</sub> (Seastar Chemical, Baseline). The acidified samples were subsequently passed through the anion exchange columns. At a pH of ~3.5, As(V) is anionic and is retained by the resin in the column, whereas As(III), which remains a neutral species, passes through the column and is collected in pre-cleaned HDPE bottles (Wilkie and Hering, 1998). Arsenite is then measured in the eluted fractions and total dissolved As is quantified using separate filtered sample aliquots preserved by acidification to pH <2 using ultra-pure HNO<sub>3</sub> (Wilkie and Hering, 1998). Arsenate is subsequently determined by difference from the As<sub>T</sub> and As(III) concentration measurements for each sample. A field blank and 4 duplicate samples for As(III) were collected. All samples were stored at 4°C prior to analysis.

Arsenic was quantified by inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer/Sciex Elan 6100 DRC). The instrument contains a reaction cell, which allows for precise measurements of As at ultra-low levels (i.e., low nanomolal to high picomolal concentrations) in natural waters where Cl normally can interfere with As

detection using standard quadrupole mass spectrometry (Perkin ElmerSCIEX, 2003). Other ICP-MS methods for As analysis in natural waters have included use of nitrogen as a carrier gas instead of argon (Branch et al., 1991) and application of the high resolution mode in magnetic sector instruments (Klaue and Blum, 1999) to avoid or resolve interferences on  $^{75}\text{As}$  by  $\text{ArCl}^+$ . In addition, corrections for isobaric interferences are also commonly made (Johannesson et al., 1996). The DRC method is designed, however, to greatly reduce the number of  $\text{ArCl}^+$  ions prior to introduction of the sample to the quadrupole mass spectrometer.

The ICP-MS was calibrated and the sample concentrations verified using a series of As calibration standards of known concentrations (0.40, 0.67, 3.20, 14.7, 105 and 213.6  $\text{nmol kg}^{-1}$ ). The calibration standards were prepared from Perkin Elmer Pure plus As standard (i.e., 10  $\text{mg kg}^{-1}$ , Lot #25-61 AS). In addition, a QC standard of 96.1  $\text{nmol kg}^{-1}$  was determined by using NIST traceable High Purity Standards (Charleston, SC). The QC standard was run routinely during the sample analysis to monitor instrument drift and overall quality of the analysis. Analytical precision was typically better than 6% RSD (relative standard deviation). The method detection limit for As, based on  $3\sigma$  of the blank measurement, is 0.36  $\text{nmol kg}^{-1}$  (27  $\text{ng kg}^{-1}$ ).

## 2.4 Results

### *2.4.1 Results of field measurements*

The analytical results for groundwaters from the Carrizo aquifer are presented in Tables 2.1 and 2.2, and Figs. 2.2 and 2.3. Figure 2.2 demonstrates that the pH of Carrizo groundwaters was consistent during the sampling period beginning in 2002 and ending in

2004. Because the current contribution concerns As speciation and concentration data collected in 2004, only corresponding data from the 2004 sampling campaign will be considered hereafter. The pH values of Carrizo groundwaters range from 6.1 to 8.5, and exhibit systematic changes along the flow path that include an initial decrease from 6.6 to 6.1 in the first 10 km, before increasing to  $\text{pH} > 8$  at a distance  $> 41$  km down-gradient along the flow path (Fig. 2.2). Alkalinity (DIC) ranges from 0.65 to 7.6  $\text{mmol kg}^{-1}$  as  $\text{HCO}_3^-$  (Table 2.1). Alkalinity (i.e.,  $\text{HCO}_3^-$ ) also varies along the flow path by first decreasing from 1.64  $\text{mmol kg}^{-1}$  to 0.65  $\text{mmol kg}^{-1}$  in the initial 10 km of the flow path before increasing again and reaching 7.6  $\text{mmol kg}^{-1}$  at a distance of 66 km along the flow path (Fig. 2.2).

The  $\text{Fe}_T$  concentrations in groundwaters from the Carrizo aquifer range from  $\sim 1.3$  to 184  $\mu\text{mol kg}^{-1}$  (Table 2.2). In the portion of the aquifer proximal to the recharge zone (i.e.,  $\sim 0$  to  $\sim 15$  km),  $\text{Fe}_T$  concentrations and Fe speciation is highly variable. More specifically, at 0.5 km along the flow path (well F-1), the  $\text{Fe}_T$  concentration is 28  $\mu\text{mol kg}^{-1}$ . The total Fe concentration increases  $\sim 6.6$  fold by 4.3 km along the flow path (well N-1) to 184  $\mu\text{mol kg}^{-1}$  (Fig. 2.3). With continued flow down-gradient to well KS-1 (7.4 km), Fe concentrations drop to 1.4  $\mu\text{mol kg}^{-1}$ , which are among the lowest Fe concentrations measured in groundwater from the aquifer. Total Fe concentrations again rise with flow to a distance of  $\sim 13$  km (well G-1) reaching a value of 40  $\mu\text{mol kg}^{-1}$  (Table 2.2; Fig. 2.3). For the remainder of the flow path,  $\text{Fe}_T$  first exhibits a sharp decrease (Poteet well) and then remains relatively constant between 11 and 17  $\mu\text{mol kg}^{-1}$  until 41 km along the flow path (Peeler-1 well) before falling to 1.3  $\mu\text{mol kg}^{-1}$  at 59 km (well

AC74R-2; Fig. 2.3). The Fe(II) concentrations, which are the dominant form of Fe in groundwaters of the Carrizo aquifer, range from below detection limit ( $\sim 0.54 \mu\text{mol kg}^{-1}$ ) to  $134 \mu\text{mol kg}^{-1}$ . The Fe(III) levels also range from below the detection [i.e., based on difference between  $\text{Fe}_T$  and Fe(II)] to  $50 \mu\text{mol kg}^{-1}$ . In the portion of the aquifer closest to the recharge zone, groundwaters generally exhibit higher Fe(II) concentrations (Fig. 2.3) except for well KS-1 at 7.4 km, where all dissolved Fe (i.e.,  $1.43 \mu\text{mol kg}^{-1}$ ) is Fe(III). In addition, although Fe(II) predominates in groundwater from well N-1 at 4.3 km, Fe(III) concentrations are significant ( $50 \mu\text{mol kg}^{-1}$ ), accounting for  $\sim 27\%$  of  $\text{Fe}_T$  (Fig. 2.3). Beyond well KS-1, essentially all dissolved Fe is Fe(II), except for groundwater from the Peeler-1 well at 41 km, where Fe(III) exceeds that of Fe(II) (Table 2.2).

Hydrogen sulfide concentrations in groundwaters from the Carrizo aquifer range from below the detection limit ( $\sim 0.29 \mu\text{mol kg}^{-1}$ ) to  $\sim 50 \mu\text{mol kg}^{-1}$ . Between 0.5 and 4.3 km along the flow path (wells F-1 and N-1),  $\text{H}_2\text{S}$  concentrations remain constant at  $1.9 \mu\text{mol kg}^{-1}$  (Table 2.2). With flow beyond well N-1 (4.3 km), the concentration of  $\text{H}_2\text{S}$  decreases to the detection limit where it remains until roughly 14.5 km (Poteet well) along the flow path (Fig. 2.3). With flow beyond 14.5 km, the  $\text{H}_2\text{S}$  concentrations of Carrizo groundwaters begin to increase and eventually reach a maximum of  $50 \mu\text{mol kg}^{-1}$  at  $\sim 66$  km down-gradient (well SMA74R-1; Table 2.2, Fig. 2.3). Between 26 and 59 km along the flow path (i.e., between the PCW-1 and AC74R-2 wells), the  $\text{H}_2\text{S}$  concentration increases at a relatively constant rate of approximately  $0.17 \mu\text{mol kg}^{-1} \text{ km}^{-1}$ . From 59 to

66 km along the flow path (i.e., from the AC74R-2 well to the SMA74R-1 well), H<sub>2</sub>S concentration increases at a rate of 6.5 μmol kg<sup>-1</sup> km<sup>-1</sup>, an increase of 38 times.

The DO concentration remains relatively low throughout the aquifer except for well N-3, at ~9.4 km, where DO is 123 μmol kg<sup>-1</sup> (Fig. 2.3). The oxidation-reduction potential (Eh) values for Carrizo groundwaters range from -137 to 282 mV. Although the Eh measured for sample F-1 (0.5 km) was relatively low (-40 mV) the other groundwaters from the first ~15 km of the flow path had relatively high Eh values. More importantly, groundwaters from near the recharge area generally exhibit higher Eh values than the down-gradient groundwaters beyond ~15 km (Table 2.2, Fig. 2.3). It is important to note that Eh measurements are, however, at best only a qualitative indicator of groundwater redox (e.g., Lindberg and Runnels, 1984).

#### *2.4.2 Arsenic concentrations and speciation*

Total dissolved inorganic arsenic concentrations [ $As_T = As(III) + As(V)$ ] and the As speciation results are presented in Table 2.2 and Fig. 2.3. In groundwaters from the Carrizo,  $As_T$  ranges from ~0.37 to 2.5 nmol kg<sup>-1</sup> (Table 2.2), and exhibits a mean of 1.6 nmol kg<sup>-1</sup>. Along the flow path,  $As_T$  concentrations initially decrease by a factor of ~2.3 from 2.2 nmol kg<sup>-1</sup> at 0.5 km (well F-1) to 0.97 nmol kg<sup>-1</sup> approximately 7.4 km down-gradient (well KS-1; Table 2.2, Fig. 2.3). Total As concentrations subsequently rise sharply to 2.4 nmol kg<sup>-1</sup> at 9.4 km (well N-3) and reach a maximum of 2.5 nmol kg<sup>-1</sup> at roughly 13 km (i.e., well G-1). With further flow down-gradient along the flow path,  $As_T$  concentrations again decrease to ~2.3 nmol kg<sup>-1</sup> at 14.5 km (Poteet well) before dropping to ~0.4 nmol kg<sup>-1</sup> at 26 km (PCW-1 well; Fig. 2.3). The total As concentration remains

relatively low along the flow path until 66 km (well SMA74R-1) where it again sharply increases to  $1.9 \text{ nmol kg}^{-1}$ . In general,  $\text{As}_T$  concentrations are higher along the first 14.5 km of the flow path (mean  $\text{As}_T = 2.1 \text{ nmol kg}^{-1}$ ) compared to the remainder of the flow path, where the mean  $\text{As}_T$  concentration is  $0.9 \text{ nmol kg}^{-1}$ .

In groundwaters from the Carrizo aquifer  $\text{As(III)}$  concentrations range from 0.29 to  $0.87 \text{ nmol kg}^{-1}$ , whereas  $\text{As(V)}$  concentrations, which are calculated based on difference between  $\text{As}_T$  and  $\text{As(III)}$ , range from below detection to  $\sim 2.0 \text{ nmol kg}^{-1}$ . The calculated mean  $\text{As(V)}$  and  $\text{As(III)}$  concentrations for the entire flow path are 1.2 and  $0.55 \text{ nmol kg}^{-1}$ , respectively. The highest concentrations of  $\text{As(V)}$  [ $2.0 \text{ nmol kg}^{-1}$ ] and  $\text{As(III)}$  [ $0.87 \text{ nmol kg}^{-1}$ ] occur at  $\sim 9.4$  and  $\sim 13$  km, respectively, along the flow path. From 0.5 km to 14.5 km (well F-1 to the Poteet well),  $\text{As(V)}$  is the dominant form of dissolved As in Carrizo groundwaters (Fig 2.3). With flow beyond 14.5 km and until 59 km (well AC74R-2),  $\text{As(III)}$  dominates, whereas in groundwater from well SMA74R-1 at 66 km,  $\text{As(V)}$  again predominates (Fig. 2.3).

Table 2.1 Dissolved organic carbon (DOC) concentrations and pH values of groundwaters from the Carrizo Sand aquifer collected in 2002 and 2003. DOC and 2002 pH data are from Tang and Johannesson (2005a), and 2003 pH data are from Vessely (2004).

Sample	Distance (Well Depth) km (m)	2002 DOC mg kg <sup>-1</sup>	2002 pH	2003 pH
RF-1	0 (61)	0.35	7.32	
F-1	0.50 (NA <sup>#</sup> )			6.40
N-1	4.29 (159)	0.43	6.79	7.00
R-1	6.9 (168)	0.30	6.55	
KS-1	7.40 (122)	0.17	6.64	6.36
N-3	9.37 (183)	0.31	6.13	
G-1	12.8 (244)			6.14
Poteet	14.5 (290)	0.82	6.48	6.33
PCW-1	26.1 (488)	0.26	7.38	6.95
Peeler-1	41.1 (655)	0.19	8.34	8.13
AC74R-2	59.0 (1317)	0.65	8.68	8.34
SMA74R-1	65.8 (1420)	0.28	8.12	8.40

# Not Available

Table 2.2 2004 Data, Carrizo Sand aquifer, South Texas.

Sample	Distance (Well Depth) km (m)	As <sub>T</sub> nmol kg <sup>-1</sup>	As(III) nmol kg <sup>-1</sup>	As(V) nmol kg <sup>-1</sup>	Fe <sub>T</sub> μmol kg <sup>-1</sup>	Fe(II) μmol kg <sup>-1</sup>	Fe(III) μmol kg <sup>-1</sup>	H <sub>2</sub> S μmol kg <sup>-1</sup>	Cond μS cm <sup>-1</sup>	Temp °C	DO μmol kg <sup>-1</sup>	TDS mg kg <sup>-1</sup>	pH	Eh mV	Alk as HCO <sub>3</sub> mmol kg <sup>-1</sup>
FB <sup>o</sup>		BDL*	BDL	BDL											
F-1	0.50 (NA <sup>#</sup> )	2.19±0.12	0.60±0.03	1.59±0.09	27.8	27.2	0.54	1.87	555	24.6	8.75	355	6.56	-40.0	1.64
N-1	4.29 (159)	2.08±0.11	0.56±0.03	1.52±0.08	184	134	50.1	1.87	587	25.4	8.13	372	6.58	78.0	1.80
KS-1	7.40 (122)	0.97±0.05	0.41±0.02	0.56±0.03	1.43	BDL	1.43	BDL	319	24.6	11.3	204	6.30	282	0.78
N-3	9.37 (183)	2.44±0.13	0.45±0.02	1.99±0.11	27.8	21.0	6.80	0.62	11.5	30.4	123	6.95	6.07	166	0.65
G-1	12.8 (244)	2.47±0.13	0.87±0.05	1.60±0.08	39.6	34.8	4.83	0.94	289	26.5	4.69	185	6.21	137	0.78
Poteet	14.5 (290)	2.33±0.13	0.60±0.03	1.73±0.10	16.5	14.5	1.97	0.31	362	28.2	8.75	231	6.13	170	0.78
PCW-1	26.1 (488)	0.37±0.02	0.43±0.02	BDL	10.7	8.06	2.69	0.94	555	34.5	16.4	356	7.22	48.0	3.92
Peeler-1	41.1 (655)	0.91±0.05	0.69±0.04	0.22±0.01	14.3	3.22	11.1	2.81	507	27.9	6.25	325	8.46	-114	6.00
AC74R-2	59.0 (1317)	0.41±0.02	0.29±0.02	0.12±0.00	1.25	1.43	BDL	6.24	919	55.0	5.63	586	8.50	-137	4.80
SMA74R-1	65.8 (1420)	1.92±0.10	0.55±0.03	1.37±0.07	3.40	2.15	1.25	49.9	1025	41.6	4.06	648	8.24	-122	7.60

# Not Available

<sup>o</sup> Field Blank



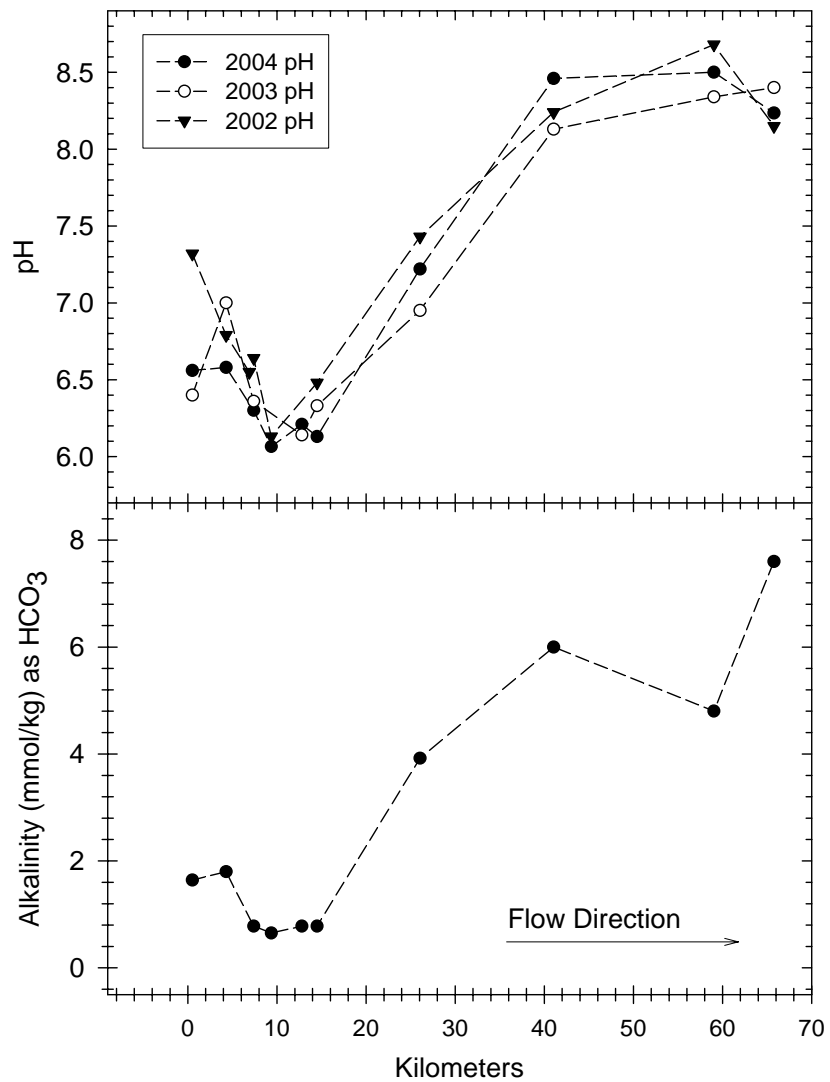


Figure 2.2: Carrizo Sand aquifer data (a) pH; (b) alkalinity ( $\text{mmol kg}^{-1}$ ) as a function of distance from recharge zone (km).

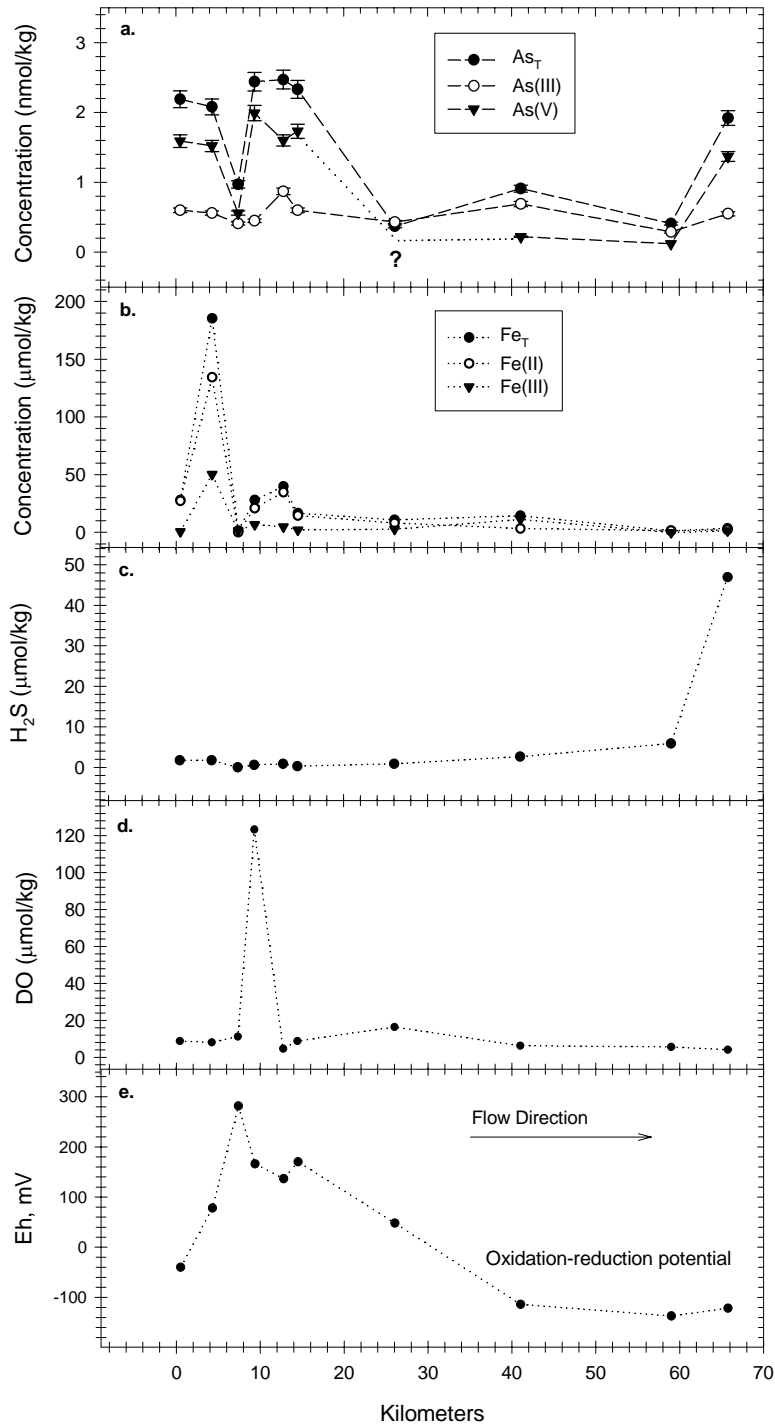


Figure 2.3: Carrizo Sand aquifer data 2004 (a) As speciation ( $\text{nmol kg}^{-1}$ ); (b) Fe speciation ( $\mu\text{mol kg}^{-1}$ ); (c)  $H_2S$  concentrations ( $\mu\text{mol kg}^{-1}$ ); (d) DO concentration ( $\mu\text{mol kg}^{-1}$ ); (e) Eh (mV) as a function of distance from recharge zone (km).

## 2.5 Discussion

### *2.5.1 Redox conditions along the Carrizo flow path*

Iron concentrations and speciation, dissolved sulfide and oxygen concentrations, measured oxidation-reduction potential (Eh), as well as concentrations of redox sensitive trace elements (i.e., U, Re; Vessely, 2004) in Carrizo groundwaters are consistent with changing redox conditions along the groundwater flow path in the aquifer (Fig. 2.3). Within the first 10 – 15 km of the flow path, for example, total Fe concentrations vary greatly (i.e., more than an order of magnitude) as do the measured Eh values and the dissolved oxygen concentrations. Moreover, within the first 10-15 km of the flow path the dissolved Fe concentrations fluctuate between relatively high and low values (1.43 to 184  $\mu\text{mol kg}^{-1}$ ) compared to portions of the aquifer that are further down-gradient along the flow path (1.25 to 39.6  $\mu\text{mol kg}^{-1}$ ; Fig. 2.3). These Fe data suggest that Fe(III) reduction is occurring in the Carrizo aquifer proximal to the recharge zone and further down-gradient because: (1) Fe concentrations are generally high (except well KS-1, see below); and (2) Fe(II) is the predominant dissolved Fe species in groundwaters with high total Fe concentrations (i.e., F-1 and N-1; Fig. 2.3). More specifically, between well F-1 (0.5 km) and well N-1 (4.3 km) along the flow path in the Carrizo aquifer the data indicate that substantial Fe(III) reduction occurs as the Fe(II) concentration increases by a factor of almost 7. However, between well N-1 and well KS-1 (7.4 km) along the flow path the Fe concentration falls precipitously, suggesting that Fe(II) oxidation has occurred between these wells with subsequent precipitation of Fe(III) oxyhydroxides/oxides. The decrease in Fe(II) concentration does not appear to reflect

precipitation of Fe(II)–sulfide minerals as dissolved S<sup>2-</sup> concentrations are low and have not changed compared to groundwaters collected up-gradient of well KS-1 (Fig. 2.3). Moreover, the oxidation-reduction potential measured in groundwaters from KS-1 (i.e., 282 mV) is the highest observed along the entire flow path indicating relatively oxidizing conditions.

The predominance of Fe(II) in Carrizo aquifer groundwaters demonstrates that Fe(III) reduction is an important process in the aquifer. Various investigators have shown that dissimilatory Fe reducing microbes such as *Geobacter sp.* and *Shewanella putrificiens* can oxidize organic matter by using Fe(III) as a terminal electron acceptor, generating Fe(II) as a metabolic product (e.g., Lovley et al. 1991; Cummings et al., 1999). Iron reducing microbes such as *Geobacter sp.* have been recovered from the deep subsurface in other Atlantic and Gulf Coastal Plain aquifers (Lovley et al., 1990), and their presence in the Carrizo aquifer could explain the Fe speciation data shown in Table 2.2 and Fig. 2.3. The Carrizo contains abundant reduced carbon in the form of lignite (Pearson and White, 1967; Tang and Johannesson, 2005a), which has been identified as driving microbial mediated redox reactions in other coastal plain aquifers (Chapelle et al., 1987; Chapelle and Lovley, 1990). However, at present, we can only infer the existence of such microbes in the Carrizo aquifer as we have not yet conducted any direct sampling of the in situ microbial consortium. It is also possible that the variable redox conditions within the aquifer proximal to the recharge zone may reflect infiltration of meteoric water with relatively high dissolved oxygen concentrations (Fig. 2.3) and/or percolation of soil

zone waters with relatively high dissolved organic carbon (DOC) concentrations, which could facilitate Fe(III) reduction (Harvey et al., 2002).

With flow beyond well KS-1, the data are consistent with the establishment of redox zones (i.e., region of the flow path dominated by Fe reduction followed by a region dominated by sulfate reduction) within the aquifer (e.g., Back and Barnes, 1965; Champ et al., 1979; Edmunds et al., 1984; Lovely and Goodwin, 1988; Smedley and Edmunds, 2002). Between wells KS-1 and N-3 (9.4 km), for example, Fe(II) concentrations in Carrizo groundwaters increase from below the detection limit to  $21 \mu\text{mol kg}^{-1}$ , indicating that Fe(III) reduction is important. Ferrous iron concentrations further increase to  $35 \mu\text{mol kg}^{-1}$  at well G-1 (12 km), decrease to  $14.5 \mu\text{mol kg}^{-1}$  at the Poteet well, and then exhibit a slow decline in concentration until the Peeler-1 well at 41 km (Fig. 2.3). Thereafter, Fe(II) concentrations and hence,  $\text{Fe}_T$ , drop to even lower values ( $1\text{-}2 \mu\text{mol kg}^{-1}$ ) for the remainder of the flow path. As mentioned above, total Fe concentrations are approximately constant between the Poteet and Peeler-1 wells, a distance of over 26 km (Fig. 2.3). The data is consistent with redox conditions being buffered by Fe(III) reduction in this portion of the aquifer.

Similar to Fe, dissolved sulfide concentrations are also below detection in groundwater from well KS-1, remain low (i.e.,  $<1 \mu\text{mol kg}^{-1}$ ) in groundwater from well N-3 (9.4 km) to the PCW-1 well (26 km), where  $\text{H}_2\text{S}$  then begins to increase (Fig. 2.3). However, unlike dissolved Fe concentrations, the  $\text{H}_2\text{S}$  concentration increases by a factor of 3 between the PCW-1 and Peeler-1 wells (41 km). Furthermore, between the Peeler-1 and the AC74R-2 wells (59 km down-gradient) dissolved sulfide concentrations more

than double and subsequently increase by a factor of 8 between the AC74R-2 and SMA74R-1 wells (66 km). Sulfate reduction likely buffers the redox condition of groundwaters between these two wells. Consequently, we submit that the Fe and the sulfide data for the Carrizo aquifer are consistent with a zone of predominantly Fe(III) reduction between well N-3 (9.4 km) and the Peeler-1 well (41 km) and a zone of chiefly sulfate reduction beyond well AC74R-2 (59 km). In between the Peeler-1 and the AC74R-2 wells, total Fe concentrations decrease, whereas H<sub>2</sub>S concentrations increase, indicating a transitional zone between Fe(III) reduction and sulfate reduction where neither process dominates. Moreover, the sulfide data are consistent with initiation of sulfate reduction between the PCW-1 and Peeler-1 wells along the groundwater flow path, as within this portion of the aquifer, H<sub>2</sub>S concentrations first begin to rise (Fig. 2.3).

In the absence of direct evidence of microbes in the deep surfaces of the Carrizo aquifer (e.g., microbes collected from the aquifer) it is only possible to infer the presence of microbes and their associated metabolic processes from the geochemical data. As discussed by Chapelle (2001), the application of the geochemical composition of groundwater in this manner is based on the presumption that microbial processes occurring within an aquifer will influence the groundwater chemistry in specific ways. Hence, increases and decreases in the concentrations of certain geochemical markers such as dissolved oxygen, Fe and H<sub>2</sub>S can be employed to infer microbial processes like aerobic respiration, ferric iron reduction, and sulfate reduction, respectively (Chapelle, 2001). An excellent example of this approach is the study by Lovely and Goodwin (1988) that used accumulation of dissolved H<sub>2</sub> along groundwater flow paths to infer the

establishment, by microbial metabolic processes, of redox zoning in a coastal plain aquifer in South Carolina. Following this approach, we suggest that the low dissolved oxygen concentrations (except well N-3) in groundwaters along the flow path in the Carrizo aquifer probably reflect consumption of oxygen by microbes via aerobic respiration (e.g., Smedley and Edmunds, 2002). The predominance of Fe(II) in the majority of the groundwater samples suggests the presence of Fe(III) reducing bacteria within the aquifer, and the increasing dissolved sulfide concentrations from ~41 km onward support the presence of sulfate reducing bacteria in the Carrizo aquifer. It should be mentioned that sulfate reduction is generally considered to chiefly be biologically mediated (e.g., Berner, 1970; Smedley and Edmunds, 2002).

Chapelle et al. (1987) and Chapelle and Lovley (1990) suggest that microbial metabolism along flow paths in Coastal Plain aquifers may partially explain the reported increases in dissolved inorganic carbon (i.e., CO<sub>2</sub>) in these aquifers. Figure 2.2 demonstrates that, in general, alkalinity, and hence dissolved inorganic carbon, increases in the Carrizo aquifer from about 15 km onward. Following the approach of Chapelle et al. (1987), where increases in dissolved inorganic carbon (i.e., CO<sub>2</sub>) were solely attributed to microbial oxidation of organic carbon, we estimate microbial metabolic rates, based on our alkalinity measurement (Table 2.1) and the average groundwater velocity of 2 m yr<sup>-1</sup> determined by Stute et al. (1992) that range between 7.6x10<sup>-2</sup> mmol L<sup>-1</sup> yr<sup>-1</sup> to 8.2 x10<sup>-1</sup> mmol L<sup>-1</sup> yr<sup>-1</sup>. These values are higher than those estimated by Chapelle et al. (1987) and Chapelle and Lovley (1990) [i.e., ~10<sup>-6</sup> to ~10<sup>-3</sup> mmol L<sup>-1</sup> yr<sup>-1</sup>] and probably indicate additional sources of dissolved inorganic carbon to Carrizo

groundwaters, such as, chemical weathering that include calcite dissolution and cation exchange reactions (e.g., Pearson and White, 1967). It is important to point out that in their study of groundwater ages in the Carrizo Sand aquifer, Pearson and White (1967) estimated that the percentage of total dissolved carbonate ( $\text{HCO}_3^- + \text{CO}_3^{2-}$ ) that was datable (i.e., from atmosphere and soil zone) ranged from ~83% proximal to the recharge area in northwest Atascosa County to ~14% in northern McMullen and Live Oak Counties near the down-dip limit of potable water in the aquifer. The mean datable carbonate content of the Carrizo Sand aquifer groundwaters based on their work is ~42%. Consequently, on average, the remainder of the dissolved carbonate in Carrizo Sand aquifer (~58%) represents carbonate (i.e., “dead” carbon) added to groundwaters from chemical weathering reactions and microbial metabolism of lignite in the aquifer sediments. As the Carrizo Sand is of Eocene age, oxidation of lignite in these sediments by microbes would also dilute the  $^{14}\text{C}$  content of the groundwaters in a similar fashion to carbonate mineral dissolution as any  $^{14}\text{C}$  in these organic materials has long since decayed. Hence, our first pass estimates of microbial metabolic rates in the Carrizo Sand aquifer groundwaters must be at least an average of 58% less than the estimates calculated using measured alkalinity concentrations, that is,  $4.4 \times 10^{-2}$  to  $4.8 \times 10^{-1} \text{ mmol L}^{-1} \text{ yr}^{-1}$ . These values are still greater than estimates for other Atlantic and Gulf Coastal Plain aquifers of the USA (Chapelle et al., 1987; Chapelle and Lovley, 1990) because the fraction of carbonate added to Carrizo Sand groundwaters from chemical weathering reactions remains in these calculated microbial metabolism rates. Additional geochemical



modeling is planned to better constrain these estimates of microbial metabolism in the Carrizo Sand aquifer.

### *2.5.2 Controls on the distribution of total arsenic and As species in the aquifer*

In the environment the major processes controlling concentrations, speciation, mobility, and toxicity of As are pH and/or redox driven mineral dissolution/precipitation, adsorption/desorption reactions, and ion exchange (e.g., Welch et al., 1988; Ahmann et al., 1994; Jain and Ali, 2000; Hering and Kneebone, 2002; Smedley and Kinniburgh, 2002; Hamon et al., 2004; McArthur et al., 2004; O'Day et al., 2004). In groundwaters, redox conditions are largely mediated by microbes in the presence of organic matter, and/or H<sub>2</sub> gas, which are both potential electron donors, and major redox active species such as O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn(IV), Fe(III), and SO<sub>4</sub><sup>2-</sup> that serve as electron acceptors during metabolic processes (Champ et al., 1979; Chapelle et al. 1987, 1988; Lovley and Goodwin, 1988; Lovley et al., 1990; Chapelle and McMahon, 1991). In the Carrizo aquifer, total As concentrations clearly change along the flow path, and these changes appear to be influenced by changing redox conditions (Fig. 2.3). More specifically, in the portion of the aquifer nearest to the recharge area, As<sub>T</sub> concentrations remain high (2.19 nmol kg<sup>-1</sup>) under what we interpret to be mildly reducing conditions as indicated by dissolved Fe concentrations [dominantly Fe(II)], and to a lesser extent, the Eh and DO data (Fig. 2.3; see also Berner, 1981). It is important to stress that because H<sub>2</sub>S concentrations are at or below the detection limit, sulfate reduction has not occurred in Carrizo groundwaters proximal to the recharge zone (first ~15 km of flow path). Consequently, these groundwaters can be classified as suboxic (i.e., 1 μmol kg<sup>-1</sup> ≤ O<sub>2</sub> <

30  $\mu\text{mol kg}^{-1}$ ; Berner, 1981; Anderson et al., 1994). Figure 3 demonstrates that As(V) predominates in Carrizo groundwaters from near the recharge zone (first ~15 km along the flow path). The relatively high dissolved Fe concentrations [again, dominantly Fe(II)] in these groundwaters suggest that adsorbed and/or coprecipitated As(V) is being released to solution in this portion of the Carrizo aquifer by reductive dissolution of Fe(III) oxyhydroxides/oxides (Cummings et al., 1999; McArthur et al., 2001, 2004; Islam et al., 2004). There appears to be a slight decrease in total As concentration between the first two wells (F-1 and N-1), which could signal adsorption of negatively charged As(V) species onto the aquifer substrate. However, it is important to point out that the apparent decrease in As species concentrations between these wells actually falls within the measurement error (Fig. 2.3).

Ferrous iron concentrations in groundwater from the next well along the flow path (KS-1) are below detection and As concentrations are the lowest observed along the first 26 km of the Carrizo aquifer flow path (Fig. 2.3). The difference in As concentrations between wells N-1 and KS-1 is chiefly due to a dramatic decrease in the As(V) concentrations. Furthermore, the decrease in Fe(II) and As(V) concentrations at well KS-1 suggests that Fe(II) oxidation may occur, followed by precipitation of Fe(III) oxyhydroxides/oxides and consequent scavenging of As(V) by coprecipitation and/or adsorption onto newly formed Fe(III) solids. With flow beyond well KS-1, As(V) concentrations and Fe(II) concentration sharply increase, whereas As(III) shows a comparatively small increase (Fig. 2.3). Consequently, the relationship between Fe(II) and As(V) concentrations in these groundwaters provides strong evidence that As(V)

concentrations are most likely controlled by Fe(III) reduction in this portion of the aquifer. Because Fe reduction in the Carrizo aquifer is likely driven by microbial processes (e.g., Lovley et al., 1990; Lovley, 1997), the close coupling between Fe(II) and As(V) concentrations suggest that the in situ microbial consortium also plays an important role, either directly or indirectly, in As cycling in the Carrizo aquifer system. Additional investigations of As speciation of the solid phases from the aquifer as well as microbial sampling of the deep subsurface are necessary, however, to identify and resolve the processes responsible for the relatively high As(V) concentrations in groundwaters along the first ~15 km of the Carrizo aquifer (e.g., Hamon et al., 2004; Islam et al., 2004).

It is important to note that in addition to Fe oxyhydroxides/oxides, both As(III) and As(V) can also strongly adsorb onto surfaces of other aquifer materials, including clay minerals and organic matter (e.g., Pierce and Moore, 1982; Goldberg and Glaubig, 1988; Fuller et al., 1993; Manning and Goldberg, 1996; 1997; Goldberg, 2002; Sracek et al., 2004). Factors such as pH, concentration of mineral and organic matter surface sites, and concentration of competing ions can affect the adsorption/desorption of As onto these substrates (Pierce and Moore, 1982; Wilkie and Hering, 1996; Dzombak and Morel, 1990; Cummings et al., 1999; Zheng et al., 2004). A recent study of rare earth element (REE) adsorption onto the Carrizo suggests that clays within the aquifer play an important role in REE sorption (Tang and Johannesson, 2005b). Consequently, clay minerals may also be important in As cycling in the Carrizo aquifer.

As mentioned above, the Fe data indicate that Fe(III) reduction is important with flow beyond well KS-1 (Fig. 2.3). Arsenate concentrations also increase in groundwaters

from wells immediately down-gradient of well KS-1, again suggesting that reductive dissolution of Fe(III) oxyhydroxides/oxides is releasing Fe(II) and As(V) to Carrizo groundwaters. Ferrous iron concentrations reach a local maximum at 12.8 km (well G-1) and then decrease at 14.5 km (Poteet well) along the flow path, where it remains relatively constant until ~41 km. Again, we interpret that Fe reduction is the chief redox process occurring along this reach of the Carrizo aquifer. The abrupt decrease in Fe(II) concentrations observed between well G-1 and the Poteet well may reflect a decrease in the available Fe(III) oxyhydroxides/oxides concentrations in the aquifer sediment or may signal a shift in the microbial population. However, without additional information we can only speculate as to the reasons for the change. Nevertheless, the substantial decrease in As concentrations in this region of the Carrizo aquifer (Fig. 2.3) is perhaps best explained by readsorption of As onto the aquifer substrate (minerals/organic matter). Throughout the mid-reaches of the aquifer, the As(III) concentrations remain low and relatively constant. However, as mentioned above, the data indicate that between 26 km (the PCW-1 well) and 59 km (well AC74R-2), As(III) is the predominant As species in Carrizo groundwaters. The As(V) concentrations (calculated by difference) are essentially at or below the detection limit (Fig. 2.3). In groundwaters from the Peeler-1 well (41 km), As(III) concentrations increase by a factor of ~1.6 compared to groundwaters from the previous well (PCW-1). The increase of As(III) at the Peeler-1 well could reflect As(V) reduction in the aquifer, however, the Fe data indicate Fe(III) concentrations exceed those of Fe(II) in this sample. Although we have no direct evidence, it is also possible that dissimilatory As(V) reducing microbes could exist in the

Carrizo aquifer and be responsible for As(V) reduction. These microbes use arsenic as a source of energy and have been isolated from a wide variety of environments (Ahmann et al., 1994; Newman et al., 1997; Stolz and Oremland, 1999; Oremland et al., 2000; Zobrist et al., 2000; Hering and Kneebone, 2002; Oremland and Stolz, 2003; Islam et al., 2004). Recently, Islam et al. (2004) suggested that As mobilization from sediments collected from the Bengal Delta into groundwaters was the result of microbial reduction of As(V) to As(III). Investigations of the in situ microbial consortium of the Carrizo aquifer are necessary to resolve this possibility.

Between wells Peeler-1 and AC74R-2 (59 km),  $As_T$  concentrations [i.e., predominantly As(III)] decrease by a factor of  $\sim 2.2$  and then increase by a factor of  $\sim 4.7$  at well SMA74R-1 (66 km). Remarkably, in the sulfidic, and hence, anoxic (i.e.,  $H_2S \geq 1 \mu\text{mol kg}^{-1}$ ; Berner, 1981) groundwaters from well SMA74R-1, As(V) predominates accounting for greater than 71% of  $As_T$  (Fig. 2.3). Indeed, between wells AC74R-2 and SMA74R-1, As(V) concentrations increase by a factor of 11.4. The high As(V) concentrations compared to As(III) concentrations in these groundwaters dominated by sulfate reduction appear to be at odds with earlier investigations suggesting the application of As species as indicators of groundwater redox conditions (e.g., Cherry et al., 1979). However, one possible explanation for the increase in As(V) concentrations between wells AC74R-2 and SMA74R-1 is pH related desorption of As(V) followed by slow transformation of As(V) to As(III) as dictated by the sluggish kinetics of As oxidation/reduction reactions. The pH of groundwater from the Peeler-1 well, and the remainder of the flow path sampled, is well above 8 (Table 2.1; Fig. 2.2). The surface

charge of quartz, clay minerals, and Fe oxides, all of which occur in the Carrizo (Pearson and White, 1967), will be negative at these pH values based on their isoelectric points (Drever, 1997). In addition, the isoelectric point of pyrite is estimated to range between 5 and 6 (Raichur et al., 2001), suggesting that any precipitated Fe sulfide minerals in this region of the aquifer would also have a negative surface charge. Consequently, negatively charged, adsorbed As(V) species will desorb from mineral surface sites under these relatively high pH conditions, and be subsequently released into the Carrizo groundwaters. Moreover, the negative surface charge of aquifer minerals would also inhibit adsorption of As(V) already in solution. It is also possible that As(III) may desorb at these pH values (Dzombak and Morel, 1990; Drever, 1997). It is important to note, however, that McArthur et al. (2004) argue that pH dependant desorption of As is not likely to be significant in groundwaters for which  $\text{pH} < 8.5$ , and may only occur via contact of high pH ( $\sim 10$ ) landfill leachates with aquifer materials.

O'Day et al. (2004) found that in sulfate reducing environments characterized by micromolar levels of As, low Fe, and high S, As concentrations can be limited by the formation of As-sulfides (e.g. orpiment). In addition, their synchrotron x-ray adsorption spectra suggests that As is not included, at the molecular level, in Fe sulfides precipitated in such sedimentary environments (O'Day et al., 2004). Consequently, our Fe and As concentration data for Carrizo groundwater between wells AC74R-2 and SMA74R-1 support, in a general sense, the findings of O'Day et al (2004). Specifically, the decrease in dissolved Fe concentrations in this region of the Carrizo aquifer characterized by high dissolved sulfide concentrations, suggests that Fe sulfide minerals are precipitating in this

region of the aquifer. However, the increase in As concentrations indicates that As does not coprecipitate with Fe sulfides in the Carrizo aquifer, which again is consistent with the observations of O'Day et al. (2004). Although these investigators argue that As-sulfide minerals are likely important controls on dissolved As concentrations in low temperature environments, to the best of our knowledge, As-sulfide minerals, such as realgar and orpiment, have not been identified in the Carrizo aquifer.

Experimental data from a study of As speciation in sulfidic waters found that under near neutral to mildly alkaline pH conditions, thioarsenic species can dominate (Wilkin et al., 2003). In the reducing, sulfidic groundwaters ( $\sim 50 \mu\text{mol kg}^{-1}$ ) from well SMA74R-1, it is also possible that thioarsenite species are important. A rough calculation using the stability constants of Wilkin et al. (2003) and As, alkalinity and  $\text{S}^{2-}$  concentrations and the pH for well SMA74R-1, suggests that thioarsenite could account for up to  $\sim 20\%$  of the total dissolved As (results not shown). Consequently, because charged thioarsenite may bind onto the anion exchange resins on the column, the As(V) value reported for this well may be overestimated (Jay et al., 2004).

## 2.6 Conclusions

Concentrations of dissolved Fe species,  $\text{H}_2\text{S}$ , and oxygen, along with measured oxidation-reduction potential (i.e., Eh) in groundwaters of the Carrizo aquifer of southeastern Texas, USA indicate redox conditions change along the flow path. Portions of the aquifer that are proximal to the recharge area in northwest Atascosa County, Texas (first  $\sim 15$  km of flow path) are characterized by variable redox states that fluctuate between relatively oxic ( $\text{O}_2 \gg 30 \mu\text{mol kg}^{-1}$ ) to mildly reducing, or suboxic (i.e.,  $1 \mu\text{mol kg}^{-1} \leq \text{O}_2 < 30 \mu\text{mol kg}^{-1}$ ). With flow down-gradient, Fe species concentrations,  $\text{H}_2\text{S}$

concentrations, and to a lesser extent, dissolved oxygen concentrations and redox potential measurements (Eh), indicate a zone of predominantly Fe(III) reduction in the mid reaches of the aquifer (~9.4 to 41 km along the flow path), followed by sulfate reduction with flow further down-gradient. Arsenic concentrations in groundwater from the Carrizo aquifer are below the World Health Organization's recommended levels and the currently approved U.S. EPA's maximum contaminant level for As in drinking water of 133 nmol kg<sup>-1</sup> (10 ppb). Arsenic concentrations and the relative proportion of inorganic As species, As(III) and As(V), vary along the groundwater flow path in the Carrizo aquifer. Arsenate predominates in the groundwaters from the first 15 km of the flow path, and then again in groundwaters collected 66 km along the flow path. Arsenite is the chief form of dissolved As in groundwaters from the mid-reaches of the aquifer (beyond 15 km to ~59 km). Our data suggest that biogeochemical processes impacting groundwaters in the recharge zone are complex and location specific. Reduction of Fe(III) oxyhydroxides/oxides and subsequent release of adsorbed and/or coprecipitated As(V) is inferred to control As(V) concentrations within the first 15 km of the groundwater flow path, followed by readsorption of As(V) in the mid-reaches of the aquifer. Further down-gradient, the observed increase in As(V) concentrations may be due to pH related desorption as pH increases to 8.5. These results provide important insights into the evolution of As(V) concentrations and speciation in a relatively pristine, unconsolidated, sedimentary aquifer and are expected to supplement future work on development of a reactive transport and biogeochemical cycling model of As in sedimentary aquifers.

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## CHAPTER 3

### CONCENTRATIONS AND SPECIATION OF ARSENIC ALONG A GROUNDWATER FLOW PATH IN THE UPPER FLORIDAN AQUIFER, FLORIDA, USA

#### 3.1 Introduction

Globally, public concerns over arsenic (As) in groundwaters have increased in recent years owing to recognition of numerous cases of widespread As poisoning from consumption of high As groundwater (e.g., Bangladesh; West Bengal, India; Vietnam; Taiwan; Smedley and Kinniburgh 2002). In the past, many studies of As in groundwaters focused on documenting the extent of elevated total dissolved As concentrations or identifying potential mineralogical sources (Peters et al. 1999; Welch et al. 2000; McArthur et al. 2001). However, to quantitatively understand the mechanisms that control As mobilization in groundwater systems, it is essential to determine its concentrations and speciation in the aquifer system. Speciation is critical because the sorption behavior, mobility and toxicity of As differ between inorganic arsenite [As(III)] and arsenate [As(V)], as well as the methylated forms (Anderson and Bruland 1991; Bowell 1994). Moreover, previous investigations of As in groundwater focused on sampling wells without regard to groundwater flow paths or whether hydrogeologic connection existed between the wells. Although such an approach can effectively

characterize the areal extent of elevated As concentrations, it reveals little as to how As concentrations and speciation “evolve” along groundwater flow paths in aquifers. Indeed, a more systematic approach to the study of As in groundwater flow systems that involves careful sampling and analysis of As concentrations and speciation, along with ancillary geochemical parameters including redox indicators is necessary for an improved understanding of the important biogeochemical processes controlling As mobilization in aquifers (e.g., Oremland and Stolz 2005; Haque and Johannesson 2006). Such studies, in conjunction with microbial investigations of groundwater aquifer systems are expected to illuminate the biogeochemical cycle of As in the deep subsurface.

Here, As concentrations and speciation are determined in groundwaters from a series of wells along a well characterized groundwater flow path in the relatively pristine Upper Floridan aquifer (UFA) in west-central Florida, USA. In addition to As concentrations and speciation, ancillary geochemical data [Fe(II) and Fe(III), dissolved sulfide, pH, dissolved oxygen, and oxidation-reduction potential] are presented for groundwaters from the same wells along the flow path, from which redox-related biogeochemical processes that likely influence the distribution and mobility of As along the flow path are inferred.

## 3.2 Experimental section

### *3.2.1 Study area*

In west-central Florida (Fig. 3.1), the Upper Floridan aquifer consists of a highly permeable carbonate rock succession that includes: Suwannee Limestone (Oligocene), Ocala Limestone (upper Eocene), and the Avon Park (middle Eocene) Formation

(Stringfield 1966; Miller 1986; many others). The thickness of the UFA ranges from 60

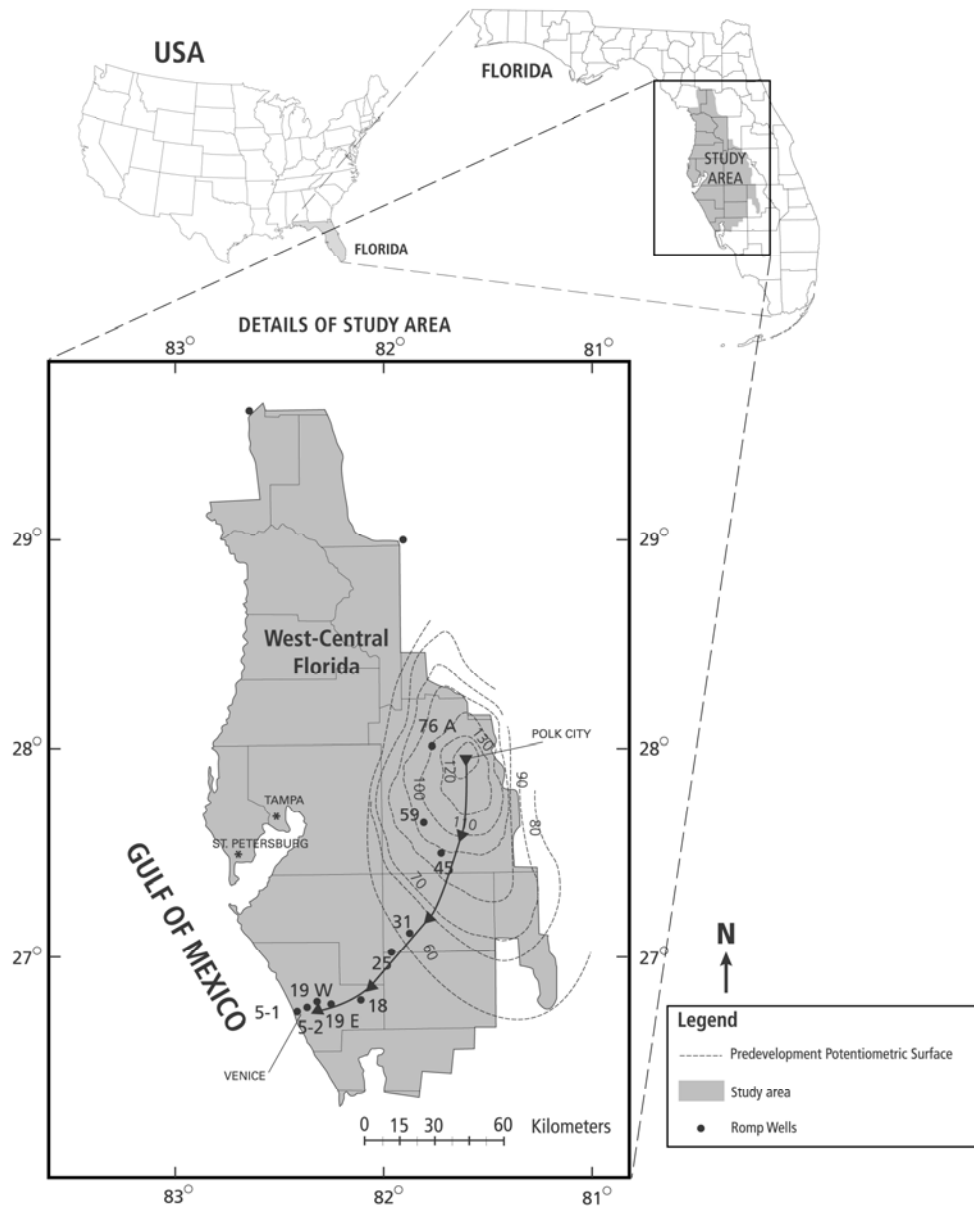


Figure 3.1: Map of the USA showing location of the study region in Florida. Inset presents the study area within west-central Florida showing investigated groundwater flow path, location of sampled wells and predevelopment potentiometric surfaces. Altitude of predevelopment potentiometric surface in feet (1 ft = 0.0348 m) based on, and modified after, Stringfield (1936), Hanshaw et al (1965), Back and Hanshaw (1970), Johnston et al. (1980), and Plummer and Sprinkle (2001).

to 640 m within the study region (Miller 1986). The dominant minerals in the UFA are calcite (~66%) and dolomite (~33%), along with minor amounts of gypsum, anhydrite, chert, quartz, apatite, metal oxides, sulfides, lignite and clay minerals (Hanshaw et al. 1965; Rye et al. 1981; Plummer et al 1983; Sacks et al. 1995). The Miocene Hawthorn Group, which is ~30 m thick along much of the flow path studied (Wicks and Herman 1994), overlies and confines the UFA. The Hawthorn Group is composed of sand, marl, clay, limestone and dolomite along with phosphatic deposits (Wilson and Gerhart 1979; Miller 1986; Lamoreaux 1989; Sacks et al. 1995). The middle confining unit, which consists of eight separate stratigraphic units, separates the UFA from the Lower Floridan aquifer (Miller 1986). In the study area, the middle confining unit is ~30-120 m thick, and is chiefly composed of middle Eocene dolomite with intergranular anhydrite/gypsum (Miller 1986).

Groundwater samples were collected from the UFA along a well characterized flow path (Back and Hanshaw 1970; Sacks et al 1995; Plummer and Sprinkle 2001), which commences from the predevelopment potentiometric high at Polk City (Stringfield 1936) and subsequently flows toward the southwest Gulf coast (Fig. 3.1). The sampled wells were all open to the UFA and the flow path chosen for this study closely follows Path II of Plummer and Sprinkle (2001) as well as the flow path investigated in the classic study by Back and Hanshaw (1970). Recharge to the flow path mainly occurs in the vicinity of Polk City, where the confining Hawthorn Group is thin or non-existent (Stringfield 1936; Back and Hanshaw 1970). The groundwaters subsequently flow south and west toward the Gulf Coast and discharge into the Gulf of Mexico near Venice,

Florida (Wicks and Herman 1994). Using digital simulation of predevelopment sub-regional flow in the study region, Ryder (1985) showed that historical discharge from the UFA mainly occurred at springs and streams, with lesser amounts of discharge occurring by diffuse upward leakage along the Gulf Coast, and seepage to submarine springs and coastal swamps. The  $^{14}\text{C}$  ages of UFA groundwaters range from a mean age of 1,400 a for groundwaters in the Polk City area, to around 30,000 a further down-gradient (Plummer and Sprinkle 2001), suggesting flow velocities of 6 to 9 m yr<sup>-1</sup> (Plummer et al. 1983). The  $^{14}\text{C}$  ages of the groundwaters further imply that much recharge to the UFA occurred during the last glacial period with little additional modern recharge water reaching the lower portions of the UFA.

### *2.2.2 Field sampling*

Prior to transport to the study site, all sample bottles (HDPE), Poly-Prep chromatography columns, and Teflon® tubing used during sample filtration were thoroughly cleaned using trace element clean procedures (Haque and Johannesson 2006). Groundwater samples were collected (July 2004) from 10 wells in the UFA located along a previously characterized flow path in west-central Florida (Fig. 3.1; Back and Hanshaw 1970; Plummer and Sprinkle 2001). The sampled wells (all monitoring wells) were purged for at least three well volumes prior to sampling. To further ensure that samples represented groundwaters from the aquifer and not from the well bore, pH, specific conductance, and water temperature were continuously monitored during the purging, and sample collection did not commence until these field parameters were stable.

In addition to pH, specific conductance, and temperature, onsite measurements include: alkalinity, dissolved oxygen, oxidation-reduction potential (Eh in mV), iron speciation [Fe(II) and Fe(III)], and dissolved sulfide ( $S^{2-}$ ) concentrations. In the field, dissolved oxygen, Eh, pH, specific conductance, and temperature were quantified using a Hydrolab MiniSonde4 with a flow through cell. The MiniSonde4 was attached to all of the wells sampled by connecting the flow through cell to the well outflow with a polyethylene tube, which allowed dissolved oxygen and Eh for each sample to be measured without exposing the groundwater sample to the atmosphere.

Iron species and dissolved sulfide were quantified on separate sample aliquots via UV/VIS spectrophotometry using a portable spectrophotometer (Hach DR/890). The spectrophotometer was calibrated and the sample concentrations verified using a series of Fe and  $S^{2-}$  calibration standards. More specifically, Fe(II) was determined using the 1,10 Phenanthroline method (Eaton et al. 1995a) and total dissolved iron [Fe(II)+Fe(III), hereafter referred to as  $Fe_T$ ] was determined by the FerroVer method (Eaton et al. 1995a). Ferric iron was subsequently calculated by difference. The method detection limit for  $Fe_T$  and Fe(II) is  $0.54 \mu\text{mol kg}^{-1}$  (Eaton et al. 1995a). Dissolved sulfide was determined on separate aliquots using the methylene blue method (Eaton et al. 1995b). The method detection limit for  $S^{2-}$  is  $0.29 \mu\text{mol kg}^{-1}$  (Eaton et al. 1995b).

### *3.2.3 Sampling for arsenic concentrations and speciation*

Dissolved inorganic As [As(III) and As(V)] species were separated in the field using a previously established anion exchange chromatography method, which employed Poly-Prep 0.8 x 4 cm chromatography columns packed with Bio-Rad AG® 1 x 8; 50-100

mesh resin in the acetate form (Wilkie and Hering 1998). Groundwaters samples were first collected into collapsible pre-cleaned LDPE cubitainers® (Hedwin Corporation) and were immediately filtered through in-line groundwater-filter capsules (Gelman Sciences, 0.45 µm, polyether sulfone membrane) by drawing water from the cubitainers® through previously cleaned Teflon® tubing using a peristaltic pump. Prior to passing through the anion exchange column, the filtered samples were acidified to a pH of ~3.5 by adding ultra-pure HNO<sub>3</sub> (Seastar Chemical, Baseline). At a pH of ~3.5, As(III) occurs as H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> and passes through the column and is collected in pre-cleaned HDPE bottles. However, As(V), which is anionic (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>), is retained by the resin in the column (Wilkie and Hering 1998). Arsenite is then quantified in the eluted fractions and total dissolved As [As(III)+As(V), hereafter referred to as As<sub>T</sub>] is measured using separate filtered sample aliquots preserved by acidification to pH <2 using ultra-pure HNO<sub>3</sub> (Wilkie and Hering 1998). Subsequently, As(V) is determined by difference. In addition to a field blank, four duplicate samples for As(III) were collected. Samples were stored at 4 °C and in the dark until analyses.

#### *3.2.4 Analyses*

All As analyses were carried out by inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer/Sciex Elan 6100 DRC). The DRC reaction cell allows for precise measurements of As at high picomolar to low nanomolar concentrations in natural waters where Cl can interfere with As detection using standard quadrupole mass spectrometry (Perkin Elmer/SCIEX Elan DRC II 2003). The DRC

reaction cell greatly reduces the number of  $\text{ArCl}^+$  ions in samples prior to introduction of the sample to the quadrupole mass spectrometer.

The instrument was calibrated and the sample concentrations confirmed using a series of As calibration standards of known concentrations (0.40, 0.67, 3.2, 14.7, 105 and 213.6  $\text{nmol kg}^{-1}$ ). The calibration standards were prepared from Perkin Elmer Pure plus As standard (10  $\text{mg kg}^{-1}$ , Lot #25-61AS). Additionally, a QC As standard of 96.1  $\text{nmol kg}^{-1}$  was prepared from a NIST traceable High Purity Standards (Charleston, SC). During sample analysis, the QC standard was routinely run to monitor for instrument drift and overall quality of the analysis. Analytical precisions for As(III) and  $\text{As}_T$  were better than 1.2% and 3.2% RSD (relative standard deviation), respectively. The method detection limit for As, based on  $3\sigma$  of the blank measurement, is 0.75  $\text{nmol kg}^{-1}$  (56  $\text{ng kg}^{-1}$ ).

### 3.3 Results and discussion

#### *3.3.1 General Chemistry*

Hydrogeochemical data for the UFA groundwaters are presented in Figure 3.2, and Tables 3.1 and 3.2. The sampled groundwaters are near-neutral, with pH values ranging from 7.1 to 7.9. More specifically, pH exhibits a decreasing trend along the flow path, which includes an initial decrease from 7.9 to 7.7 in the first 79 km, before decreasing to  $\text{pH} < 7.4$  beyond 79 km (Fig. 3.2). Measured alkalinity (reported as  $\text{HCO}_3^-$ ) ranges from 37 to 68  $\mu\text{mol kg}^{-1}$  (Table 3.1). Previous geochemical modeling indicates that the observed trends in pH and alkalinity are the result of gypsum and dolomite dissolution with subsequent calcite precipitation (i.e., dedolomitization) along the flow path (Plummer et al. 1983).



Table 3.1 Hydrogeochemical data of groundwaters from Upper Floridan aquifer, Florida<sup>a</sup>: SPC, Alk, Eh, DO and TDS are specific conductance, alkalinity, oxidation-reduction potential, dissolved oxygen, and total dissolved solids, respectively.

Distance	km	0.00	32.2	46.3	78.8	90.8	112	123	133	138	144
Well No. (All ROMP)		76A	59	45	31	25	18	19E	19W	5-2	5-1
Well depth	m	80.5	61.0	101	140	91.4	154	125	125	155	150
SPC	$\mu\text{S cm}^{-1}$	283	323	356	510	1122	818	1246	1588	2692	2695
Temp	$^{\circ}\text{C}$	23.5	22.8	27.0	29.4	27.7	27.1	25.9	26.8	27.6	26.1
pH		7.93	7.82	7.83	7.70	7.42	7.38	7.30	7.26	7.07	7.12
Alkalinity ( $\text{HCO}_3$ )	$\mu\text{mol kg}^{-1}$	36.6	39.3	43.9	55.1	64.3	68.2	47.2	48.5	52.5	44.6
Eh	mV	265	73	-30	-68	-34	-83	-43	-84	-53	-71
DO	$\mu\text{mol kg}^{-1}$	23.8	71.6	13.1	3.44	4.38	3.75	9.69	3.75	3.44	4.38
TDS	$\text{g kg}^{-1}$	0.18	0.21	0.23	0.33	0.72	0.52	0.80	1.10	1.72	1.72

<sup>a</sup>A previous study reports major solute data for the same flow path (Tang and Johannesson, 2005a)

A previous study (Tang and Johannesson, 2005a) of rare element concentrations in groundwaters along the same flow path reports that from the recharge area near Polk City (0 km) to ~46 km, groundwaters from the UFA are Ca(Mg)- $\text{HCO}_3$  type waters, with flow beyond 46 km, the groundwater composition changes to Ca-Mg- $\text{SO}_4$ - $\text{HCO}_3$  type waters, and finally become Ca-Mg- $\text{SO}_4$  near the end of the studied flow path. Other investigators report that in the coastal area of the Floridan peninsula, Ca-,  $\text{SO}_4$ -, Mg- and Cl- rich groundwaters, resulting from gypsum dissolution, upwell from the base of the UFA and mixes with UFA groundwaters (Rye et al. 1981; Sacks et al. 1995; Plummer and Sprinkle 2001). The increase in our measured conductivity values along the studied

flow path (283 to 2,695  $\mu\text{S cm}^{-1}$ ; Table 3.1) supports upwelling of higher conductivity waters from below and is thus in agreement with these previous investigations. However, it is also possible that elevated conductivity values may result from saltwater intrusion near Sarasota. Future geochemical modeling studies are planned to help better identify and constrain the dominant mechanisms controlling groundwater quality along the studied flow path.

### *3.3.2 Redox characteristics*

The dissolved oxygen concentration is 24  $\mu\text{mol kg}^{-1}$  in groundwaters from the most up-gradient well in the recharge area near Polk City (0 km; ROMP 76A). With flow down-gradient, dissolved oxygen initially increases reaching a maximum of 72  $\mu\text{mol kg}^{-1}$  at 32 km (ROMP 59). At this location it is possible that the three-fold increase in dissolved oxygen concentration may reflect infiltration of oxygenated meteoric water into the aquifer or aeration of groundwater during sampling. However, with flow beyond 32 km, the dissolved oxygen concentration abruptly decreases to 13  $\mu\text{mol kg}^{-1}$  (46 km; ROMP 45) and remains relatively low and uniform throughout remainder of the flow path (Fig. 3.2). The measured Eh values range from -84 to 265 mV, exhibiting a maximum in the recharge area. Between 0 to 46 km, Eh decreases from 265 to -30 mV. With flow beyond 46 km, the Eh values are also generally low and relatively constant (Fig. 3.2). Both dissolved oxygen and the Eh measurements suggest that relatively oxidizing conditions characterize the aquifer from 0 to 32 km, whereas more reducing conditions dominate further down-gradient. It is important to note, however, that karstic

Table 3.2 Concentrations and speciation data for dissolved iron, sulfides and arsenic in groundwaters from the Upper Floridan aquifer, Florida.

Distance	Km	0.00	32.2	46.3	78.8	90.8	112	123	133	138	144
Well No. (All ROMP)		76A	59	45	31	25	18	19E	19W	5-2	5-1
Fe(II)	$\mu\text{mol kg}^{-1}$	0.54	1.07	BDL*	0.54	BDL	0.54	BDL	BDL	0.90	BDL
Fe(III)	$\mu\text{mol kg}^{-1}$	1.79	0.36	BDL	BDL	BDL	BDL	BDL	BDL	0.00	BDL
Fe <sub>T</sub>	$\mu\text{mol kg}^{-1}$	2.33	1.43	BDL	0.54	BDL	0.54	BDL	BDL	0.90	BDL
S <sup>2-</sup>	$\mu\text{mol kg}^{-1}$	BDL	2.00	34.0	106	100	105	86.0	82.0	63.0	70.0
As(III)	$\text{nmol kg}^{-1}$	1.55±0.13	11.5±0.13	1.31±0.13	2.88±0.13	1.39±0.07	0.97±0.07	1.23±0.13	1.29±0.27	1.81±0.40	1.83±0.13
As(V)	$\text{nmol kg}^{-1}$	17.0±0.47	4.16±0.67	0.44±0.00	-2.16±0.00	-0.35±0.06	0.12±0.06	-0.23±0.00	-0.25±0.14	0.98±0.13	-0.19±0.14
As <sub>T</sub>	$\text{nmol kg}^{-1}$	18.6±0.60	15.7±0.80	1.75±0.13	0.72±0.13	1.04±0.13	1.09±0.13	1.00±0.13	1.04±0.13	2.79±0.27	1.64±0.27

\*Below Detection Limit for Fe<sub>T</sub> and Fe(II) is 0.54  $\mu\text{mol kg}^{-1}$ , and for S<sup>2-</sup> is 0.29  $\mu\text{mol kg}^{-1}$

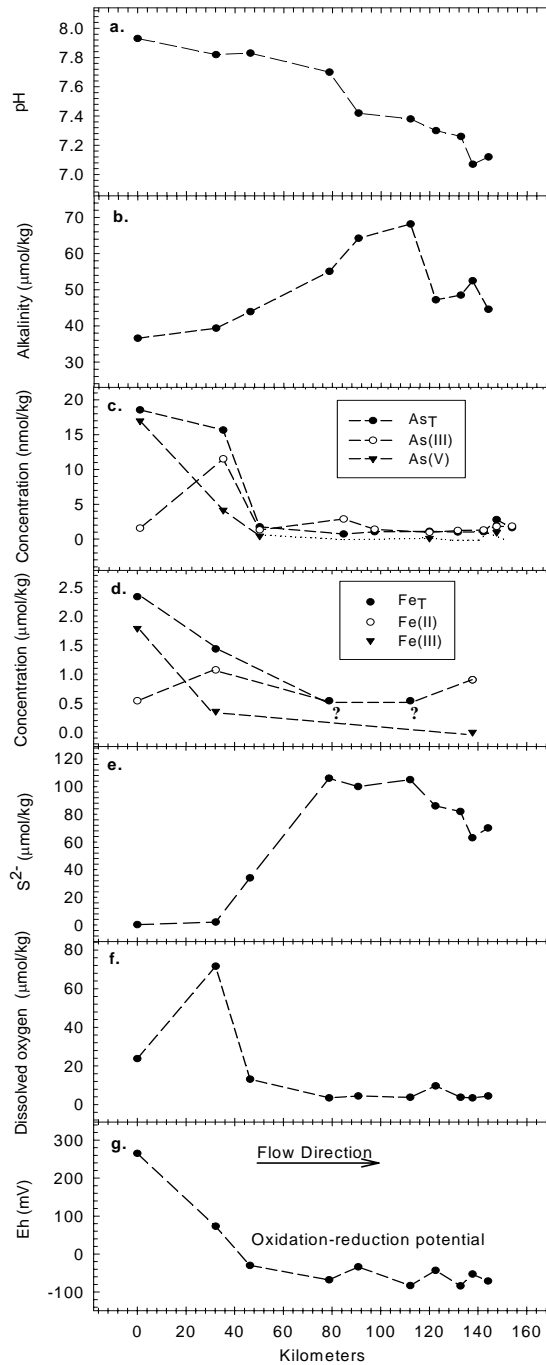


Figure 3.2: Upper Floridan aquifer data: (a) pH; (b) alkalinity; (c) As speciation; (d) Fe speciation; (e)  $S^{2-}$ ; (f) Dissolved oxygen; (g) Eh as a function of distance from recharge zone (km). Dashed lines are actual data and dotted lines represent values below the detection limit. The analytical error bars for the As data are smaller than the key symbols.

features are common in the UFA, and it is thus possible that fractures could allow infiltration of oxygenated meteoric water at various places along the flow path (Leve 1983), leading to local mixing of oxygenated water with the more reducing groundwaters (e.g., 32 and 123 km; Fig. 3.2).

Nonetheless, the dissolved oxygen and the Eh measurements are consistent with a general decrease in redox conditions along the flow path, and essentially reducing conditions in the lower reaches of the UFA (Back and Hanshaw 1970). It is important to note that Eh measurements are not necessarily representative of the groundwater redox equilibria, and are at best only a qualitative indicator of in situ redox conditions (Lindberg and Runnells 1984).

Total dissolved Fe range from below detection limit ( $0.54 \mu\text{mol kg}^{-1}$ ) to  $2.33 \mu\text{mol kg}^{-1}$  (Table 3.1). Total Fe concentrations are highest in groundwaters from the recharge area ( $\text{Fe}_T = 2.33 \mu\text{mol kg}^{-1}$ ), and subsequently decrease thereafter with flow down-gradient (Fig. 3.2). More specifically, beyond 32 km (i.e.,  $\text{Fe}_T = 1.43 \mu\text{mol kg}^{-1}$ ),  $\text{Fe}_T$  concentrations drop and remain low such that in 7 out of 8 wells sampled,  $\text{Fe}_T$  concentrations are either at or below the detection limit. It is possible that from 0 to 32 km, the relatively higher dissolved oxygen concentrations facilitate oxidative dissolution of Fe sulfides within the aquifer substrate and subsequent release of Fe to the groundwaters.

Ferrous and ferric iron concentrations range from below detection ( $0.54 \mu\text{mol kg}^{-1}$ ) to  $1.1 \mu\text{mol kg}^{-1}$  and from below detection to  $1.79 \mu\text{mol kg}^{-1}$ , respectively (Fig. 3.2). Within the recharge area, Fe(III) dominates and accounts for 77% of the  $\text{Fe}_T$ . However,

for groundwater collected down-gradient, Fe(II) predominates, accounting for 75% of the  $Fe_T$ , for example, in groundwater at 32 km. With flow beyond 32 km, concentrations of both Fe(II) and Fe(III) are below detection except at 79 km (ROMP 31), 112 km (ROMP 18), and 138 km (ROMP 5-2), where all dissolved iron is Fe(II). The Fe data suggest that reduction of Fe(III) oxides/oxyhydroxides is an important process occurring in groundwaters proximal to the recharge area (0 to 32 km), as the dominant form of dissolved Fe in UFA groundwater changes from Fe(III) at 0 km to Fe(II) at 32 km (Fig. 3.2; Chapelle and Lovley 1990). Beyond 32 km, the generally low Fe concentrations likely reflect reductive dissolution of Fe(III) to Fe(II) and subsequent removal of Fe(II) by precipitation as Fe-sulfide minerals (e.g., pyrite; Lennie and Vaughan 1996).

Dissolved sulfide concentrations range from 2.0 to 106  $\mu\text{mol kg}^{-1}$  (mean  $S^{2-} = 72 \mu\text{mol kg}^{-1}$ ). Dissolved sulfide is lowest near the recharge area, increases by 17 fold at 46 km down-gradient, and reaches a maximum of 106  $\mu\text{mol kg}^{-1}$  at 79 km. Beyond 32 km, the dramatic increase in  $S^{2-}$  concentrations suggests that  $SO_4$  reduction is the principal redox reaction occurring along the mid to lower reaches of the flow path. Plummer and Sprinkle (2001) report  $SO_4$  and  $S^{2-}$  data for a similar flow path in the UFA and the  $S^{2-}$  data presented here are in agreement with their reported  $S^{2-}$  data. Consequently, based on the Fe and  $S^{2-}$  data, it is inferred that a zone of dissimilatory Fe(III) reduction dominates between 0 and 32 km, followed by a zone of chiefly dissimilatory  $SO_4$  reduction from beyond 32 km. Numerous studies have also reported distinct redox zones in aquifers (Back and Barnes 1965; Champ et al. 1979; Lovley and Goodwin 1988; Haque and Johannesson 2006). The relatively high  $S^{2-}$  concentrations in groundwaters beyond 32 km

indicate that the groundwaters become increasingly sulfidic and anoxic ( $S^{2-} \geq 1 \mu\text{mol kg}^{-1}$ ) (Berner 1981) with flow down-gradient. Dissolved  $S^{2-}$  remains relatively constant between 79 and 112 km, and subsequently  $S^{2-}$  decreases with flow beyond 112 km (Fig. 3.2).

Previous studies suggest that it is possible for a “mixed metabolic zone” to develop in aquifers (Lovley and Goodwin 1988; Kirk et al. 2004). Specifically, under sufficiently reducing conditions, limitation on  $\text{SO}_4$  availability may result in simultaneous  $\text{SO}_4$  reduction and methanogenesis (Lovley and Goodwin 1988; Kirk et al. 2004). The observed decrease in  $S^{2-}$  concentration in groundwaters beyond 112 km may indicate a region in the UFA where both  $\text{SO}_4$  reducers and methanogens are potentially active (Fig. 3.2). Other investigators have also suggested that methanogenesis may be important in portions of the Floridan aquifer (Rye et al. 1981; Plummer et al. 1983).

### 3.3.3 Distribution of arsenic concentrations and speciation

Arsenic concentrations in the UFA groundwaters are presented in Figure 3.2, and Table 3.2. Total As concentrations range from  $0.72 \pm 0.13$  to  $18.6 \pm 0.60 \text{ nmol kg}^{-1}$ , and exhibit a mean ( $\pm$ standard deviation) of  $4.5 \pm 0.27 \text{ nmol kg}^{-1}$ . Between 0 and 32 km,  $\text{As}_T$  concentrations are greater [mean  $\text{As}_T = 17 \text{ nmol kg}^{-1}$ ] than in groundwaters down-gradient of 32 km [mean =  $1.4 \text{ nmol kg}^{-1}$ ]. Along the flow path, the maximum observed As concentration is a factor of  $\sim 7$  below the current US EPA’s maximum contaminant level (MCL) of  $133 \text{ nmol kg}^{-1}$  ( $10 \mu\text{g kg}^{-1}$ ) for As in drinking water.

Arsenite concentrations range from  $0.97 \pm 0.07$  to  $11.5 \pm 0.13 \text{ nmol kg}^{-1}$  [mean  $\text{As(III)} = 2.6 \text{ nmol kg}^{-1}$ ]. Except for groundwater from the recharge area,  $\text{As(III)}$  is the

predominant form of dissolved As in the studied groundwaters (Fig. 3.2 and Table 3.2). One notable feature of the As data is that with flow beyond 32 km, concentrations [chiefly As(III)] remain relatively low compared to that of the up-gradient groundwaters. For example, the mean As(III) concentrations of groundwaters from 0 and 32 km is  $6.5 \text{ nmol kg}^{-1}$  compared to  $1.6 \text{ nmol kg}^{-1}$  for groundwater beyond 32 km. It is important to point out that the 2.2 fold increase in the As(III) concentration at 79 km is at odds with the  $\text{As}_T$  concentration. It is unclear if the higher As(III) concentrations in groundwater collected from 79 km reflects a problem with the  $\text{As}_T$  analysis or contamination of the As(III) sample aliquot. With flow beyond 79 km, As(III) concentrations continue to decrease reaching  $0.97 \pm 0.07 \text{ nmol kg}^{-1}$  at 112 km. Beyond 112 km, the As(III) concentrations gradually rise again, attaining a value of  $1.8 \pm 0.13 \text{ nmol kg}^{-1}$  at 144 km (ROMP 5-1).

Arsenate concentrations range from below detection ( $0.75 \text{ nmol kg}^{-1}$ ) to  $17 \pm 0.47 \text{ nmol kg}^{-1}$  (Table 3.2), and exhibit a mean of  $2.0 \text{ nmol kg}^{-1}$ . It is important to note that in 50% of the samples, As(V) concentrations are below detection [i.e.,  $\text{As}_T \approx \text{As(III)}$ ]. Arsenate concentrations are highest in groundwaters from the first two wells sampled along the flow path [mean As(V) =  $11 \text{ nmol kg}^{-1}$ ] compared to the down-gradient waters [mean As(V) =  $0.19 \text{ nmol kg}^{-1}$ ]. Arsenate accounts for >91% of  $\text{As}_T$  in groundwaters from 0 km, but only ~30% of  $\text{As}_T$  in the next well (32 km) down-gradient (Table 3.2).

#### *3.3.4 Mechanisms controlling speciation, transformation and mobilization of arsenic*

Dedolomitization, microbial oxidation of organic matter, reductive dissolution of Fe(III) oxides/oxyhydroxide,  $\text{SO}_4$  reduction, and pyrite precipitation reactions, which



govern the biogeochemical evolution of UFA groundwaters (Plummer et al. 1983; Plummer and Sprinkle 2001), also influence the “evolution” of As concentrations and speciation along the studied flow path (Fig. 3.2). Specifically, the distribution pattern of As species along the flow path reveals three features: (1) relatively higher As concentrations prevail in groundwaters from the recharge area (0 km) compared to groundwaters collected down-gradient of 32 km; (2) beyond 32 km, As concentrations remain low and relatively uniform, with As(III) predominating in solution; and (3) these differences in As concentrations and speciation correspond to distinct redox zones along the flow path (Fig. 3.2).

For groundwaters from the recharge area, which the Eh measurements and dissolved oxygen concentrations indicate are relatively oxidizing, the thermodynamically more favorable As species, As(V) predominates, accounting for >91% of  $As_T$  (Fig. 3.2). The predominance of Fe(III) in the recharge area groundwater (ROMP 76A) is inconsistent with release of sorbed As(V) via reductive dissolution of Fe(III) oxides/oxyhydroxides. Another explanation, however, is that the relatively high As concentration and dominance of As(V) may reflect the release of As due to chemical weathering of minerals or pH related (pH = 7.9) As(V) desorption (Allard and Grimvall 1988; Fuller et al. 1993). Arsenate sorption is expected to be inhibited at pH values near the point of zero charge (PZC) of important sorbing mineral such as Fe(III) oxides/oxyhydroxides and calcite ( $CaCO_3$ ; Stumm and Morgan 1996; Appelo et al. 2002). At 0 km, where the pH (~7.9) is close to the PZC for Fe oxides/oxyhydroxides (~8; Appelo et al. 2002) and  $CaCO_3$  (8 to 9.5; Somasundaran and Agar 1967), it is

reasonable to expect that the near-neutral surface charges of these minerals can inhibit adsorption of the dissociated As(V) oxyanions. Consequently, the relatively high As concentration measured at 0 km may reflect, in part, pH induced desorption or adsorptive inhibition of As(V). With flow beyond the recharge area, the decrease in As(V) concentrations may reflect adsorption of the negatively charged As(V) species onto the aquifer substrate as pH decreases (from ~8 to ~7; Fig. 3.2). This would induce a progressive increase in the positive charge of surfaces of Fe(III) oxides/oxyhydroxides and CaCO<sub>3</sub> (Somasundaran and Agar 1967; Hamon et al. 2004). It is also possible that As(V) is adsorbed onto clay mineral surfaces (Goldberg 2002) within the UFA, as kaolinite, palygorskite, and sepiolite clays occur within the aquifer matrix (Sacks et al. 1995).

At 32 km, the change in As species composition from As(V) towards As(III) is accompanied by a change in the predominant dissolved Fe species from Fe(III) at 0 km to Fe(II) at 32 km. Although  $As_T$  and  $Fe_T$  decrease between 0 and 32 km, they remain relatively high (15.7 nmol kg<sup>-1</sup> and 1.43 nmol kg<sup>-1</sup>, respectively) compared to groundwaters collected further down-gradient (Table 3.2). Again, an important difference between groundwater from 0 and 32 km (ROMP 76A and 59, respectively) is the change from oxidized to reduced As and Fe species (Fig. 3.2). The As and Fe data for these two wells are thus consistent with release of sorbed As via reductive dissolution of Fe(III) oxides/oxyhydroxides, followed by reduction of As(V) to As(III), although sorbed As(III) is also likely to be released by this mechanism (Cummings et al. 1999; Dixit and Hering 2003; Islam et al. 2004; Oremland and Stolz 2005).

Beyond 32 km, the decrease in  $\text{Fe}_T$  concentrations and concomitant increase in  $\text{S}^{2-}$  concentrations indicate a zone of redox transition from Fe(III) reduction up-gradient to  $\text{SO}_4$  reduction down-gradient (Fig. 3.2). Between 32 and 46 km, concentrations of both As(III) and As(V) decrease sharply (by a factor of  $\sim 8.8$  and  $9.5$ , respectively) reaching  $1.3 \pm 0.13$  and  $0.44 \text{ nmol kg}^{-1}$ , respectively. With flow beyond 46 km, As(III) and As(V) concentrations remain low (except at  $\sim 79$  km) and relatively constant thereafter (Fig. 3.2). In sulfidic environments, such as the mid to lower reaches of the UFA, As(V) reduction is expected to be enhanced leading to As(III) predominance in solution (Newman et al. 1997). The mobility of As(III) is strongly controlled by its sorption onto sulfide minerals in sulfidic groundwaters (Newman et al. 1997; Bostick and Fendorf 2003). Furthermore, As mobilization is also affected by formation of arsenopyrite in highly sulfidic environments, and via orpiment precipitation in less sulfidic waters (Bostick et al. 2003; O'Day et al. 2004). It is generally agreed that sedimentary pyrite acts as a sink for As even when only a minor amount of pyrite forms (Huerta-Diaz and Morse 1992). Research on mechanisms of As(III) retention on galena and sphalerite also demonstrate that As(III) adsorption increases sharply with increasing pH (Bostick et al. 2003); similar behavior was observed for As(III) sorption onto troilite and pyrite (Zouboulis et al. 1993; Bostick and Fendorf 2003). It is important to point out that As(III) sorption behavior on metal sulfides is distinct from As(III) sorption on metal oxides/oxyhydroxides, which is greatest at circum-neutral pH and substantially lower at high pH (Dzombak and Morel 1990). Arsenite sorption onto galena and sphalerite can occur in neutral pH waters where the As(III) species is still neutral ( $\text{pK}_a = \sim 9.2$ ), and

electrostatic effects contribute less to its adsorption (Bostick et al. 2003). Consequently, it is possible that in the region of the UFA where  $\text{SO}_4$  reduction predominates ( $>32$  km), As(III) is removed from solution by adsorption onto sulfide minerals, of which pyrite is likely the most abundant. The likelihood that As(III) is removed from UFA groundwaters by sorption onto metal sulfide minerals is further supported by the negative correlation between As(III) and dissolved sulfide ( $r = -0.72$ ).

It has recently been suggested that mobilization of As from sediments collected from the Ganges Delta into groundwaters occurs as a result of anaerobic respiration by Fe(III) reducing bacteria (Islam et al. 2004). Moreover, numerous investigators confirm the presence of dissimilatory As(V) reducing prokaryotes in a variety of natural environments (Newman et al. 1997; Oremland and Stolz 2005) including aquifer sediments from Bangladesh (Saikat et al. 2001). Furthermore, during metabolism, some As(V)-reducing bacteria, such as *Sulfurospirillum barnesii* and *Desulfotomaculum auripigmentum*, are capable of utilizing other electron acceptors such as Fe(III) and  $\text{SO}_4$ , respectively (Dowdle et al. 1996; Newman et al. 1997; Oremland and Stolz 2005). *Desulfotomaculum auripigmentum* is the first example of a bacterium that, in the presence of both As(V) and  $\text{SO}_4$ , reduces both As(V) and  $\text{SO}_4$  (Newman et al. 1997). However, with time, *D. auripigmentum* showed a preference for As(V), achieving a  $\sim 2.4$  fold higher molar growth ( $\text{g cells mol lactate}^{-1}$ ) compared to when grown on  $\text{SO}_4$  alone (Newman et al. 1997). Additionally, in laboratory culture, in the presence of  $\text{S}^{2-}$  generated from  $\text{SO}_4$  reduction, *D. auripigmentum* metabolism led to the precipitation of reduced As(III) as orpiment (Newman et al. 1997). Although currently there is a lack of

direct evidence of microbial metabolism involving As in the UFA, it is possible that microorganisms capable of utilizing Fe(III), SO<sub>4</sub> and As(V) as terminal electron acceptors could exist in the UFA. Previously, Tang and Johannesson (2005a) found that in groundwaters along the same flow path dissolved organic carbon (DOC) concentrations increased with flow down-gradient. A possible explanation could be meteoric and/or soil zone water with relatively high DOC concentrations infiltrate into the carbonate aquifer along the flow path, facilitating microbial metabolism (Harvey et al., 2002). Investigations of the in situ microbial consortium of the UFA, however, are necessary to confirm such a possibility.

### 3.4 Conclusions

The principal source of drinking water in west-central Florida is groundwater extracted from the UFA. In the groundwaters collected along a flow path in UFA, dissolved As concentrations are well below the current US EPA's MCL of 133 nmol kg<sup>-1</sup> (10 µg kg<sup>-1</sup>) for As in drinking water. Sorption onto Fe(III) oxides/oxyhydroxides and sulfides and co-precipitation in sulfide solid phases are likely the dominant physico-chemical processes governing the distribution of As in the UFA. Because microbes likely control redox reactions and thus the abundance of Fe(III) oxides/oxyhydroxides and sulfide minerals in the UFA, it is suggested that the in situ microbial consortium plays a crucial role in the evolution of As concentrations and speciation in these groundwaters. More specifically, in the oxic to suboxic groundwaters near the recharge area, where dissimilatory Fe(III) reduction is important, As exhibits its highest concentration. Further down-gradient, where sulfide concentrations are significant owing to presumed

microbially mediated  $\text{SO}_4$  reduction, As is likely removed from solution by sulfide minerals.

Although at present, dissolved As concentrations in these groundwaters are considerably below the approved MCL, in future, continued groundwater mining in west-central Florida, mining of phosphates, and salt water intrusion along the coast, may alter the distribution of dissolved As along the flow path. A comprehensive understanding of the biogeochemical evolution of As in these groundwaters is thus vital for management of this major drinking water resource.

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## CHAPTER 4

### EVALUATING MOBILIZATION AND TRANSPORT OF ARSENIC IN SEDIMENTS AND GROUNDWATERS OF AQUIA AQUIFER, MARYLAND, USA

#### 4.1 Introduction

Arsenic (As) is widely recognized as among the most toxic chemical elements and is also generally considered to be the prime naturally occurring carcinogen found in the environment (Smith et al., 1992; NRC, 1999, 2001; Nriagu, 2002). As a consequence, the chief cause of As poisoning to human populations is via consumption of drinking water with elevated As concentrations (Nickson et al., 2000; Chakraborti et al., 2002). Indeed, the catastrophic poisoning of ~40 million people in the Ganges-Brahmaputra Delta region of Bangladesh, and the Indian state of West Bengal is attributed to the consumption, as drinking water, of groundwaters from a local, shallow aquifer (Smedley and Kinniburgh, 2002). In addition to the Ganges-Brahmaputra Delta region, well documented cases of elevated As in groundwater sources of drinking water are also reported from other regions of southeast Asia, including Vietnam and Cambodia, as well as for Ghana, eastern Europe, Chile, Argentina, north-central México, and portions of the USA (Smedley and Kinniburgh, 2002). Groundwater with high As concentrations abstracted from many of these regions are associated with young (i.e., Quaternary) alluvial/deltaic sedimentary deposits and are characterized by reducing conditions with high dissolved

iron (Fe) concentrations and low nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4$ ) levels (Smedley, 2003; Nordstrom, 2002). A number of biogeochemical processes have been advanced to explain the elevated As concentrations in these aquifers including oxidative dissolution of As-rich pyrite (Chowdhury et al., 1999; largely disproved by Nickson et al., 2000), displacement of adsorbed As by phosphate originating from surface application of fertilizers (Acharyya et al., 1999), and dissimilatory reduction of Fe(III) oxide/oxyhydroxides and the consequent release of sorbed and/or co-precipitated As (Nickson et al., 1998, 2000; Acharyya et al., 1999; McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002).

Groundwaters and surface waters with elevated As concentrations [i.e., exceeding the US EPA maximum contaminant level (MCL) for drinking waters of  $133 \text{ nmol kg}^{-1}$  (10 ppb)] are relatively common to regions of the western USA characterized by hydrothermal fluids as well as locations with a history of mining activities (Welch et al., 1988; Welch et al., 2000). However, two notable, unconsolidated sediment aquifers within the USA that produce groundwaters with elevated As concentrations are the unconfined Ogallala aquifer in portions of western Texas (Hudak, 2000, 2006; USGS, 2003) and the confined Aquia aquifer from coastal Maryland. In the case of the Ogallala aquifer, various researchers have speculated that the source of high As concentrations in some local groundwaters may be related to past application of arsenical herbicides and/or pesticides to cotton fields on the High Plains (USGS, 2003). However, as the Aquia aquifer is largely confined, and groundwaters are reported to range up to 100,000 years in age (Purdy et al., 1996), an anthropogenic origin for the elevated As concentrations of



Aquia groundwaters is unlikely. Instead, the high As concentrations reported for some Aquia groundwaters must reflect natural, biogeochemical processes occurring within the aquifer that act to enhance dissolved As concentrations (Haque and Johannesson, 2006c).

This contribution focuses on portions of Aquia aquifer located chiefly on Maryland's eastern shore, where groundwater As concentrations were previously reported to reach values close to  $667 \text{ nmol kg}^{-1}$  (50 ppb; D. Bolton, Maryland Geological Survey (MGS), personal communication, 2004). A series of groundwater samples were collected along a flow path, identified based on the pre-development potentiometric surface for the aquifer (Drummond, 2001; Curtin et al., 2002), and analyzed for inorganic As species [As(III) and As(V)], along with ancillary geochemical parameters, including a number of redox sensitive parameters. In order to address whether changes in aqueous concentrations and speciation of As in Aquia groundwaters reflect adsorption/desorption reactions with mineral surface exchange sites (labile fraction) versus As originating from the non-labile pool (release by mineral dissolution) due to varying pH and/or redox conditions along flow, aquifer sediments were subjected to a sequential extraction scheme developed specifically to evaluate As speciation in sediments (Wenzel et al., 2001).

#### 4.2. Study Area

The Aquia aquifer in Maryland (MD) is an unconsolidated, chiefly confined Coastal Plain aquifer. The Aquia crops out along a southwest to northwest trend from near Washington, DC, toward Annapolis, MD, and into northern Kent County on

Maryland's eastern shore (Fig. 4.1; Chapelle, 1983; Aeschbach-Hertig et al., 2002). The Aquia aquifer dips to the southeast beneath the Chesapeake Bay and terminate in a facies

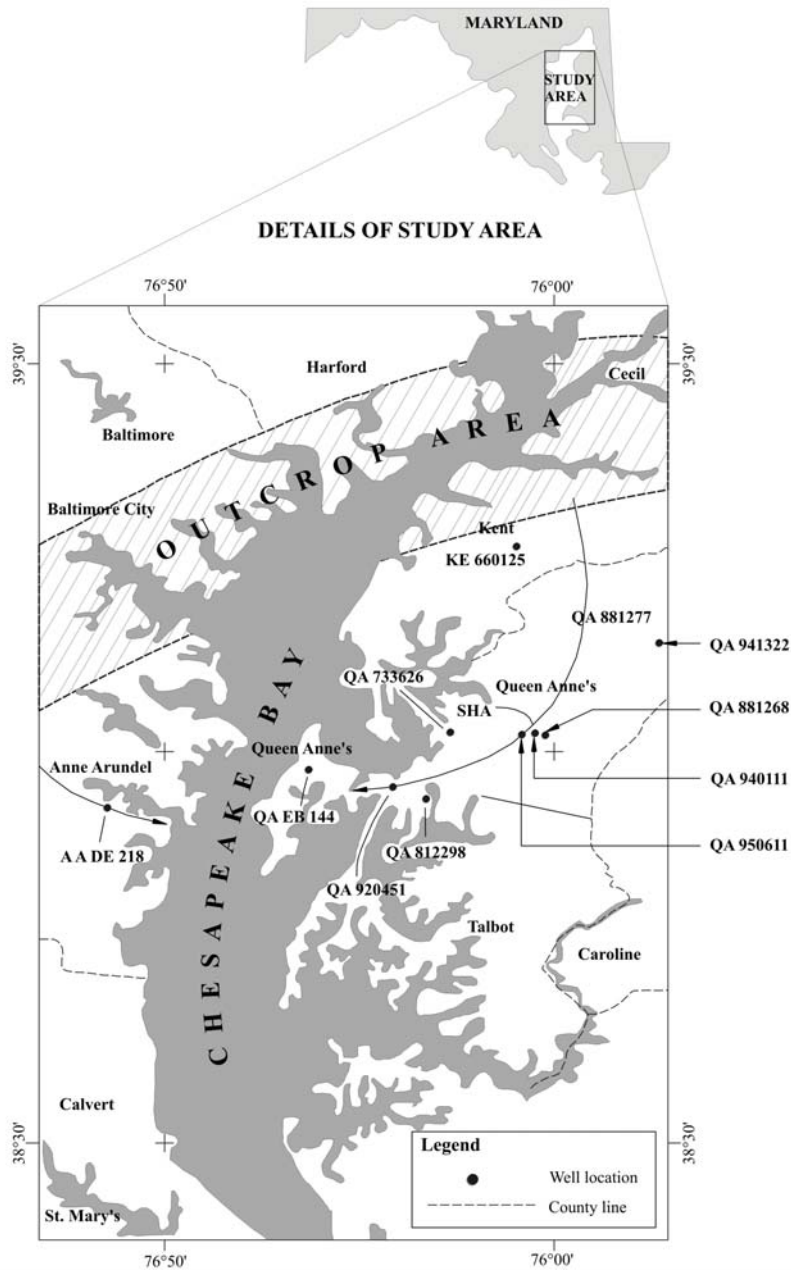


Figure 4.1: Map of the USA showing location of the study region in Maryland. Inset presents the study area within central and east central Maryland showing location of outcrop area, investigated groundwater flow path, and location of sampled wells.

change to more clay-rich and, hence, relatively impermeable sediment roughly 90 km from the outcrop area (Fig. 4.1; Chapelle, 1983; Aeschbach-Hertig et al., 2002). The Aquia aquifer, which is a hydrostratigraphic unit defined within the broader Aquia Formation, is overlain by the Marlboro clay and underlain by the Severn Formation (Chapelle, 1983). The Aquia, a Paleocene marine deposit, is composed of fine- to medium-grained quartz sand (~55%), glauconite (~30%), and shell fragments (~8%), along with minor amounts of lignite, clay minerals, garnet, magnetite, hornblende, and pyrite (Page, 1957; Wolff 1967; Hansen, 1974; Chapelle, 1983). The thickness of the Aquia aquifer ranges from 23 to 30 m near the Chesapeake Bay (Harsh and Laczniak, 1990).

Here, we focus on portions of Aquia aquifer located chiefly on Maryland's eastern shore (Fig. 4.1) where groundwater As concentrations were previously reported to exceed the US EPA's current MCL for drinking water of  $133 \text{ nmol kg}^{-1}$  (D. Bolton, MGS, personal communication, 2004). In August 2006, a series of groundwater samples were collected along a broadly defined flow path, identified with assistance from the Maryland Department of the Environment and based on the pre-development potentiometric surface-levels for the aquifer (Drummond, 2001). The pre-development potentiometric surface indicates that groundwater recharged to the Aquia aquifer in its outcrop area in northern Kent County on Maryland's eastern shore flows south and southwest towards the Chesapeake Bay, discharging, in part, to the Bay in the vicinity of the shoreline (Drummond, 2001; Curtin et al., 2002). For the purpose of comparison, an

additional groundwater sample was collected (well AA DE 218) from the western shore of Chesapeake Bay in Anne Arundel County, Maryland (Fig. 4.1). Future investigations of As concentrations and speciation in Aquia groundwater from the western shore are currently in the planning stage.

Based on  $^{14}\text{C}$  and  $^{36}\text{Cl}/\text{Cl}$  measurements of Aquia groundwaters, Purdy (1991) suggested that the upper part of the aquifer (first ~40 km) was recharged following the last glacial maximum (~18,000 a), whereas in the lower part of the aquifer, the groundwater age may be on the order of 100,000 a (Purdy et al., 1996). It is important to note that Purdy and colleagues (Purdy, 1991; Purdy et al., 1996) as well as a number of other important hydrogeochemical studies of groundwaters within the Aquia aquifer (e.g., Chapelle, 1983; Chapelle and Knobel, 1983, 1985) focused on flow paths originating near Washington, DC, and subsequently flowing southeast along the length of the southern Maryland Peninsula bounded by the Chesapeake Bay on the east and the Potomac River to the south and west (e.g., portions of Calvert and St. Mary's Counties on Fig. 4.1). The length of these flow paths exceed that studied here (97 km vs. 86 km), which is important to note when making comparison between these flow paths.

### 4.3. Materials and methods

#### *4.3.1 Sample collection*

##### 4.3.1.1 Groundwater sampling and field analyses

Prior to transport to the study site, all sample bottles (HDPE), field containers (e.g., Teflon® tubing) and lab-ware were thoroughly cleaned using trace element clean (i.e., “trace clean”) procedures (Johannesson et al., 2004). All sampled wells were purged

for at least 30 minutes prior to sample collection to ensure that the water samples represented groundwaters from the Aquia aquifer and not from the well bore. In addition, sample collection did not commence until the specific conductance, pH, and temperature measurements stabilized.

Groundwater samples were analyzed in the field for a number of parameters including pH, alkalinity, electrical conductivity, dissolved oxygen, oxidation-reduction potential (Eh in mV), dissolved N species ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ), total dissolved Mn, dissolved Fe species (II and III), and sulfide ( $\text{S}^{2-}$ ). Oxidation-reduction potential (Eh), pH, specific conductance, and temperature were quantified using a Hydrolab MiniSonde 5 with a flow-through cell. The flow-through cell was connected to the well outflow using a polyethylene tube, which allowed the Eh to be measured without exposure of groundwater to the atmosphere. Dissolved oxygen, N species, total Mn, Fe species and dissolved  $\text{S}^{2-}$  were quantified on separate sample aliquots via UV/VIS spectrophotometry using a portable spectrophotometer (Hach DR/890). For each parameter, the spectrophotometer was calibrated and the sample concentrations were verified using a series of calibration standards of known concentrations. Briefly, Fe(II) was determined using the 1,10 Phenanthroline method (Eaton et al., 1995a), total Fe [ $\text{Fe}_T$ ] was determined by the Ferrozine method (Stookey, 1970; Hach, 2004), and Fe(III) was subsequently calculated by difference. The method detection limits for  $\text{Fe}_T$  and Fe(II) are  $0.16 \mu\text{mol kg}^{-1}$  and  $0.36 \mu\text{mol kg}^{-1}$ , respectively (Hach, 2004). Dissolved  $\text{S}^{2-}$  was measured on separate aliquots using the portable spectrophotometer and the Methylene Blue method (Eaton et al., 1995a). The method detection limit for  $\text{S}^{2-}$  is  $0.16 \mu\text{mol kg}^{-1}$  (Eaton et al.,

1995a). Concentrations of dissolved oxygen were determined on separate aliquots using the High Range dissolved oxygen (method detection limit:  $18.8 \mu\text{mol kg}^{-1}$ ; Hach, 2004) and Indigo Carmine methods (method detection limit:  $0.38 \mu\text{mol kg}^{-1}$ ; Gilbert et al., 1982) for high and low ranges, respectively. Concentrations of Si, Mn,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were determined on separate aliquots using the same portable spectrophotometer and the Heteropoly Blue method (Schelske et al., 1984), 1-(2-Pyridylazo)-2-Naphthol method (Manzoori et al., 1999), Cadmium 16 Reduction method (Gal et al., 2004) and Salicylate method (Krom, 1980), respectively. The method detection limits for Si, Mn,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were  $0.36 \mu\text{mol kg}^{-1}$ ,  $0.13 \mu\text{mol kg}^{-1}$ ,  $0.16 \mu\text{mol kg}^{-1}$ ,  $0.55 \mu\text{mol kg}^{-1}$ , respectively (Hach, 2004).

In situ separation of soluble inorganic species of As (III and V) was performed using a previously established anion exchange chromatography method (for details see Wilkie and Hering 1998; Haque and Johannesson, 2006a, b). The anion exchange method employed Poly-Prep 0.8x4 cm chromatography columns packed with Bio-Rad AG<sup>®</sup> 1x8, 50-100 mesh, anion exchange resin converted to the acetate form (see Wilkie and Hering, 1998 for details). Groundwater samples for As species determination were first collected from the well head into collapsible “trace clean” LDPE cubitainers<sup>®</sup> and were immediately filtered through  $0.45 \mu\text{m}$  in-line filter-capsules (Gelman Sciences, polyether sulfone membrane) by drawing water from the cubitainers<sup>®</sup> through “trace clean” Teflon<sup>®</sup> tubing using a peristaltic pump. To avoid photocatalyzed oxidation of As(III), all filtered samples were collected in 500 mL opaque, amber HDPE bottles (McCleskey et al., 2004), and subsequently acidified to pH  $\sim 3.5$  by addition of ultra-pure  $\text{HNO}_3$

(Seastar Chemical, Baseline). The acidified samples were then passed through the anion exchange columns. At a pH of  $\sim 3.5$ , the resins in the column retain As(V), which occurs as anionic  $\text{H}_2\text{AsO}_4^-$ , and As(III), occurring as  $\text{H}_3\text{AsO}_3^0$ , passes through the column. Arsenite is quantified in the collected eluted fractions. Total soluble As [As(III)+As(V), hereafter referred to as  $\text{As}_T$ ] samples were collected in 1 L amber HDPE bottles using separate filtered ( $0.45 \mu\text{m}$ , polyether sulfone membrane) sample aliquots preserved by acidification to  $\text{pH} < 2$  (Wilkie and Hering 1998; Haque and Johannesson, 2006a, b). Subsequently, As(V) is calculated by subtracting As(III) from  $\text{As}_T$  concentrations of the sample. In addition to a field blank, three duplicate samples for As species analyses were also collected. Prior to analysis, all samples were stored in the dark and “on ice” at  $\sim 4^\circ\text{C}$ .

#### 4.3.1.2 Sediment sampling

To examine and study the solid phase speciation of As in the Aquia sediments, we collected a number of sub-samples, including duplicates of aquifer sediments from a drill core archived at the Maryland Geological Survey. The core (ID# Ken-Bf 180) was collected from Kent County, MD, and the sedimentology and stratigraphy of the core is described in detail by Hansen (1992). Our samples represented sediments from sampling depths of 57 m, 65 m, 97 m, and 104 m within the Aquia. Collected sediment samples were stored on ice at  $\sim 4^\circ\text{C}$  until they arrived at the laboratory, where they were subsequently transferred to a laboratory refrigerator. All samples were collected to minimize contamination by using gloved hands, stainless steel (or plastic) tools, and clean polyethylene sampling bags.

### 4.3.2 Analyses

#### 4.3.2.1 Groundwater arsenic analysis

All groundwater samples collected for dissolved As concentrations and speciation were analyzed by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Finnigan MAT ELEMENT 2). The high resolution mode of the HR-ICP-MS allows As to be distinguished from potential interference from  $\text{ArCl}^+$ . The instrument was calibrated and the sample concentrations were verified using a series of As calibration standards of known concentrations, and analytical precision was typically better than 3.42% RSD (relative standard deviation). The method detection limit for As, based on  $3\sigma$  of the blank measurement, is  $0.14 \text{ nmol kg}^{-1}$ . Arsenic calibration standards of known concentrations, i.e., 2.67, 26.7, 134, and 267  $\text{nmol kg}^{-1}$ , were prepared from high purity single-element stock solutions (High-Purity Standards, Charleston, SC, USA). All standard and sample solutions were spiked with 4.0 ppb indium as an internal standard to correct for instrument drift.

#### 4.3.2.2 Sequential extraction analysis

To characterize the distribution of As in the Aquia sediments, all sediment samples were evaluated using a modified sequential extraction method for As described by Wenzel et al. (2001). The extraction procedure and subsequent quantification by ICP-MS has sufficient sensitivity to quantify  $\text{nmol kg}^{-1}$  concentrations (i.e.,  $<0.5 \text{ ppb}$ ) of As in sediments. The procedure is used to examine the As concentrations associated with five “operationally defined phases” within the sediment, including non-specifically bound (outer sphere surface complexed), specifically bound (inner sphere surface complexed),



amorphous hydrous Fe (Mn, Al) oxides (e.g., ferrihydrite), crystalline (hydrous) Fe (Mn, Al) oxides (e.g., goethite, hematite and magnetite), and residual (e.g., aluminosilicates; framework silicates, such as quartz; Wenzel et al., 2001). Moreover, the sequential extraction technique employs reagents that were chosen to selectively attack the specific soil phases with minimal dissolution of non-target phases, and the sequence of reagents is applied from relatively weaker to increasingly stronger to dissolve progressively more refractory mineral phases (Wenzel et al., 2001). Table 4.1 summarizes the extraction procedure, along with the “operationally defined” sediment phases targeted by each extractant. It should be noted, however, that as with all sequential extraction schemes (e.g., Tessier et al., 1979), which are subject to possible artifactual results arising from incomplete dissolution and/or re-adsorption of trace elements, the results are best viewed as semi-quantitative (Tipping et al., 1985).

Table 4.1 Summary of sequential extraction procedure.

Fraction	Extractant	Target phase	Possible mechanism*
1	0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; 4 hr shaking (20°C)	Physisorbed As (outer sphere surface complexes), commonly referred to as labile or reactive As (Hamon et al., 2004)	Anion exchange of SO <sub>4</sub> for As
2	0.05 M NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> ; 16 hr shaking (20°C)	Chemisorbed As (inner sphere surface complexes; also labile)	Anion exchange of PO <sub>4</sub> for oxyanion As
3	0.2 M NH <sub>4</sub> -oxalate buffer, pH 3.25; 4 hr shaking (dark; 20°C)	Non labile As associated with amorphous and poorly crystallized Fe (Mn, Al) oxide/oxyhydroxides	Ligand-promoted dissolution
4	0.2 M NH <sub>4</sub> -oxalate buffer + 0.1 M ascorbic acid (pH 3.25); 30 min in water basin at 96±3°C	Non-labile As associated with well crystallized Fe (Mn, Al) oxide/oxyhydroxides	Reduction of Fe(III) and Al(III)
5	a. 16 N HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> ; Microwave assisted acid digestion (EPA method 3050B; <a href="http://www.epa.gov/SW-846/pdfs/3050b.pdf">www.epa.gov/SW-846/pdfs/3050b.pdf</a> )	a. Liberate As associated with residual minerals such as orpiment (Keon et al., 2001)	a. Oxidation of sulfides and organic matter
	b. 16 N HNO <sub>3</sub> + HF (Tessier et al., 1979; Tang et al., 2004)	b. Release As associated within aluminosilicate minerals (Johannesson and Zhou, 1999)	b. Dissolution of aluminosilicates

\* Wenzel et al. (2001)

Here, we briefly outline the procedure for each extraction step (see Wenzel et al., 2001 for details). Prior to extraction, all sediment samples were air-dried at ambient temperature in a Class 100 laminar flow hood. The dried sediments were then passed through a 2-mm sieve and homogenized. Reagents (reagent or trace element grade) were obtained from Sigma-Aldrich and were prepared using ultra-pure Milli-Q water (18.2  $\Omega$ -cm). The volume of all extraction solutions used was 25 mL.

Fraction 1. A 1.0 gm (dry weight) aliquot of each sediment sample was placed into a 50 mL centrifugation tube (Fisher Scientific), along with 25 mL of 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  reagent (Table 4.1). The mixture was subsequently agitated for 4 hours at 20°C on a shaker (VWR Mini Shaker), and then centrifuged (Labofuge 400, Heraeus Instruments) for 15 minutes at 2000 rpm. The resultant supernates were filtered (0.4  $\mu\text{m}$  membrane Nuclepore® filters), acidified with ultra-pure  $\text{HNO}_3$  (Seastar Chemical, Baseline), and stored at 4°C prior to analysis. The residual soil was used for the subsequent extraction step.

Fraction 2. The residue from fraction 1 was placed in a 50 mL centrifuge tube along with 25 mL of 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  solution, and subsequently agitated for 16 hours at 20°C on the Mini Shaker as described above. The sediment-reagent slurry was then centrifuged, filtered, and acidified as described above.

Fraction 3. The residue from fraction 2 was placed in a 50 mL centrifuge tube along with 25 mL of 0.2 M  $\text{NH}_4$ -oxalate buffer solution and the pH was adjusted to 3.25 using oxalic acid. The mixture was subsequently shaken for 4 hours at 20°C in the dark,

and then centrifuged, filtered, and acidified as described above. To account for potential carryover to the next extraction steps, we employed a wash step to recover As remaining in the rest of the solution and re-adsorbed onto amorphous metal oxides. The residue from the primary extraction was placed in a 50 mL centrifuge tube along with the same reagents and the wash step solution was subsequently shaken for 10 min in the dark, followed by centrifugation, filtration, and acidification as described above.

Fraction 4. The residual from fraction 3 was placed in a 50 mL centrifuge tube along with a 0.2 M  $\text{NH}_4$ -oxalate buffer solution and 0.1 M ascorbic acid adjusted to pH 3.25. The centrifuge tube containing the sediment-reagent solution slurry was then placed in a heated water bath ( $96 \pm 3^\circ\text{C}$ ) for 30 minutes. After cooling, the sediment-reagent slurry was then centrifuged, filtered, and acidified as described above. A wash step using the same reagents was employed to recover As remaining in the rest of the solution and re-adsorbed onto crystalline Fe and Al oxide minerals. Here, a 50 mL centrifuge tube containing the residue from the primary extraction along with the same reagents was subsequently shaken for 10 min in the dark, and centrifuged, filtered, and acidified as described above.

Fraction 5. The residue from fraction 4 was subsequently digested using a two step process. First, the EPA acid digestion method 3050B (see [www.epa.gov/SW-846/pdfs/3050b.pdf](http://www.epa.gov/SW-846/pdfs/3050b.pdf)) was used whereby the sediment residue was placed in a 25 mL mixture of 16 N  $\text{HNO}_3$  (Seastar Chemical, Baseline) and 30%  $\text{H}_2\text{O}_2$  (Fluka), which was then placed in a heated water bath ( $95^\circ\text{C} \pm 5^\circ\text{C}$ ) for 4 hours. After cooling, the sediment-reagent solution slurry was centrifuged, filtered, and acidified as described above.

Secondly, the remaining residue was subsequently digested in a Teflon® beaker with 20 mL ultrapure HF (Seastar chemicals, Baseline), and the mixture was evaporated to near dryness, followed by 20 mL of ultrapure 16 N HNO<sub>3</sub>, which was again evaporated to near dryness. Subsequently, an additional 20 mL of ultrapure HF was added and the mixture was evaporated to near dryness. The residue was then redissolved with Milli-Q water and diluted up to 25 mL with Milli-Q water. The sediment-reagent solution slurry was subsequently centrifuged, filtered, and acidified as described above. The concentration of total extractable As in the residual phase was then determined by the sum of the combined digestion techniques.

All supernatants of the sequential extraction procedure were analyzed for As by ICP-MS (Perkin Elmer/Sciex Elan DRC II). The instrument was calibrated and the sample concentrations were confirmed using a series of As calibration standards of known concentrations ranging from 0.133, 1.33, 13.3, 134, and 1335 nmol kg<sup>-1</sup>. The calibration standards were prepared from high purity single-element stock solutions at 134 μmol kg<sup>-1</sup> (High-Purity Standards, Charleston, SC, USA). The method detection limit for As, based on 3σ of the blank measurement, is 0.40 nmol kg<sup>-1</sup>. Because we are also interested in the relative solid phase distribution of Fe, Mn, and Al within these sediment fractions as a means of confirming the phases attacked by each sequential extraction, these three metals were also determined concurrently with As by ICP-MS.

All standard and sample solutions were spiked with 10 ppm of an internal standard mix (Li, Sc, Ge, In, Tb, and Bi; PerkinElmer Life and Analytical Science),

specifically employing Ge as the internal standard for As, to monitor and correct for instrumental drift.

## 4.4 Results

### *4.4.1 Groundwater chemistry*

Hydrogeochemical data for groundwaters from the Aquia aquifer are listed in Tables 4.2 and 4.3 and shown in Figures 4.2 and 4.3. Aquia groundwaters are near-neutral to slightly alkaline, with pH values ranging between 7.6 and 8.4. Alkalinity, expressed as HCO<sub>3</sub>, ranges from 2.0 to 4.2 mmol kg<sup>-1</sup> (Table 4.2), and exhibits an overall increasing trend with flow down-gradient along the flow path (Fig. 4.2).

Table 4.2 Hydrogeochemical data of groundwaters from Aquia aquifer: temperature (Temp), alkalinity as HCO<sub>3</sub> (Alk), pH, specific conductivity (Cond), total dissolved solids (TDS), oxidation-reduction potential (Eh), and dissolved oxygen (DO).

Sample	Distance km	Temp °c	Alk ( HCO <sub>3</sub> ) mmol kg <sup>-1</sup>	pH	Cond µScm	TDS mg kg <sup>-1</sup>	Eh mV	DO µmol kg <sup>-1</sup>
<i>Eastern shore wells</i>								
KE 66 0125	22.5	16.6	1.99	7.57	222	143	25.5	51.0±1.80
QA 88 1277	33.5	15.6	2.79	7.69	296	189	44.0	13.5±0.21
QA 94 1322	36.2	18.6	3.08	8.01	330	211	-11.0	19.6±0.10
QA 88 1268	51.2	16.7	3.19	8.08	303	194	-10.5	16.8±0.07
State Hwy Admin	52.0	19.7	2.91	8.38	305	196	-46.0	21.4±0.11
QA 94 0111	52.5	16.2	3.79	7.91	366	234	-3.00	11.1±0.05
QA 95 0611	55.0	16.1	2.98	8.02	302	194	-18.0	50.0±0.00
QA 73 3626	64.5	16.9	3.46	7.84	351	213	27.5	23.3±0.12
QA 81 2298	70.7	17.5	3.79	8.30	296	189	-11.0	20.3±0.05
QA 92 0451	75.1	17.8	4.16	7.93	422	267	11.5	12.0±0.10
QA EB 144	86.3	15.9	3.24	8.12	366	271	-53.0	9.38±0.08
<i>Western shore well</i>								
AA DE 218	40.0	14.5	2.48	7.81	300	192	60.5	124±1.80

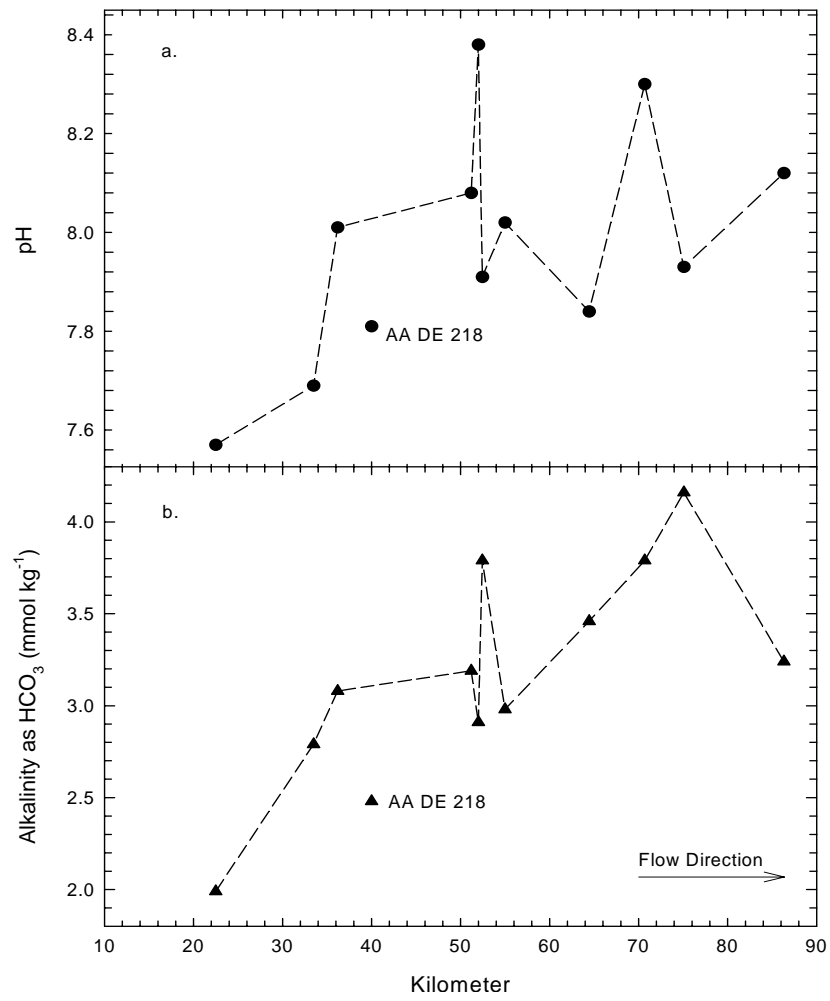


Figure 4.2: Aquia aquifer data: (a) pH; (b) alkalinity as a function of distance from recharge zone (km).

Table 4.3 Concentrations and speciation data for dissolved Fe, S<sup>2-</sup>, Mn, N, and Si in groundwaters from the Aquia aquifer

Sample	Distance	Fe <sub>T</sub>	Fe(II)	Fe(III)	S <sup>2-</sup>	Mn	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Si
	Km	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	μmol kg <sup>-1</sup>	mmol kg <sup>-1</sup>
<i>Eastern shore wells</i>									
KE 66 0125	22.5	12.7±0.21	0.90±0.03	11.8±2.58	BDL <sup>*</sup>	1.02±0.00	BDL <sup>‡</sup>	0.42±0.19	1.26±0.05
QA 88 1277	33.5	17.7±0.01	7.70±0.00	10.0±0.27	0.23±0.18	0.15±0.01	0.48±0.00	2.03±0.19	0.41±0.00
QA 94 1322	36.2	15.4±0.05	2.87±0.10	12.5±0.34	BDL	BDL <sup>†</sup>	1.13±0.00	14.8±0.00	0.32±0.00
QA 88 1268	51.2	14.7±0.08	0.18±0.00	14.5±0.39	0.10±0.18	0.42±0.01	0.32±0.00	9.12±0.93	0.44±0.00
State Hwy Admin	52.0	7.01±0.06	2.38±0.10	4.63±0.12	0.40±0.02	0.00±0.00	3.23±0.00	6.77±0.00	0.24±0.00
QA 94 0111	52.5	11.4±0.10	6.80±0.10	4.60±0.12	BDL	BDL	0.00±0.00	3.22±0.00	0.23±0.00
QA 95 0611	55.0	3.35±0.02	3.35±0.09	BDL <sup>°</sup>	BDL	BDL	0.76±0.09	4.83±0.00	0.57±0.00
QA 73 3626	64.5	BDL <sup>°</sup>	BDL <sup>¶</sup>	BDL	BDL	0.44±0.01	1.13±0.00	7.73±0.00	0.44±0.00
QA 81 2298	70.7	9.94±0.03	9.94±0.27	BDL	0.34±0.03	0.04±0.01	0.65±0.00	15.1±0.00	0.20±0.00
QA 92 0451	75.1	9.01±0.01	9.01±0.24	BDL	BDL	BDL	0.48±0.00	9.02±0.00	0.38±0.00
QA EB 144	86.3	8.29±0.01	4.71±0.13	3.58±0.00	0.16±0.00	0.11±0.01	0.48±0.00	1.39±0.19	0.22±0.00
<i>Western shore well</i>									
AA DE 218	40.0	14.0±0.01	5.32±0.10	8.70±0.23	0.52±0.18	0.76±0.02	0.32±0.00	BDL <sup>‡</sup>	0.37±0.00

<sup>°</sup>BDL for Fe<sub>T</sub> = 0.16 μmol kg<sup>-1</sup>

<sup>¶</sup>BDL for Fe(II) = 0.36 μmol kg<sup>-1</sup>

<sup>\*</sup>BDL for S<sup>2-</sup> = 0.16 μmol kg<sup>-1</sup>

<sup>†</sup>BDL for Mn = μmol kg<sup>-1</sup>

<sup>‡</sup>BDL for NO<sub>3</sub><sup>-</sup> = 0.16 μmol kg<sup>-1</sup>

<sup>‡</sup>BDL for NH<sub>4</sub><sup>+</sup> = 0.55 μmol kg<sup>-1</sup>

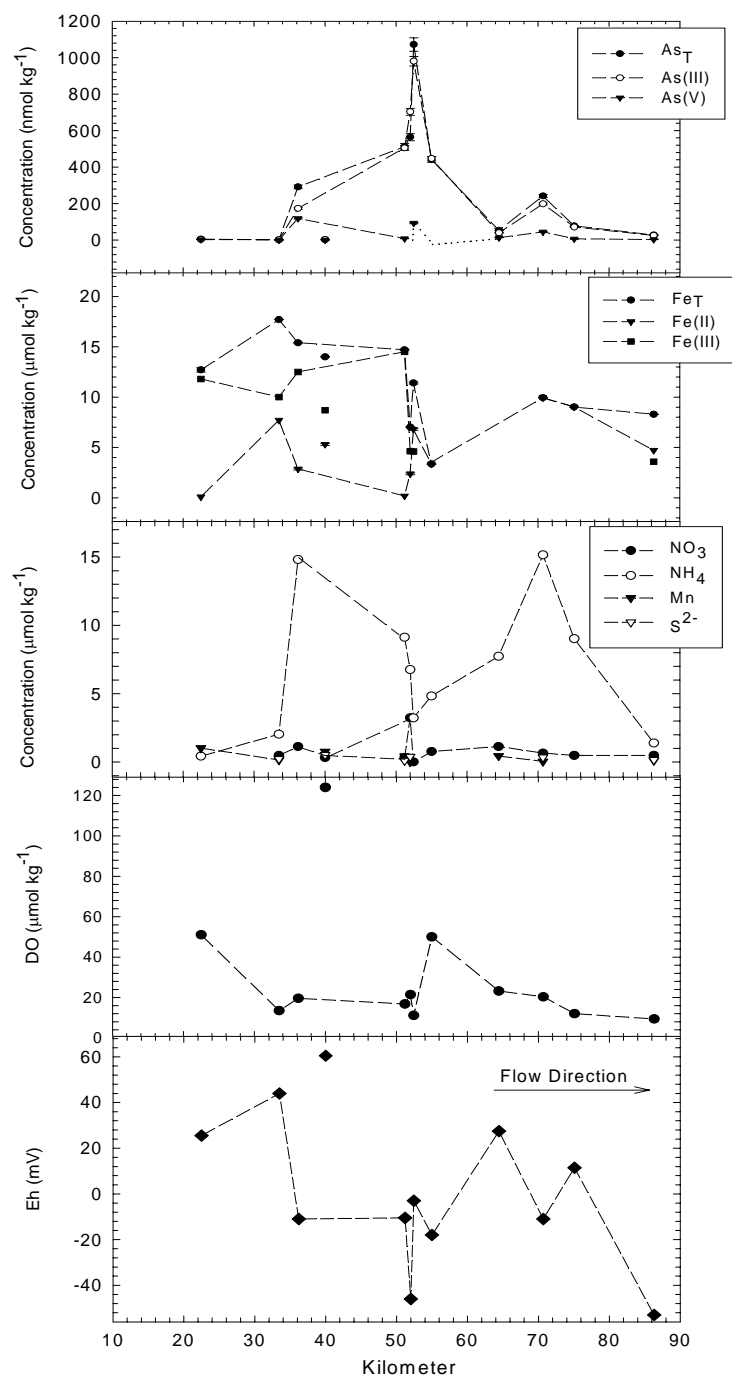


Figure 4.3: Aquia aquifer data: (a) As speciation; (b) Fe speciation; (c) N speciation, Mn and S<sup>2-</sup>; (d) Dissolved oxygen; (e) Eh as a function of distance from recharge zone (km). Dashed lines are actual data and dotted lines represent values below the detection limit.



Dissolved oxygen (DO) concentrations in Aquia groundwaters range between 9.4 and 124  $\mu\text{mol kg}^{-1}$ . Dissolved oxygen concentrations are relatively low throughout the aquifer except at well AA DE 218 on the western shore, where the DO concentration is 124  $\mu\text{mol kg}^{-1}$  (Fig. 4.3). Measured Eh values range between -53 to 61 mV and generally exhibit higher values near the recharge zone compared to groundwater samples collected further down-gradient along the flow path (Fig. 4.3). Dissolved  $\text{NO}_3^-$  concentrations range from below detection to 3.2  $\mu\text{mol kg}^{-1}$  (mean  $\text{NO}_3^- = 0.7 \mu\text{mol kg}^{-1}$ ), and remain relatively low throughout the length of the flow path, except at 52 km (State Hwy Admin well) where  $\text{NO}_3^-$  exhibits its highest concentration. Dissolved  $\text{NH}_4^+$  concentrations range from below detection to 15  $\mu\text{mol kg}^{-1}$  (Table 4.3), and in general exhibit higher concentrations with flow beyond 36 km along the flow path (Fig. 4.3).

Total dissolved Fe concentrations (i.e.,  $\text{Fe}_T$ ) range from below detection to 18  $\mu\text{mol kg}^{-1}$  (Table 4.3). Ferrous iron concentrations range from below detection to 9.9  $\mu\text{mol kg}^{-1}$ , and Fe(III) concentrations range from below detection to 14.5  $\mu\text{mol kg}^{-1}$ . From the recharge area to 52 km down-gradient along the flow path (State Hwy Admin well), Fe(III) predominates within the Aquia groundwaters, whereas with flow beyond the State Highway Administration well, Fe(II) is the chief form of Fe in Aquia groundwaters. An outstanding feature of the Fe speciation data of Aquia groundwaters is this sharp transition at 52 km where the chief form of Fe in Aquia groundwater changes from Fe(III) to Fe(II). Dissolved sulfide ( $\text{S}^{2-}$ ) concentrations range from below detection to  $\sim 0.52 \mu\text{mol kg}^{-1}$  (Table 4.3). In general,  $\text{S}^{2-}$  concentrations remain low along the flow path and are below detection in 6 out of 12 wells sampled.

Table 4.4 and Fig. 4.3 present the As species concentrations and their distribution in the Aquia groundwaters as a function of distance from the recharge area in Kent County, Maryland. Total dissolved As concentrations range from ~0.8 to 1072 nmol kg<sup>-1</sup>, and exhibit a mean of ~274 nmol kg<sup>-1</sup>. Arsenic concentrations are highest along the mid-reaches of the flow path (36 to 55 km; mean As<sub>T</sub> = 480 nmol kg<sup>-1</sup>). In 50% of the groundwater wells sampled, As<sub>T</sub> concentrations exceed the EPA's MCL (133 nmol kg<sup>-1</sup>) for As in drinking water. In general, the elevated As concentration in Aquia groundwaters are much lower than those measured in groundwaters of Bangladesh and West Bengal, where As concentrations as high as 4.4 μmol kg<sup>-1</sup> are reported (Acharyya et al., 1999; Nickson et al., 2000; McArthur et al., 2001).

Table 4.4 Concentrations and speciation data for dissolved inorganic As in groundwaters from the Aquia aquifer.

Sample	Distance km	As <sub>T</sub> nmol kg <sup>-1</sup>	As(III) nmol kg <sup>-1</sup>	As(V) nmol kg <sup>-1</sup>
<i>Eastern shore wells</i>				
KE 66 0125	22.5	4.92±0.17	2.71±0.07	2.21±0.07
QA 88 1277	33.5	0.75±0.03	0.59±0.02	0.15±0.00
QA 94 1322	36.2	291±9.95	173±4.64	118±3.60
QA 88 1268	51.2	512±17.5	505±13.5	7.25±0.22
State Hwy Admin	52.0	564±19.3	703±18.8	BDL*
QA 94 0111	52.5	1072±36.7	980±26.3	91.9±2.80
QA 95 0611	55.0	441±15.1	446±11.9	BDL
QA 73 3626	64.5	52.7±1.80	39.4±1.06	13.2±0.40
QA 81 2298	70.7	241±8.24	198±5.31	44.0±1.34
QA 92 0451	75.1	76.8±2.63	70.7±1.89	6.05±0.18
QA EB 144	86.3	27.3±0.93	24.8±0.66	2.51±0.08
<i>Western shore well</i>				
AA DE 218	40.0	1.66±0.06	1.50±0.04	0.17±0.01

\* BDL for As = 0.14 nmol kg<sup>-1</sup>

In Aquia groundwaters, As(III) concentrations range from 0.24 to 980 nmol kg<sup>-1</sup> (mean = 242 nmol kg<sup>-1</sup>), whereas As(V) concentrations range from below detection to ~118 nmol kg<sup>-1</sup> (mean = 28.5 nmol kg<sup>-1</sup>). A notable feature of the Aquia As data is that the highest concentrations are attained where the predominant form of Fe in the groundwater changes from Fe(III) to Fe(II; Fig 4.3).

#### *4.4.2 X-Ray diffraction analysis of Aquia sediments*

Photomicrographs of Aquia aquifer sediments from 105 m and 57 m depths are presented in Fig 4.4 showing the abundance of quartz and glauconite, as well as Fe(III) oxide/oxyhydroxides occurring within the sediments. X-Ray diffraction (XRD) analysis of the Fe-rich coatings (Fig. 4.4) on mineral grains, and other materials too fine to be resolved by petrographic microscope, were conducted on oriented mounts of clay-sized particles (<2 μm) of Aquia sediment from each depth (i.e., 57, 65, 97 and 104 m). Figure 4.5 presents results of the XRD analysis obtained using a Rigaku D/max-rA diffractometer with Cu-Kα radiation, a voltage of 40 kV, and an intensity of 25 mA. Aquia sediment samples were scanned with the goniometer from 3° to 36° 2θ under air-dried conditions. Identification of clay minerals was made mainly according to the position of the (001) series of basal reflections on the XRD diagrams (Moore and Reynolds, 1989). XRD analysis indicates that the Fe-rich coatings on quartz, glauconite, and other minerals within the Aquia (Fig. 4.4) are chiefly composed of the clay mineral illite and goethite, with lesser amounts of hematite (Fig. 4.5). Our results are broadly consistent with the study by Penn et al. (2001) of coastal plain sediments from Virginia's eastern shore.

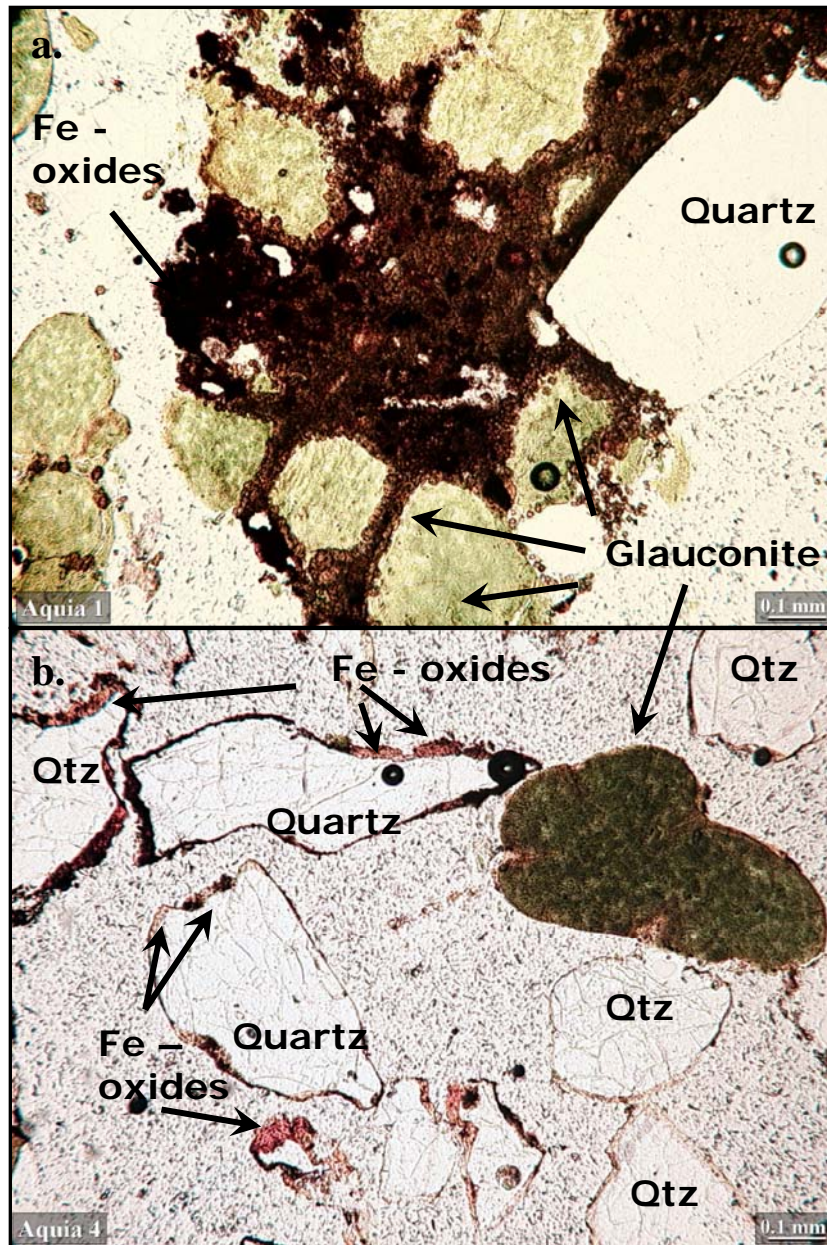
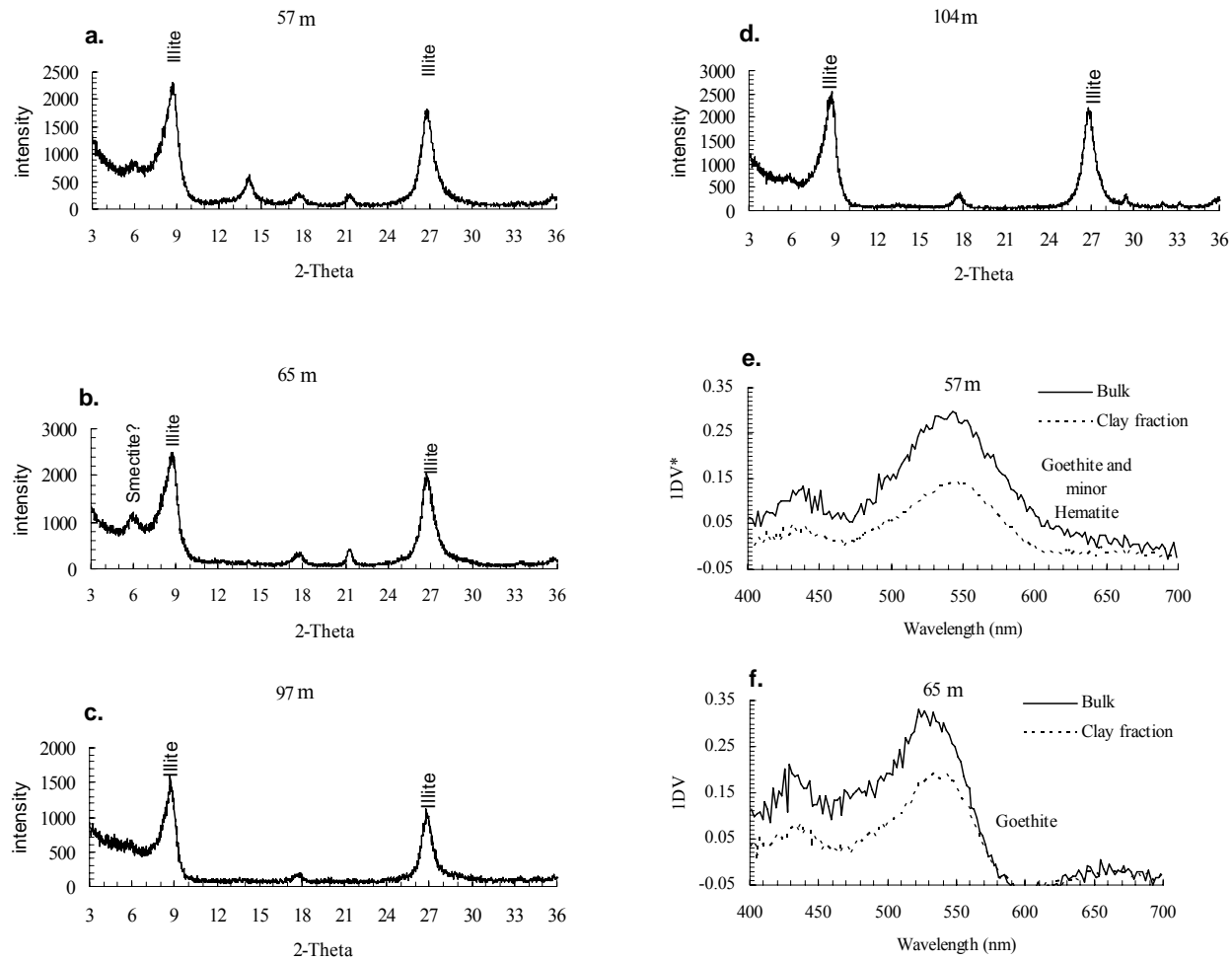


Figure 4.4: Photomicrograph (plain light) of Aquia aquifer sediments (core Ken-Bf 180; Hansen, 1992) from (a) 105 m depth and (b) 57 m depth. The Aquia aquifer sediments contain abundant subangular to well rounded quartz grains and various sized glauconite “pellets” exhibiting a range of degree of weathering. In addition, the photomicrograph shows the ubiquitous presence of Fe oxide phases that occurs as (a) masses cementing glauconite and quartz grains as well as (b) coatings on quartz, glauconite, and other minerals within the sediments.



\*IDV = Value of first derivative

Figure 4.5: X-Ray diffraction diagram of Aquia sediments at (a) 57 m; (b) 65 m; (c) 97 m; (d) 104 m; diffuse reflectance spectrum diagram of Aquia sediment (e) 57 m; (f) 65 m.

#### *4.4.3 Sequential extraction analysis of Aquia sediments*

The results of the sequential extraction analysis for As in Aquia aquifer sediments are summarized in Tables 4.5 and 4.6, along with concentrations of Fe, Mn and Al in each fraction. Below we present the results of the sequential extractions in the order of each successive fraction:

Fraction 1. In Aquia sediment samples, concentrations of total extractable, physisorbed (outer sphere surface complexed) As range from 5.42 to 36.8 nmol kg<sup>-1</sup> (Table 4.5). At sampling depths of 57, 65, 97, and 104 m, the physisorbed fractions of As account for 1.86, 1.54, 0.52, and 0.56% of the total As concentrations of Aquia sediments, respectively (Table 4.6). Overall, the physisorbed portion of As represents the lowest concentrations of the total extractable As (Table 4.6). Extractable fractions of Mn, Fe, Al range from 0.031 to 21.4%, 0.09 to 0.20%, and 0.07 to 0.48%, respectively.

Fraction 2. Concentrations of total extractable chemisorbed (inner sphere surface complexed) As range from 0.42 to 348 nmol kg<sup>-1</sup> (Table 4.5). The chemisorbed As fraction also accounts for relatively low proportions of the total extractable As in Aquia sediments albeit, greater than the physisorbed fractions. For example, in sediments from depths of 57, 65, 97, and 104 m, the chemisorbed fraction of As accounts for 7.44, 17.3, 10.4, and 14.1% of the total extractable As, respectively (Table 4.6). Extractable Mn, Fe, and Al fractions range from 0.83 to 2.80%, 0.03 to 0.93%, 0.04 to 1.95%, respectively.

Fraction 3. Concentrations of total extractable non-labile As associated with amorphous and/or poorly crystallized oxides of Fe (e.g., ferrihydrite; Fuller et al., 1993), Mn and/or Al range from 343 to 473 nmol kg<sup>-1</sup> (Table 4.5). The fraction of As associated

with amorphous and/or poorly crystalline oxides of Fe, Mn, and/or Al accounts for a substantial portion of the extracted As in Aquia sediments. For example, in sediment samples from depths of 57, 65, 97, and 104 m, extractable fractions of As account for 23.9, 17.2, 39.7, and 35.2% of the total extractable As, respectively (Table 4.6). Manganese, Fe and Al fractions range from 40.1 to 85.0%, 5.53 to 63.4%, and 11 to 23.1%, respectively.

Fraction 4. The concentrations of total extractable As bound to well crystallized oxide/oxyhydroxides of Fe (e.g., hematite, magnetite, lepidocrocite; Ford et al., 1997; Dixit and Hering, 2003; Pedersen et al., 2006), Mn (e.g., birnessite, cryptomelane; Deschamps et al., 2005) and Al oxides (e.g., Gibbsite; Ladeira et al., 2001) with Aquia sediments range from 217 to 978 nmol kg<sup>-1</sup> (Table 4.5). The fractions of extractable As are 45.7, 48.6, 21.7, and 22.3% in sediment samples collected at depths of 57, 65, 97, and 104 m, respectively (Table 4.6). Overall, the non-labile As bound to crystallized Fe and Mn oxides represent the major fraction of the total extractable As. Extracted fractions of Mn, Fe and Al range from 3.11 to 15.4%, 13.8 to 45.6%, and 12.0 to 19.5%, respectively.

Fraction 5: Concentrations of total extractable As in the residual phase range from 271 to 415 nmol kg<sup>-1</sup> (Table 4.5). Fractions of extractable As at depths of 57, 65, 97, and 104 m are 21.0, 15.4, 27.8, 27.8 %, respectively (Table 4.6). Extracted fractions of Mn, Fe, and Al range from 2.17 to 23.5%, 21.6 to 64.7%, and 55.7 to 71.1%, respectively.

Table 4.5 Concentrations of extractable As, and Mn, Fe and Al in sediment samples collected from the Aquia aquifer.

Sample Depth (m)	Element	Unit	F1	F2	F3	F4	F5	Total (F1-F5)
57	As	nmol kg <sup>-1</sup>	36.8	147	473	903	415	1975
	Mn	μmol kg <sup>-1</sup>	43.9	7.33	446	16.3	11.4	524
	Fe	μmol kg <sup>-1</sup>	8.75	53.1	1483	3589	2744	7878
	Al	μmol kg <sup>-1</sup>	8.35	23.8	465	393	1121	2011
65	As	nmol kg <sup>-1</sup>	30.9	348	346	978	309	2012
	Mn	μmol kg <sup>-1</sup>	3.25	0.42	6.11	1.86	3.58	15.2
	Fe	μmol kg <sup>-1</sup>	7.78	20.9	293	1548	3432	5302
	Al	μmol kg <sup>-1</sup>	19.1	32.4	446	484	3013	3995
97	As	nmol kg <sup>-1</sup>	5.91	117	448	245	314	1130
	Mn	μmol kg <sup>-1</sup>	0.68	0.64	21.0	2.70	7.15	32.2
	Fe	μmol kg <sup>-1</sup>	55.6	260	17659	3849	6018	27842
	Al	μmol kg <sup>-1</sup>	3.28	57.5	583	371	1927	2942
104	As	nmol kg <sup>-1</sup>	5.42	137	343	217	271	973
	Mn	μmol kg <sup>-1</sup>	0.18	0.48	39.6	8.95	8.84	58.1
	Fe	μmol kg <sup>-1</sup>	21.4	5.85	12729	3269	6899	22924
	Al	μmol kg <sup>-1</sup>	2.06	1.29	557	314	2152	3027

Table 4.6 Fraction of As and some major elements in Aquia sediments.

Sample Depth (m)	% Element	F1	F2	F3	F4	F5
57	% As	1.86	7.44	23.9	45.7	21.0
	% Mn	8.37	1.40	85.0	3.11	2.17
	% Fe	0.11	0.67	18.8	45.6	34.8
	% Al	0.42	1.18	23.1	19.5	55.7
65	% As	1.54	17.3	17.2	48.6	15.4
	% Mn	21.4	2.8	40.1	12.2	23.5
	% Fe	0.15	0.39	5.53	29.2	64.7
	% Al	0.48	0.81	11.0	12.0	75.0
97	% As	0.52	10.4	39.7	21.7	27.8
	% Mn	2.11	1.99	65.3	8.39	22.2
	% Fe	0.20	0.93	63.4	13.8	21.6
	% Al	0.11	1.95	19.8	12.6	65.5
104	% As	0.56	14.1	35.2	22.3	27.8
	% Mn	0.31	0.83	68.2	15.4	15.2
	% Fe	0.09	0.03	55.5	14.3	30.1
	% Al	0.07	0.04	18.4	10.4	71.1



## 4.5. Discussion

### *4.5.1 Controls on redox in Aquia groundwaters*

Aquia aquifer groundwaters are characterized by increasing pH and alkalinity with flow down-gradient along the flow path (Fig. 4.2), which are in agreement with previous studies that attribute the geochemical evolution of Aquia aquifer groundwaters to chemical weathering of glauconite and dissolution of shell materials along flow paths (Wolff 1967; Chapelle and Knobel, 1983; Chapelle, 1983). Glauconite is an Fe-rich, mixed-layer aluminous illite-smectite clay mineral, although commonly composed almost entirely of illite layers, and is analogous to end-member illite-smectite clays both chemically as well as structurally (Thompson and Hower, 1975). Weathering reactions involving glauconite consume protons, form goethite and authigenic kaolinite as secondary phases, and lead to increasing pH values along flow paths (Wolff, 1967). It is possible that the predominance of illite within Aquia sediments as indicated by the XRD studies (Fig. 4.5) reflects the presence of glauconite within the Aquia, or alternatively, the illitization of authigenic kaolinite produced by the breakdown of glauconite (Chermak and Rimstidt, 1990; Huang, 1993). The observed increase in alkalinity with flow down-gradient along the flow path is attributed to chemical weathering reactions and the dissolution of shell fragments that occur within the Aquia aquifer sediments (Chapelle, 1983).

Previous investigations also demonstrated that the chemical composition of Aquia groundwaters change systematically with flow down-gradient. For example, in their study of a relatively larger flow path on Maryland's western shore, Chapelle and Knobel (1983)

reported that Aquia groundwaters were of the Ca-Mg-HCO<sub>3</sub> type for the first ~42 km of the flow path. With flow beyond 42 km, Aquia groundwaters became progressively lower in Ca and Mg, and higher in Na concentrations, but exhibited relatively little change in HCO<sub>3</sub> concentrations (Chapelle and Knobel, 1983; Purdy et al., 1996). Approximately 80 km from the recharge area, the groundwaters had evolved to Na-HCO<sub>3</sub> type waters (Chapelle and Knobel, 1983, 1985; Purdy et al., 1996). The evolution of Aquia groundwaters along the flow path in south Maryland studied by Chapelle and Knobel (1983; 1985) is consistent with cation exchange of Ca and Mg for Na, dissolution of carbonate shells and subsequent precipitation of secondary calcite near the recharge zone, as well as carbonate mineral dissolution further down-gradient in the aquifer. Similar conclusions concerning the geochemical evolution of Aquia groundwaters were advanced for this or adjacent flow paths on Maryland's western shore (Chapelle, 1983; Chapelle and Knobel, 1983, 1985; Purdy, 1991; Purdy et al., 1992, 1996). The overall increasing trend in our pH, alkalinity and specific conductance values with flow down-gradient along our studied flow path support, in a general sense, the findings of these previous investigators.

Concentrations of dissolved oxygen in the Aquia groundwaters from Maryland's eastern shore indicate that these waters are generally suboxic ( $1 \mu\text{mol kg}^{-1} \leq \text{O}_2 < 30 \mu\text{mol kg}^{-1}$ ; Berner, 1981; Anderson et al., 1994), although oxic conditions ( $\text{O}_2 > 30 \mu\text{mol kg}^{-1}$ ) are observed in wells KE 66-0125 (~22 km) and QA 95-0611 (~50 km). None of the wells sampled in the Aquia aquifer produced anoxic/sulfidic waters (i.e.,  $\text{S}^{2-} > 1 \mu\text{mol kg}^{-1}$ ; Berner, 1981), thus setting the Aquia aquifer apart from groundwaters of the Carrizo

(Texas) and Upper Floridan (Florida) aquifers, which attain anoxic/sulfidic conditions and for which we previously investigated the As geochemistry (Haque and Johannesson, 2006a, b). Measurements of Eh are highly variable in the Aquia groundwaters, but in general exhibit relatively higher values (mean Eh = 35 mV) proximal to the recharge area compared to groundwaters further down-gradient (i.e., beyond ~34 km; Fig. 4.3). Overall, the measured Eh values are consistent with suboxic conditions along the majority of the Aquia aquifer flow path studied. It is important to stress, however, that measurements of Eh should only be viewed as qualitative indicators of the overall redox conditions (Whitfield, 1974; Lindberg and Runnels, 1984). Lindberg and Runnels (1984), for example, report that Eh measurements made with platinum (Pt) electrodes are commonly not consistent with Eh values calculated using the Nerst equation. The disagreement between calculated (i.e., equilibrium) Eh values and those determined by measurement using a Pt electrode can arise from a number of factors including misbehavior of the electrode resulting from, for example, sulfide deposition on the surface in sulfidic waters, the slow or irreversible kinetics affecting many redox couples in natural waters (i.e., disequilibrium), and the likelihood of mixed potentials in these environments (e.g., Langmiur, 1997).

The suboxic groundwaters of the Aquia aquifer are further characterized by relatively high  $\text{NH}_4^+$  concentrations and low, but measurable, concentrations of  $\text{NO}_3^-$  (Fig. 4.3). The depletion of  $\text{NO}_3^-$  and accumulation of  $\text{NH}_4^+$  along the flow path indicates that post dissimilatory  $\text{NO}_3^-$  reducing conditions exist in groundwaters of Aquia (Burdige, 2006). Furthermore, the concentrations and speciation of Fe in these groundwaters

suggest that Fe(III) reduction is an important process in the Aquia aquifer. For example, at 34 km down-gradient along the flow path, the high  $Fe_T$  concentration along with significant soluble Fe(II) concentration ( $> 43.5\%$  of  $Fe_T$ ), indicate initiation of Fe(III) reduction at this location in the aquifer (Fig. 4.3). Moreover, at 52 km down-gradient along the flow path, the pronounced transition in Fe speciation, which shifts from predominantly Fe(III) to soluble Fe(II), is consistent with redox conditions being buffered by Fe(III) reduction for the remainder of the studied flow path. Given the suboxic nature of these groundwaters, it is possible that Fe(III) reducing microbes such as (e.g., *Geobacter sp.* and *Shewanella putrifaciens*) may be active, utilizing Fe(III) oxides as an electron acceptor to oxidize organic matter (e.g., Lovley et al., 1990; Lovley et al. 1991; Cummings et al., 1999). Studies on the biochemistry of dissimilatory Fe(III) reduction have focused on members of the genera *Shewanella* and *Geobacter*, which release soluble Fe(II) as a metabolic product (Lovley et al. 1991; Cummings et al., 1999). Members of the genus *Geobacter* have been recovered from a variety of sedimentary environments in which Fe(III) reduction is a dominant electron accepting process (Lovley et al., 1990), and their presence in the Aquia aquifer could explain the Fe speciation data shown in Fig. 4.3. Lignite which is common in the Aquia aquifer sediments (Chapelle, 1983) may act as electron donor and carbon source for microbial processes in the deep subsurface as can dissolved organic carbon (Chapelle et al., 1987; Chapelle and Lovley, 1990; Detmers et al., 1991).

With flow beyond 34 km, and as reductive dissolution of Fe(III) proceeds, catalytic action (i.e., electron transfer) of soluble Fe(II) may induce recrystallization of

the remaining solid Fe oxides, such as ferrihydrite and goethite, to more crystalline, and hence, more thermodynamically stable Fe(III) oxides, such as hematite and lepidocrocite, as well as mixed Fe(II/III) minerals, such as magnetite, siderite or vivianite (Zachara et al., 2002; Horneman et al., 2004; Liu, 2005; Pedersen et al., 2005). The XRD analysis of the Aquia sediments confirms the presence of goethite and hematite within aquifer sediments, but cannot detect amorphous Fe(III) oxide/oxyhydroxides (Fig. 4.5). A number of factors, such as pH, temperature, time and microbial activity control the rate of transformation of amorphous Fe oxides and the nature of the newly formed products (Baltpurvins et al., 1996; Roden and Urrutia, 2002; Hansen et al., 2005; Pedersen et al., 2006). For example, the transformation rate to goethite and/or hematite increases with increasing pH and temperature (Cornell and Schwertmann 1996; Makris et al., 2005; Baltpurvins et al., 1996). The production of hematite is favored at pH values of 7 to 8 (i.e., point of zero charge of ferrihydrite), whereas formation of goethite is favored at pH values between 4 and 12 (Baltpurvins et al., 1996). Roden and Zachara (1996) report that rates of microbial Fe(III) reduction are highest with amorphous Fe(III) phases, and decrease with increasing crystallinity of newly formed minerals.

#### *4.5.2 Assessing mobilization of arsenic from sequential extraction results*

Total As concentrations in the analyzed Aquia aquifer sediments range from 973 to 2012 nmol kg<sup>-1</sup> (mean As = 1523 nmol kg<sup>-1</sup> or 0.11 ppm), which is, on average 94% lower than the average crustal abundance of As (~24.03 μmol kg<sup>-1</sup> or 1.8 ppm; Table 4.4; Hering and Kneebone, 2002). Despite what appears to be relatively low As concentrations in these aquifer sediments, Hering and Kneebone (2002) report that only a

minor fraction (0.09%) of the total As from soils with porosity of 0.3 and an As concentrations near crustal abundance (i.e., 1.8 ppm) is necessary to produce dissolved As concentrations that exceed the drinking water MCL of 133 nmol kg<sup>-1</sup>. Consequently, although total As concentration measured in Aquia aquifer sediments are generally below average crustal values, following the arguments of Hering and Kneebone (2002), it is estimated that release of only 1.2% of the average Aquia aquifer As concentration is necessary to produce a groundwater As concentration of 1072 nmol kg<sup>-1</sup>, the highest As concentration measured in Aquia groundwaters (Table 4.4).

Arsenic is commonly associated with Fe(III) oxide/oxyhydroxides in aquifer sediments, either by co-precipitation which incorporates As into the mineral or amorphous phase structures (Tye et al., 2002; O'Day et al., 2004), or by adsorption onto surface sites (Fuller et al., 1993; Manning and Goldberg, 1996, 1997; Goldberg, 2002). Consequently, the geochemistry of As in groundwater flow systems is closely coupled to the biogeochemical cycling of Fe(III) oxide/oxyhydroxides (and to a lesser extent, Mn and Al oxide/oxyhydroxides) that are common to aquifer sediments (Moore et al., 1988; Lovley, 1991; Goldberg, 2002; Tani et al., 2004). Arsenate and As(III) bind to surface sites on Fe(III) oxide/oxyhydroxides by forming thermodynamically stable, inner sphere complexes, although specific surface coordination of these surface complexes is somewhat controversial (e.g., Pierce and Moore, 1982; Manceau, 1995; Manning et al., 1998; Waychunas et al., 1993; Sherman and Randall, 2003). For example, it is well established that both As(III; Manning et al., 1998), and As(V; Pierce and Moore, 1982; Sherman and Randall, 2003) adsorb onto Fe(III) oxide surfaces as binuclear, bidentate

complexes, although extended X-ray absorption fine structure (EXAFS) analyses indicate that for As(V), a bidentate corner sharing complex is energetically more favored over the hypothetical edge-sharing, bidentate complex (Sherman and Randall, 2003). The results of sequential extraction of Aquia sediments demonstrate that in Aquia aquifer sediment, the labile portion (i.e., surface exchangeable) of As represents a minor proportion of the total extractable As (Fig. 4.6). In comparison to physisorbed As (0.52 to 1.86% of total As), the chemisorbed As (7.44 to 17.3% of total As) represents a relatively larger proportion of the total extractable As (Table 4.6; Fig. 4.6). However, the amount of labile As is small relative to the total sediment As concentrations. Nonetheless, because As (III and V) adsorption/desorption reactions onto aquifer mineral surface sites are strongly influenced by pH (Goldberg, 2002; Dixit and Hering 2003), it is generally agreed that sorption reactions represent an important source/sink term for As in groundwater flow systems (Wenzel et al., 2001; Goldberg, 2002; Hamon et al., 2004). For example, anionic As(V) species strongly adsorb onto surfaces of Fe and Al oxide/oxyhydroxides at low pH values ( $3 \leq \text{pH} < 7$ ; Stumm and Morgan, 1996; Goldberg, 2002), but tend to desorb from these surface sites as pH rises above 7 to 8 (Pierce and Moore 1982; Goldberg, 2002; Dixit and Hering 2003). However, under environmentally relevant pH values ( $6 < \text{pH} < 8$ ), As(III), owing to its occurrence as uncharged and nondissociated arsenous acid, is generally regarded to be less surface reactive than As(V; Goldberg, 2002).

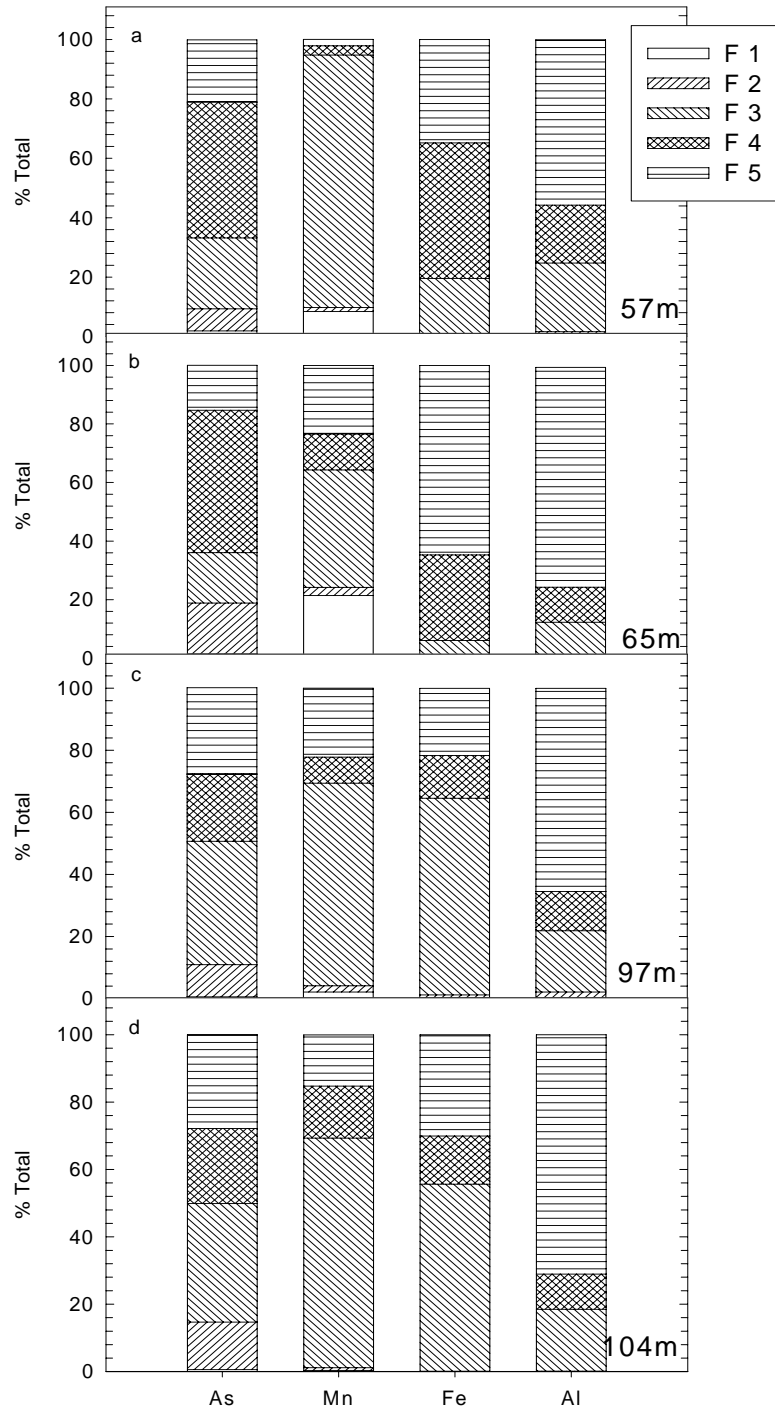


Figure 4.6: Fractionation of As, Mn, Fe, and Al in the Aquia sediments at (a) 57 m; (b) 65 m; (c) 97 m; (d) 104 m.



The sequential extraction data demonstrate that in Aquia sediments, the highest proportion of the total extractable As is present in non-labile forms, primarily associated with amorphous and crystalline Fe (Mn, Al) oxide/oxyhydroxides (Fig. 4.6). For example, in sediments collected from relatively shallower depths (57 and 65 m) within the Aquia aquifer sediment cores, the non-labile As bound to well crystallized Fe (Mn, Al) oxide/oxyhydroxides represents the largest pool of the total extractable As (~46% and 49% of  $As_T$ , respectively), whereas in the deeper sediments (97 and 104 m), the non-labile As (~40% and 35% of  $As_T$ , respectively) associated with amorphous or poorly crystallized Fe (Mn, Al) oxide/oxyhydroxides represent the highest portion of the total extractable As (Fig. 4.6). These results are consistent with previous studies that demonstrate that Fe(III) oxide/oxyhydroxides are important hosts of non-labile forms of As (e.g., Tye et al., 2002; Dixit and Hering, 2003; De Brouwere et al., 2004). For example, De Brouwere et al. (2004) found that in 27 metal contaminated soils, only a minor fraction (1.2-19.5%) of the total As was labile, whereas the remaining As was contained within the mineral structure of Fe and Al oxides. Tye et al. (2002) observed a similar finding in artificially contaminated soils, where the labile forms of As accounted for 25% of the total solid phase As, and the non-labile As was apparently incorporated within Fe oxide minerals.

Hence, although changing pH can potentially mobilize sorbed (i.e., labile) As species, mineral dissolution reactions are required to mobilize the non-labile fraction. Dissolution of Fe oxides can be achieved in especially acidic waters (e.g., pH <3; Bowers and Higgs, 1987), however in neutral to alkaline waters such as those of the Aquia

aquifer, lowering of the redox condition is necessary to dissolve these minerals, and release non-labile As to groundwaters. Specifically, microbially mediated redox induced reductive dissolution of minerals hosting As, such as Fe(III) oxide/oxyhydroxides can release non-labile As into solution (Pierce and Moore, 1982; Lovley et al., 1991; Lovley and Coates, 1997; Hamon et al., 2002; Kneebone et al., 2002; Dixit and Hering, 2003). Numerous studies of the Bengal Delta aquifers hypothesize that As incorporated within Fe(III) oxide/oxyhydroxides coatings on weathered alluvial sediments that undergo microbially mediated reductive dissolution is the primary source of As to these groundwaters (Nickson et al. 1998, 2000; Acharyya 2002; McArthur et al. 2004).

Finally, between 15 and 28% of the total As content of the Aquia aquifer sediments is residual, occurring in aluminosilicates (clay minerals), and chiefly in other chemically resistant minerals (e.g., quartz; Fig. 4.6). These minerals are relatively stable compared to pH and redox sensitive Fe (Mn, Al) oxide/oxyhydroxides, and therefore are not expected to be sources of As to Aquia groundwaters.

#### *4.5.3 Hydrogeochemical controls on arsenic distribution in Aquia groundwaters*

The distribution pattern of As in Aquia groundwaters reveals four distinct features: (i) proximal to the recharge area (<36 km), As concentrations remain relatively low (mean  $As_T = 98.9 \text{ nmol kg}^{-1}$ ); (ii) along mid-reaches of the flow path (36-71 km), As concentrations (mean  $As_T = 412 \text{ nmol kg}^{-1}$ ) are substantially higher than the current US EPA's MCL ( $133 \text{ nmol kg}^{-1}$ ) for drinking water; (iii) with flow beyond 71 km, As concentrations (mean  $As_T = 52.1 \text{ nmol kg}^{-1}$ ) decrease and remain low for the remainder of the flow path; and (iv) the more toxic and more mobile As(III) species is the dominant

form of As along the entire flow path (Fig. 4.3). The observed changes in As concentrations along the studied flow path are consistent with control by pH and localized change in redox conditions, i.e., from oxic or suboxic to more reducing (Fig. 4.2 and 4.3). For example, in the neutral pH (~7.7) upgradient groundwaters from near the recharge zone relatively low As concentrations likely result from adsorption of As (e.g.,  $\text{H}_2\text{AsO}_4^-$ ) onto positively charged surface sites of Fe oxide/oxyhydroxides, clay minerals and/or organic matter (Dzombak and Morel, 1990; Fuller et al., 1993; Manning and Goldberg, 1996; 1997; Goldberg, 2002). The maximum adsorption of labile As(III) to Fe oxide/oxyhydroxides and clay minerals occurs at pH 8 to 9, whereas for As(V), maximum adsorption to these minerals occurs at lower pH (i.e., pH ~5 for clays and ~7 for Fe oxides; Stumm and Morgan, 1996; Goldberg, 2002). Petrographic and XRD analyses of the Aquia sediments indicate the presence of various clay minerals (e.g., illite, smectite), Fe(III) oxide/oxyhydroxides (e.g., goethite, hematite) coated quartz, and glauconite within the sediments (Fig. 4.4 and 4.5). Because both As(V) and As(III) are expected to sorb to aquifer mineral surface sites at these pH values (~7.7; Dzombak and Morel, 1990; Manning et al., 1998; Goldberg, 2002), the relatively low As concentrations of Aquia groundwater from near the recharge area likely reflect adsorption/desorption reactions involving surface exchangeable (i.e., labile) As species. Moreover, as our sequential extraction data indicate that the labile fraction of As constitutes a relatively low proportion of the total extractable portion of As within Aquia aquifer sediments (Table 4.5, 4.6; Fig. 4.6), especially high As concentrations in Aquia groundwaters are

not expected to result from desorption reactions of surface complexed As species in this region of the aquifer.

Along mid-reaches (36-71 km) of the flow path, Aquia groundwaters exhibit As concentrations that exceed the current US EPA's MCL by as much as a factor of 8 (Fig. 4.3). The elevated levels of As in the Aquia groundwaters follow the onset of reductive dissolution of Fe oxide/oxyhydroxides in the Aquia as demonstrated by the correspondence in the change of Fe speciation from dominantly Fe(III) where As is low, to Fe(II) where As concentrations increase dramatically. These observations for the Aquia are in general agreement with previous investigations that demonstrate strong relationship between As and Fe (e.g., Cummings et al., 1999; McArthur et al., 2001; Smedley and Kinniburgh, 2002; Islam et al., 2004). More specifically, as reductive dissolution of Fe oxide/oxyhydroxides is initiated, adsorbed (i.e., labile) As is released due to decrease in surface area (Pedersen et al., 2006). However, as reductive dissolution of Fe(III) oxide/oxyhydroxides progresses, As incorporated (e.g., by co-precipitation) in these mineral (or amorphous) phases is also released into the groundwater along with Fe(II). The increase in dissolved As concentrations at essentially the same location along the flow path where Fe(II) becomes the chief form of Fe in Aquia groundwaters strongly suggests that the main source of the As in the groundwaters is the non-labile pool incorporated within Fe(III) oxide/oxyhydroxides and not the result of desorption of surface exchangeable (i.e., labile) As from mineral surface sites. Similar observations are reported for As mobilization from sediments collected from a reservoir in central California (Kneebone et al., 2002; Dixit and Hering, 2003). Furthermore, the sequential

extraction results for Aquia aquifer sediments indicate that the majority of As in these sediments is non-labile As incorporated within Fe (Mn, Al) oxide/oxyhydroxides (Table 4.5, 4.6; Fig. 4.6).

A number of studies demonstrate that dissolved Fe(II) catalyzes the transformation of amorphous Fe(III) oxides to more crystalline, and hence more thermodynamically stable Fe(III) oxides (Cornell and Schwertmann, 1996; Zachara et al., 2002), as well as mixed Fe(II/III) oxide minerals (Hansen et al., 2005; Pedersen et al., 2006). Consequently, re-adsorption of reductively dissolved Fe(II) onto Fe(III) oxide/oxyhydroxides within Aquia aquifer sediments is expected to promote stabilization and transformation of initially amorphous or poorly crystalline Fe oxide/oxyhydroxides to more crystalline Fe(III) oxides (e.g., hematite), and may also lead to the formation of mixed Fe(II/III) oxides (e.g., magnetite). Although various Fe(III) oxide/oxyhydroxides (hydrated ferric oxide, goethite) and mixed Fe(II/III) oxides, such as magnetite all have similar sorption affinity for As species, the surface area of Fe oxide/oxyhydroxides decreases dramatically as the crystallinity increases (Dixit and Hering, 2003; Horneman et al., 2004; van Geen et al., 2004). For example, the surface area for hydrated Fe(III) oxide, goethite, and magnetite are reported to be on the order of 600, 54, and 90 m<sup>2</sup> g<sup>-1</sup>, respectively (Dzombak and Morel, 1990; Dixit and Hering, 2003). This translates to sorption densities of 0.24 and 0.016 moles of As(V) per mole of Fe for hydrated Fe(III) oxide and goethite, respectively, and 0.31, 0.016, and 0.025 moles of As(III) per mole of Fe for hydrated Fe(III) oxide, goethite, and magnetite, respectively (Dixit and Hering, 2003). The decrease in surface area with increasing crystallinity leads to progressively

lower surface site densities available for As adsorption onto more crystalline Fe(III) oxides and mixed Fe(II/III) oxides compared to amorphous and poorly crystalline Fe(III) oxide/oxyhydroxides such as ferrihydrite (Dixit and Hering, 2003). Therefore, as poorly crystalline Fe(III) oxide/oxyhydroxides undergo reductive dissolution in the suboxic Aquia groundwaters releasing both Fe(II) and non-labile As to the groundwater, some of the released Fe(II) likely re-adsorbs onto and subsequently catalyzes the transformation of the remaining Fe(III) oxides to more crystalline forms and/or mixed Fe(II/III) oxides. Therefore, one explanation for the high As concentrations of Aquia groundwaters is that the As released during reductive dissolution of Fe(III) oxides within the sediments builds up in solution owing to the substantial decrease in the available surface complexation sites as the Fe oxides within the sediments become progressively more crystalline and/or form mixed Fe(II/III) oxides (Ford et al., 1997). Again, we stress that our sequential extraction studies show that the chief pool of As within the Aquia aquifer sediments is the non-labile fraction incorporated within Fe (Mn, Al) oxide/oxyhydroxides. It should be noted, however that as the released As is transported down gradient along the flow path, the data indicates that much of it is eventually re-adsorbed to aquifer mineral surface sites (Fig. 4.3). The observed decoupling of As and Fe (high As in conjunction with low Fe) in groundwaters at ~51 to 64 km along the flow path could reflect reprecipitation or readsorption of released Fe (II; Fig. 4.6; Horneman et al., 2004; van Geen et al., 2004). Such re-precipitation/readsorption was observed in laboratory and field studies of As mobilization from Bangladesh sediments (van Geen et al., 2004; Horneman et al., 2004). With further flow down-gradient (beyond 71 km), the decrease in As concentrations may

reflect incorporation of As into the crystalline lattice structures of secondary Fe oxide/oxyhydroxides (Ford, 2002).

Thermodynamics predict that As(V) should dominate under aerobic conditions (i.e., high Eh), whereas As(III) is the stable species for anaerobic conditions (i.e., low Eh; Ferguson and Gavis, 1972; Cherry et al., 1979; Cullen and Reimer, 1989; Saxena et al., 2004). However, disequilibrium between the dominant As species and prevailing in situ redox conditions is relatively common in natural waters, and has been attributed to the sluggish redox kinetics of the As(III)/As(V) couple and microbial processes (Ferguson and Gavis, 1972; Cutter, 1992; Ahmann et al., 1994; Wilkie and Hering, 1998; Cumming et al., 1999; Oremland and Stolz, 2005). Hence, the predominance of As(III) in the suboxic Aquia groundwater could reflect the release of co-precipitated As(III) by Fe reducing bacteria, such as *Geobacter sp.* or *Shewanella sp.* (Lovley et al. 1991; Cummings et al., 1999). In this case, As(III) would be the chief form of As in the non-labile pool [Fe(III) oxide/oxyhydroxides] within the Aquia aquifer sediments. Another possibility is that the specific microbes within the Aquia aquifer that respire by using Fe(III) as a terminal electron acceptor are also able to use As(V) as an electron acceptor (e.g., Oremland and Stolz, 2005). For example, organisms such as *Sulfurospirillum barnesii* Strain SES-3 and *Sulfurospirillum arsenophilum* can release both aqueous Fe(II) and As(III) by reducing Fe(III) and As(V) within the mineral substrate (Laverman et al., 1995; Ahmann et al., 1997; Zorbrist et al., 2000; Oremland and Stolz, 2005). In this case, As(V) would be the chief form of As in the non-labile pool of the Aquia aquifer sediments [i.e., co-precipitated within Fe(III) oxide/oxyhydroxides]. For this second

possibility, the in situ “Fe(III) reducing” microbial population in the Aquia aquifer would differ from that of the Carrizo aquifer in south Texas, where only As(V) is released to the groundwaters during reduction of Fe(III) oxides/oxyhydroxides (Haque and Johannesson, 2006b). Still another possibility is that there are distinct populations of Fe(III) reducing and As(V) reducing microbes that coexist within the Aquia aquifer. A number of recent studies have identified As(V) reducing microbes (Ahmann et al., 1994; Newman et al., 1998; Stolz and Oremland, 1999; Oremland and Stolz, 2003). Determining the speciation of As in the non-labile pool of As of the Aquia aquifer sediments (i.e., within the Fe(III) oxide/oxyhydroxides) and investigation of the in situ microbial consortia within the aquifer using genetic probes is planned to help ascertain the important processes occurring within the flow system that lead to the high dissolved As(III) concentrations in Aquia groundwaters.

#### 4.6. Conclusions

A series of groundwater samples collected along a flow path in Aquia aquifer, Maryland demonstrate that adsorbed/co-precipitated As responds readily to changes in groundwater chemistry and result in aqueous concentrations up to  $1072 \text{ nmol kg}^{-1}$ . Measurements of groundwater redox parameters, in particular, N and Fe species, dissolved  $\text{S}^{2-}$ , and dissolved oxygen concentrations and the oxidation-reduction potential, suggest that Aquia groundwaters are suboxic, and nonsulfidogenic. Sequential extraction analysis of Aquia aquifer sediments indicate that the average solid phase As concentration is 94% lower than the average crustal abundance of As, however results of our groundwater study indicate that dissolved As concentrations exceeding the EPA’s



current MCL of  $133 \text{ nmol kg}^{-1}$  are widespread along the flow path. Based on these results, we propose a working hypothesis for the occurrence of elevated As concentrations in Aquia aquifer. With flow beyond the recharge area, dissimilatory Fe(III) reduction driven by suboxic, non-sulfidogenic Aquia groundwaters release a substantial amount of As from the non-labile pool of As that is associated with amorphous and/or well crystallized Fe(III) oxide/oxyhydroxides, which comprise coatings on aquifer mineral surfaces (e.g., quartz, glauconite). As Fe(III) reduction proceeds along the flow path (>36 km), the released Fe(II) likely catalyzes recrystallization of amorphous Fe(III) oxide/oxyhydroxides into more thermodynamically stable and more crystalline Fe(III) oxides and/or mixed Fe(II/III) oxides. In turn, the newly formed minerals, owing to a substantial decrease in specific surface area, most likely contribute to further mobilization of As into the groundwaters. However, as the released As is transported further down gradient (51 to 64 km), the observed decoupling of As (high) and Fe (low) data indicates that much of the Fe(II) is eventually re-adsorbed onto sediment grain surfaces. At the end of the flow path (i.e., >71 km), elevated Fe concentrations in conjunction with low As concentrations suggest that along this section of the flow path, As is being co-precipitated/readsorbed with more crystalline structures of these newly formed Fe oxides. Along the entire flow path, the predominance of As(III) under suboxic conditions suggest the presence of microbial organisms that release adsorbed/co-precipitated As(III) by using Fe(III) and/or As(V) as terminal electron acceptor. Although currently we lack direct evidence of presence of such microbes in the

Aquia, preliminary assessment of the dissolved As concentrations and speciation data strongly suggests a microbial control on As cycling within the aquifer.

## CHAPTER 5

### CONCLUSIONS

This chapter summarizes the conclusions of this research work, and restates the key findings presented in the preceding chapters. The purpose of this research was to systematically examine and understand the biogeochemical mechanisms that control natural “evolution” of As in groundwater systems. To set up a foundation and to develop directions for the research work, an extensive literature review was conducted and, based upon the findings of the reviews, a systematic approach was taken to develop the methodology for my doctoral research project. The central hypothesis was that physico-chemical changes occurring along groundwater flow paths within aquifers that accompany chemical weathering and oxidation-reduction reactions facilitated by the in situ microbial consortium (e.g., Fe reducers, SO<sub>4</sub> reducers), catalyze both As mobilization from, and capture by, mineral/amorphous phases via adsorption/desorption reactions and/or mineral dissolution. To address this hypothesis, it was determined that this research would first focus on understanding the geochemical behavior of As along groundwater flow paths in well characterized aquifers with particular emphasis on quantifying As concentrations and speciation [As(III) and As(V)] in groundwater samples. Groundwater samples were collected along groundwater flow paths in three well

characterized aquifers: Carrizo (Texas), Upper Floridan (Florida) and Aquia (Maryland) aquifers. Results of the groundwater studies indicated that dissolved As concentrations in Carrizo and Upper Floridan aquifers remain low ( $<19 \text{ nmol kg}^{-1}$  or 1.4 ppb) and well below the US Environmental Protection Agency's maximum contaminant level (MCL) for As in drinking water of  $133 \text{ nmol kg}^{-1}$  (10 ppb), whereas in the Aquia aquifer, groundwater As concentrations were not only found to be elevated (mean  $274 \text{ nmol kg}^{-1}$ ) but also exceeded the drinking water MCL, by as much as a factor of 8. Another notable feature of the Aquia groundwater study was that all the wells sampled within the Aquia produced suboxic groundwaters ( $\text{S}^{2-} < 1 \text{ } \mu\text{mol kg}^{-1}$ ), therefore setting the Aquia aquifer apart from groundwaters of the Carrizo and Upper Floridan aquifers that reach anoxic/sulfidic conditions. The next part of the investigation focused on determining whether changes in aqueous concentrations and speciation of As reflect adsorption/desorption reactions with mineral surface exchange sites versus As originating from the non-labile pool due to varying pH and/or redox conditions along flow. To address this issue of lability, I chose to further investigate the Aquia aquifer and sediment samples collected from within the Aquia were examined petrographically and by X-Ray diffraction, and subsequently subjected to a sequential extraction scheme. From these investigations the following conclusions were drawn:

(i) The results of the Carrizo Sand groundwater study demonstrate that concentrations and speciation of As exhibit systematic changes along the flow path that correspond to changes in dissolved Fe(II) and Fe(III) concentrations, dissolved  $\text{S}^{2-}$  concentrations, pH, and alkalinity. Furthermore, the data suggest that dissimilatory

reduction of Fe(III) oxide/oxyhydroxides and subsequent release of Fe(II) along with adsorbed and/or coprecipitated As(V) is inferred to control As(V) concentrations within the initial groundwaters (<15 km), followed by rapid readsorption of As(V) onto Fe oxides/oxyhydroxide minerals in the mid-reaches of the aquifer. Further down-gradient (>41 km), the increase in As(V) concentrations could be due to pH related desorption as pH increases to 8.5.

(ii) The UFA groundwater study revealed that total As concentrations are higher in the recharge area groundwaters compared to down-gradient portions (i.e., confined) of the flow path. Mobilization of As species in UFA groundwaters is influenced by dissimilatory Fe(III) reduction and subsequent dissolution, SO<sub>4</sub> reduction, and probable pyrite precipitation that are inferred from the data to occur along distinct regions of the flow-path. In general, the distribution of As species are consistent with equilibrium thermodynamics, such that As(V) dominates in more oxidizing waters near the recharge area, and As(III) predominates in the progressively reducing groundwaters beyond the recharge area.

(iii) The Aquia aquifer study found that the highest dissolved As concentrations are attained where the predominant form of Fe in the groundwater changes from Fe(III) to Fe(II). With flow beyond the recharge area, the observed spike in As concentration is associated with dissimilatory Fe(III) reduction, which liberates As from the non-labile pool of As. The data further indicate that along mid reaches of the flow path, soluble Fe(II) likely contributes to recrystallization of amorphous Fe(III) oxide/oxyhydroxides into more crystalline Fe(III) oxides and/or mixed Fe(II/III) oxides.

The newly formed minerals, owing to a substantial decrease in surface site density, likely contribute to further mobilization of As into the groundwaters. Between 51 to 64 km, the observed decoupling of As (high) and Fe (low) data demonstrate that Fe(II) is subsequently re-adsorbed to Fe oxide/oxyhydroxides and/or mixed Fe(II/III) minerals. With flow beyond 64 km, the high Fe concentrations in conjunction with the low As concentrations suggest that As is being co-precipitated/re-adsorbed with more crystalline structures of the newly formed Fe oxide minerals. The predominance of As(III) in the suboxic groundwaters of Aquia is most likely due to presence of respiratory microbial consortia that are capable of releasing adsorbed/co-precipitated As by utilizing Fe(III) and/or As(V) as terminal electron acceptor.

Based on the abovementioned research findings, following are the major conclusions drawn regarding biogeochemical mechanisms that govern natural “evolution” of As in groundwater flow systems:

(i) In the deep subsurfaces, the major processes influencing concentrations, speciation and mobility of As are pH and/or redox driven mineral dissolution/precipitation, and adsorption/desorption reactions.

(ii) Mobilization of As depends on the type of Fe oxides present within the aquifer substrate (i.e., well crystalline vs. less or poorly crystalline oxide/oxyhydroxides of Fe). More specifically, the decrease in surface area with increasing crystallinity leads to progressively lower surface site densities available for As adsorption onto more crystalline Fe oxides compared to poorly crystalline Fe oxide/oxyhydroxides. Therefore, aquifers with more crystalline Fe(III) oxides and/or mixed Fe(II/III) oxides can develop

high dissolved As concentrations, and aquifers dominated by poorly crystalline Fe(III) oxy-hydroxides are less likely to exhibit elevated As concentrations.

(iii) The in situ microbial consortium plays a crucial role in the “evolution” of speciation of As in these groundwaters. The form of As released [i.e., As(III) vs. As(V)] largely depends on respiratory microbial consortia present within the aquifer (i.e., Fe(III) reducing bacteria, dissimilatory As(V) reducing prokaryotes (DARPs) and Fe(III) reducing DARPs).

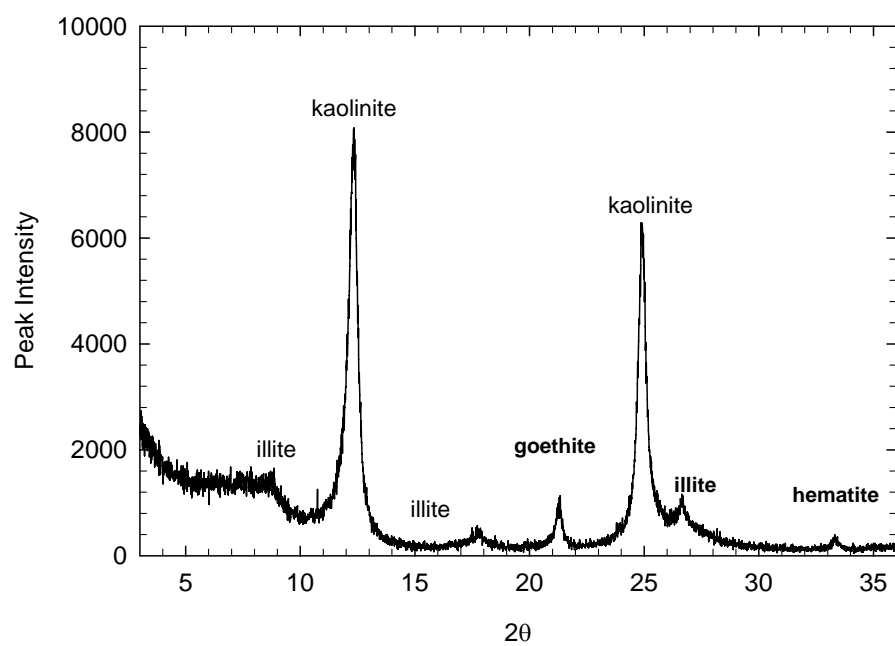
The key findings of this dissertation research were more compelling and complex than anticipated at the beginning of the project. For this reason, it would be valuable to further extend the research described herein. In particular, given the importance of microbial metabolism on As mobilization, follow on research of the in situ microbial consortium of the Aquia has already been undertaken by Dr Johannesson and her research team at The University of Texas at Arlington.

APPENDIX A

ANALYSES OF CARRIZO SAND SEDIMENTS



X-Ray diffraction diagram of Carrizo Sand sediments



Concentrations of extractable Al, and Mn, Fe and As in sediment samples collected from the Carrizo Sand aquifer.

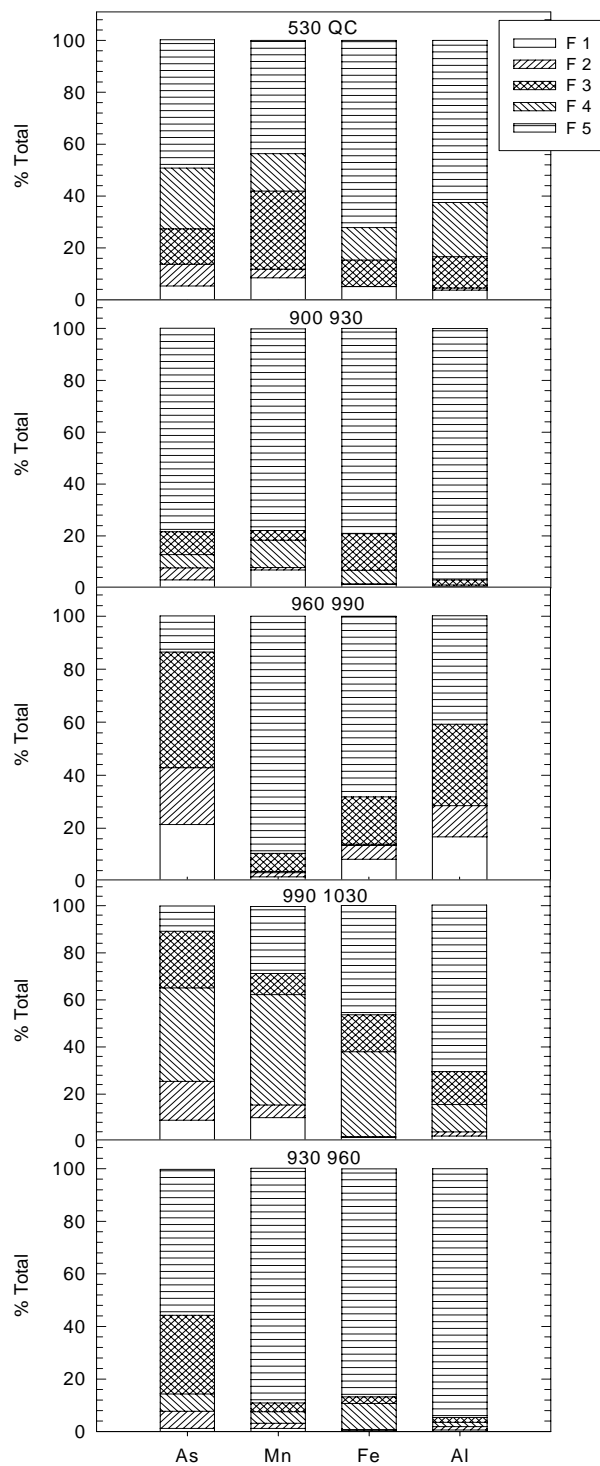
Sample	Fraction	Al	Mn	Fe	As
		$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\mu\text{mol kg}^{-1}$	$\text{nmol kg}^{-1}$
530 QC	F1	28.2	0.38	116	15.1
	F2	6.37	0.15	2.75	24.1
	F3	92.4	1.35	232	38.7
	F4	160	0.65	289	66.8
	F5	478	1.96	1658	141
	Sum	765	4.49	2297	285
900 930	F1	3.49	0.47	33.7	9.04
	F2	1.86	0.07	2.94	13.7
	F3	8.27	0.72	129	15.3
	F4	25.0	0.26	346	26.2
	F5	1232	5.34	1942	233
	Sum	1271	6.87	2453	297
960 990	F1	19.0	0.06	23.0	13.7
	F2	13.5	0.06	14.7	13.8
	F3	BDL	0.02	1.23	BDL
	F4	35.0	0.26	50.1	28.0
	F5	46.7	3.42	191	8.74
	Sum	114	3.82	280	64.2
990 1030	F1	3.55	0.28	10.1	10.7
	F2	2.89	0.15	1.29	20.0
	F3	19.0	1.32	221	48.0
	F4	23.0	0.25	96.1	29.2
	F5	116	0.80	284	12.9
	Sum	164	2.81	612	121
930 960	F1	3.03	0.06	5.66	1.31
	F2	5.99	0.09	5.70	7.30
	F3	7.67	0.21	143	7.29
	F4	8.30	0.16	36.2	33.2
	F5	443	4.26	1255	61.6
	Sum	468	4.77	1446	111

Fraction of As and some major elements in Carrizo Sand sediments.

Sample	Fraction	% Al	% Mn	% Fe	% As
530 QC	F1	3.69	8.46	5.05	5.3
	F2	0.83	3.34	0.12	8.46
	F3	12.1	30.1	10.1	13.6
	F4	20.9	14.5	12.6	23.4
	F5	62.5	43.7	72.2	49.5
900 930	F1	0.27	6.84	1.37	3.04
	F2	0.15	1.02	0.12	4.61
	F3	0.65	10.5	5.26	5.15
	F4	1.97	3.78	14.1	8.82
	F5	96.9	77.7	79.2	78.5
960 990	F1	16.7	1.57	8.21	21.3
	F2	11.8	1.57	5.25	21.5
	F3	0.00	0.52	0.44	0.00
	F4	30.7	6.81	17.9	43.6
	F5	41.0	89.5	68.2	13.6
990 1030	F1	2.16	9.96	1.65	8.84
	F2	1.76	5.34	0.21	16.5
	F3	11.6	47.0	36.1	39.7
	F4	14.0	8.9	15.7	24.1
	F5	70.7	28.5	46.4	10.7
930 960	F1	0.65	1.26	0.39	1.18
	F2	1.28	1.89	0.39	6.58
	F3	1.64	4.4	9.89	6.57
	F4	1.77	3.35	2.5	29.9
	F5	94.7	89.3	86.8	55.5

Fractionation of As, Mn, Fe, and Al in the Carrizo Sand sediments at well (a) 530

QC; (b) 900 930; (c) 960 990; (d) 990 1030; (e) 930 960:



APPENDIX B

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## REFERENCES

- Acharyya, S.K., Chakraborty, P., Lahiri, S., Raymahashay, B.C., Guha, S., Bhowmik, A., 1999. Arsenic poisoning in the Ganges delta. *Nature* 401, 545.
- Aeschbach-Hertig, W., Stute, M., Clark, M., Reuter, R.F., Schollosser, P., 2002. A Paleotemperature record derived from dissolved noble gases in groundwater of the Aquia aquifer (Maryland, USA). *Geochim. Cosmochim. Acta*, 66, 797-817.
- Ahmann D., Krumholz L.R., Hemond H.F., Lovley D.R., Morel F.M.M., 1997. Microbial mobilization of arsenic from sediments of the Aberjona watershed. *Environ. Sci. Technol.* 31, 2923-2930.
- Ahmann, D., Roberts, A.L., Krumholz, L.R., Morel, F.M.M., 1994. Microbe grows by reducing arsenic. *Nature* 371, 6500, 750.
- Akai, J., Izumi, K., Fukuhara, H., Masuda, H., Nakano, S., Yoshimura, T., Ohfuji, H., Anawar, H., Akai, K., 2004. Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. *Appl. Geochem.* 19, 215-230.
- Allard, H.X.B, Grimvall, A, 1988. Influence of pH and organic substance on the adsorption of As(V) on geological materials. *Water Air Soil Poll* 40, 293-305.
- Anderson, L.A, Bruland, K.W., 1991. Biogeochemistry of arsenic in natural waters: The importance of methylated species. *Environ. Sci. Technol.* 25, 420-427.

- Anderson, L.D., Kent, D.B., Davis, J.A., 1994. Batch experiments characterizing the reduction of Cr(VI) using suboxic material from a mildly reducing sand and gravel aquifer. *Environ. Sci. Technol.* 28, 178-185.
- Andreae, M.O., 1978. Distribution and speciation of arsenic species in natural waters and certain algae. *Deep-Sea Res.* 25, 391-402.
- Appelo, C.A.J., Van Der Weiden, M.J.J., Tournassat, C., Charlet, L., 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* 36, 3096-3103.
- Back, W., Barnes, I., 1965. Relation of electrochemical potentials and iron content to ground-water flow patterns. *U. S. Geol. Surv. Prof. Pap.* 498-C, pp. 16.
- Back, W., Hanshaw, B.B., 1970. Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. *J. Hydrol.* 10, 330-368.
- Balpurvins, K.A., Burns, R.C., Lawrance, G.A., 1996. Effect of pH and anion type on the aging of freshly precipitated iron(III) hydroxide sludges. *Environ. Sci. Technol.* 30, 939-944.
- Berner, R. A., 1970. Sedimentary pyrite formation. *Am. J. Sci.* 268, 1-23.
- Berner, R. A., 1981. A new geochemical classification of sedimentary environments. *J. Sed. Petrol.* 51, 359-365.
- Bostick, B.C., Fendorf, S. Manning, B.A., 2003. Arsenite adsorption on galena (PbS) and sphalerite (ZnS). *Geochim. Cosmochim. Acta.* 67, 895-907.

- Bostick, B.C., Fendorf, S., 2003. Arsenite sorption on troilite (FeS) and pyrite (Fe<sub>2</sub>S). *Geochim. Cosmochim. Acta.* 67, 909-921.
- Bowell, R.J., 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.* 9, 279-286.
- Bowers, A.R., Higgs, T.A., 1987. Influence of acidic environments on electrokinetic and adsorptive behavior of iron oxide rich soils. *Water Air Poll.* 32, 129-144.
- Branch, S., Ebdon, L., Ford, M., Foulkes, M., O'Neill, P., 1991. Determination of arsenic in samples with high chloride content by inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* 5, 151-154
- Burdige, D.J., 2006. *Geochemistry of marine sediments.* Princeton Univ. Press, New Jersey. pp. 105-107.
- Castro, M.C., Goblet, P., 2003. Calibration of regional groundwater flow models: working toward a better understanding of site-specific systems. *Water Resour. Res.* 39(6), 1172, doi:10.1029/2002WR001653, 2003.
- Castro, M.C., Stute, M., Schlosser, P., 2000. Comparison of 4 He ages and 14 C ages in simple aquifer systems: implications for groundwater flow and chronologies. *Appl. Geochem.* 15, 1137-1167.
- Chakraborti, D., Rahman, M.M., Paul, K., Chowdhury, U.K., Sengupt, M.K., Lodh, D., Chanda, C.R., Saha, K.C., Mukherjee, S.C., 2002. Arsenic calamity in the Indian subcontinent – What lessons have been learned? *Talanta* 58, 3-22.

- Champ, D.R., Oulens, J., Jackson, R.E., 1979. Oxidation-reduction sequences in groundwater flow systems. *Canadian J. Earth Sci.* 16, 12-23.
- Chapelle, F. H., Lovley D. R., 1990. Rates of bacterial metabolism in deep coastal-plain aquifers. *Appl. Environ. Microbiol.* 56, 1865-1874.
- Chapelle, F.H., McMahon P.B., 1991. Geochemistry of dissolved inorganic carbon in a coastal plain aquifer: 1. Sulfate from confining beds as an oxidant in microbial CO<sub>2</sub> production. *J. Hydrol.* 127, 85-108.
- Chapelle, F.H., Morris, J.T., McMahon, P.B., Zelibor, J.L., Jr., 1988. Bacterial metabolism and the  $\delta$ -13C composition of ground water, Floridan aquifer, South Carolina. *Geology* 16, 117-121.
- Chapelle, F.H., Zelibor, J.L., Grimes, D.J., Knobel, L.L., 1987. Bacteria in deep coastal plain sediments of Maryland: A possible source of CO<sub>2</sub> to ground water. *Water Resour. Res.* 23, 1625-1632.
- Chapelle, F.H., 1983. Ground-water geochemistry and calcite cementation of the Aquia aquifer in southern Maryland. *Water Resour. Res.* 19, 545-558.
- Chapelle, F.H., 2001. *Ground-water Microbiology and Geochemistry*. 2<sup>nd</sup> Edition, John Wiley & Sons, (New York), pp. 477.
- Chapelle, F.H., Knobel, L.L., 1983. Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia aquifer, Maryland. *Ground Water* 21, 343-352.

- Chapelle, F.H., Knobel, L.L., 1985. Stable carbon isotopes of bicarbonate in the Aquia aquifer, Maryland-evidence for an isotopically heavy source of carbon dioxide. *Ground Water* 23, 592-599.
- Chen, S-L., Dzung, S.R., Yang, M-H., Chiu, K-H. Shieh, G-M., Wai, C.M., 1994. Arsenic species in groundwaters of the blackfoot disease area, Taiwan. *Environ. Sci. Technol.* 28, 877-881.
- Chermak, J.A., Rimstidt, J.D., 1990. The hydrothermal transformation of kaolinite to muscovite/illite. *Geochim. Cosmochim. Acta.* 54, 2979-2990.
- Cherry, J.A., Shaik, A.U., Tallman, D.E., Nicholson, R.V., 1979. Arsenic species as an indicator of redox conditions in groundwater. *J. Hydrogeol.* 43, 373-392.
- Chowdhury, U.K., Biswas, B.K., Dhar, R.K., Samanta, G., Mandal, B.K., Chowdhury, T.R., 1999. Groundwater arsenic contamination and sufferings of people in Bangladesh. In: Chappell W.B., Abernathy C.O., Calderon R.L., (Eds.), *Arsenic Exposure and Health Effects*. Elsevier, Amsterdam, pp. 165-182.
- Cornell, R.M., Schwertmann, U., 1996. *The iron oxides: structure, properties, reactions, occurrence and uses*. Verlag VCH Verlagsgesellschaft, Weinheim, Germany.
- Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. *Chem. Rev.* 89, 713-764.
- Cummings, D.E., Caccavo, Jr., F., Fendorf, S., Rosenzweig, R.F., 1999. Arsenic Mobilization by the Dissimilatory Fe(III)-reducing bacterium *Shewanella* sp. BrY. *Environ. Sci. Technol.* 33, 723-729.

- Curtin, S.E., Andreaden, D.C., Wheeler, J.C., 2002. Potentiometric surface of the Aquia in southern Maryland. USGS Open-file Report 2003 255.
- Cutter, G.A., 1992. Kinetic controls on metalloid speciation in seawater. *Marine Chem.* 40, 65-80.
- Deschamps, E., Virginia S., Ciminelli, T., Höll, W.T., 2005. Removal of As(III) and As(V) from water using a natural Fe and Mn enriched sample. *Water Res.* 39, 5212-5220.
- Detmers, J., Schulte, U., Strauss, H., Kuever, J., 1991. Sulfate reduction at a lignite seam: microbial abundance and activity. *Microbiol. Ecol.* 42, 238-247.
- Dixit, S., Hering, J.G., 2003. Comparison of arsenic (V) and arsenic (III) sorption to iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37, 4182-4189.
- Dowdle, P.R., Laverman, A.M., Oremland, R.S., 1996. Bacterial dissimilatory reduction of arsenic (V) to arsenic (III) in anoxic sediments. *Appl. Environ. Microbiol.* 62, 1664–1669.
- Dowling, C.B., Poredo, R.J., Basu A.R., Peters S.L., 2002. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. *Water Resour. Res.* 38(9), 1173, Doi:10.1029/2001WR000968, 2002.
- Drever, J.I., 1997. *The Geochemistry of Natural Waters, Third Edition: Surface and Groundwater Environments.* Prentice-Hall, (Upper Saddle River, NJ), pp. 192-194.



- Drummond, D.D., 2001. Hydrogeology of the Coastal Plain Aquifer System in Queen Anne's and Talbot Counties, Maryland, with a Discussion of Brackish-Water Intrusion in the Aquia Aquifer. Maryland Geological Survey, Report of Investigations 72, USA.
- Dzombak, D.A., Morel, F.M.M., 1990. Surface complexation modeling--Hydrous ferric oxide. John Wiley & Sons (New York), pp. 54-58.
- Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (ed.), 1995a. Standard methods for the examination of water and wastewater. 3-67-68.
- Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (ed.), 1995b. Standard methods for the examination of water and wastewater. 4-122-123.
- Edmunds, W.M., Miles, D.L., Cook, J.M., 1984. A comparative study of sequential redox processes in three British aquifers. In: Eriksson E. (Ed.), Proceedings of Hydrochemical Balances of Freshwater Systems, Uppsala Symposium. IAHS Publication 150, pp. 55-70.
- Ferguson J.F., Gavis J., 1972. A review of the arsenic cycles in natural waters. Water Res. 6, 1259-1274.
- Ficklin, W.H., 1983. Separation of As(III) and As(V) in ground waters by ion exchange. Talanta 30, 371-373.
- Ford, R.G., 2002. Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. Environ. Sci. Technol. 36, 2459-2463.
- Ford, R.G., Bertsch, P.M., Seaman, J.C., 1997. Goethite morphologies investigated via x-ray diffraction of oriented samples. Clays Clay Mineral. 45, 769-772.

- Francesconi, K., Kuehnelt D., 2002. Arsenic compounds in the environment. In: W. T. Frankenberger, Jr. (ed.), Environmental Chemistry of Arsenic. Marcel Dekker (New York), pp. 52-93.
- Fuller, C.C., Davis, J.A., Waychunas, G.A., 1993. Surface chemistry of ferrihydrite: Part 2: Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* 57, 2271-2282.
- Gal, C., Wolfgang, F., Möller, J., 2004. Re-examination of the cadmium reduction method and optimisation of conditions for the determination of nitrate by flow injection analysis. *Microchim. Acta*. 146, 155-164.
- Gilbert, T.W., Behymer, T.D., Castaneda, H.B., 1982. Determination of dissolved oxygen in natural and wastewaters. *American Laboratory* 14, 119-134.
- Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Sci. Society of America J.* 66, 413-421.
- Goldberg, S., Glaubig, R.A., 1988. Anion sorption on a calcareous, montmorillonitic soil – arsenic. *Soil Sci. Society of America J.* 52, 1297-1300.
- Hach, 2004. The Handbook DR/2400 Portable Spectrophotometer Procedure. USA.
- Hamon, R.E., Lombi, E., Fortunati, P., Nolan, A.L., McLaughlin, M.J., 2004. Coupling speciation and isotope dilution techniques to study arsenic mobilization in the environment. *Environ. Sci. Technol.* 38, 1794-1798.
- Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability *in situ* remediation treatments. *Environ. Sci. Technol.* 36, 3991-3996.

- Hansen, H.J., 1974. Sedimentary facies of the Aquia formation in the subsurface of the Maryland Coastal Plain: Maryland Geological Survey Report of Investigations 21.
- Hansen, H.J., 1992. Stratigraphy of Upper Cretaceous and Tertiary sediments in a core-hole drilled near Chesterville, Kent County, Maryland. Maryland Geological Survey Open-file Report 93-02-7.
- Hanshaw, B.B., Back, W., Rubin, M., 1965. Radiocarbon determinations for estimating groundwater flow velocities in central Florida. *Science*. 148, 494-495.
- Haque, S., Johannesson, K.H., 2006a. Arsenic concentrations and speciation along a groundwater flow path: the Carrizo Sand aquifer, Texas, USA. *Chem. Geol.* 228, 57-71.
- Haque, S.E., Johannesson, K.H., 2006b. Concentrations and speciation of arsenic along a groundwater flow-path in the Upper Floridan aquifer, Florida, USA. *Environ. Geol.* 50, 219-228.
- Haque, S.E., Johannesson, K.H., 2006c. Speciation and distribution of arsenic in the Aquia aquifer, Maryland. *Geological Society of America Abstracts with Programs*, 38, 321.
- Harsh, J.F., Lacznik, R.J., 1990. Conceptualization and analysis of ground-water flow system in the Coastal Plain of Virginia and adjacent parts of Maryland and North Carolina. USGS Professional Paper 1404F, 100.

- Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Neidan, V., Brandander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science* 298, 1602-1606.
- Hering J., Kneebone P., 2002. Biogeochemical controls on arsenic in water. In: W. T. Frankenberger, Jr. (ed.), *Environmental Chemistry of Arsenic*. Marcel Dekker (New York), pp. 155-181.
- Horneman, A., van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Connell, S.M., Hoque, M.A., Aziz, Z., Shamsudduha, M., Seddique, A.A., Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions: Part I. Evidence from sediment profiles. *Geochim. Cosmochim. Acta* 68, 3459–3473.
- Huang, W-L., 1993. The formation of illitic clays from kaolinite in KOH solution from 225°C to 350°C. *Clay Clay Minerals* 41, 645-654.
- Hudak, P., 2000. Distribution and sources of arsenic in the southern high plains aquifer, Texas, USA. *J. Environ. Sci. Health*. 35, 899-913.
- Hudak, P., 2006. Spatial and temporal patterns of arsenic concentration in the High Plains Aquifer of Texas, USA. *International J. Environ. Studies*. 63, 201-299.
- Huerta-Diaz, M.A., Morse, J.W., 1992. Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Acta*. 56, 2681-2702.

- Islam, F., Gault, A., Boothman, C., Polya, D., Charnock, J., Chatterjee, D., Lyond, J. 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* 430, 68-71.
- Jain, C.K., Ali, I., 2000. Arsenic: occurrence, toxicity and speciation techniques. *Water Res.* 34, 4304- 4312.
- Jay, J.A., Blute, N.K., Hemond, H.F., Durant, J.L., 2004. Arsenic-sulfides confound anion exchange resin speciation of aqueous arsenic. *Water Res.* 38, 1155-1158.
- Johannesson, K.H., Hendry, M.J., 2000. Rare earth element geochemistry of groundwaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada, *Geochim. Cosmochim. Acta* 64, 1493-1509.
- Johannesson, K.H., Stetzenbach, K.J., Kreamer, D.K., Hodge, V.F., 1996. Multivariate statistical analysis of arsenic and selenium concentrations in groundwaters from south-central Nevada and Death Valley, California. *J. Hydrol.* 178, 181-204.
- Johannesson, K.H., Tang, J., Daniels, J.M., Bounds, W.J., and Burdige, D.J., 2004. Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA. *Chem. Geol.* 209, 271-294.
- Johnston, R.G., Krause, R.E., Meyer, F.W., Ryder, P.W., Tibbals, C.H., Hunn, J.D., 1980. Estimated potentiometric surface for the Tertiary limestone aquifer, southeastern United States, prior to development. *U.S. Geol. Surv. Open-file Rep.* 80-406.
- Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method. *Environ. Sci. Technol.* 35, 2778-2784.

- Kirk, M.F., Holm, T.R., Park, J., Jin, Q., Sanford, R.A., Fouke, B.W., Bethke, C.M., 2004. Bacterial sulfate reduction limits natural arsenic contamination in groundwater. *Geology*. 32, 953-956.
- Klaue, B., Blum, J.D., 1999. Trace analyses of arsenic in drinking water by inductively coupled plasma mass spectrometry: high resolution versus hydride generation. *Anal. Chem.* 71, 1408-1414.
- Kneebone, P.E., O'Day, P.A., Jones, N., Hering, J.G., 2002. Deposition and fate of arsenic in iron and arsenic enriched reservoir sediments. *Environ. Sci. Technol.* 36, 381-386.
- Krom, M.D., 1980. Spectrophotometric Determination of Ammonia: A Study of a Modified Berthelot Reduction Using Salicylate and Dichloroisocyanurate, *The Analyst* 105, 305-316.
- Kuhn, A., Sigg, L., 1993. Arsenic cycling in eutrophic Lake Greifen, Switzerland: influence of seasonal redox processes. *Limnol. Oceanogr.* 38, 1052-1059.
- Ladeira, A.C.Q., Ciminelli, V.S.T., Duarte, H.A., Alves, M.C.M., Ramos, A.Y., 2001. Mechanism of anion retention from EXAFS and density functional calculations: arsenic (V) adsorbed on gibbsite. *Geochim. Cosmochim. Acta* 65, 1211-1217.
- Lamoreauz, P.E., 1989. Water development for phosphate mining in a karst setting in Florida – a complex environmental problem. *Environ. Geol. Water Sci.* 14, 117-153.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey, USA.

- Laverman, A.M., Blum, J.S., Schaefer, J.K., Phillips, E.P., Lovley, D.R., Oremland, R.S., 1995. Growth of strain SES-3 with arsenate and other diverse electron acceptors. *Appl. Environ. Microbiol.* 61, 3556-3561.
- Le, X.C., 2002. Arsenic speciation in the environment and humans. In: W. T. Frankenberger, Jr. (ed.), *Environmental Chemistry of Arsenic*. Marcel Dekker (New York), pp. 94-116.
- Lennie, A.R., Vaughan, D.J., 1996. Spectroscopic studies of iron sulfide formation and phase relations at low temperatures. *Mineral Spectroscopy, Special Publ.* 5, 117–131.
- Leve G.W. (1983) Relation of concealed faults to water quality and the formation of solution features in the Floridan aquifer, northeastern Florida, USA. *J Hydrol* 62: 251-264
- Levy, D.B., Schramke, J.A., Esposito, J.K., Erickson, T.A., Moore, J.C., 1999. The shallow ground water chemistry of arsenic, fluorine, and major elements: Eastern Owens Lake, California. *Applied Geochemistry* 14, 1, 53-65.
- Lindberg, R.D., Runnels, D.D., 1984. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling: *Science* 225, 925-927.
- Liu, H., Wei, Y., Sun, Y., 2005. The formation of hematite from ferrihydrite using Fe(II) as a catalyst. *J. Molecular Catalysis A: Chem.* 226, 135-140.
- Lovley, D.R., 1997. Microbial Fe(III) reduction in subsurface environments. *FEMS Microbiol. Rev.* 30, 305-313.

- Lovley, D.R., Chapelle, F.H., Phillips, E.J.P., 1990. Recovery of Fe(III)-reducing bacteria from deeply buried sediments of the Atlantic coastal plain. *Geology* 18, 954-957.
- Lovley, D.R., Coates, J.D., 1997. Bioremediation of metal contamination. *Curr. Opin. Biotechnol.* 8, 285–289.
- Lovley, D.R., Goodwin, S., 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediment. *Geochim. Cosmochim. Acta* 52, 2993-3003.
- Lovley, D.R., Phillips, E.J.P., Lonergan, D.J., 1991. Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments, *Environ. Sci. Tech.* 26, 1062-1067.
- Maest, A.S., Pasilis, S.P., Miller, L.G., Nordstrom, D.K., 1992. Redox geochemistry of arsenic and iron in Mono Lake, California, USA. In: Kharaka, Y., Maest, A. S. (Eds.), *Water-Rock Interaction*, Balkema, Rotterdam, pp. 507-511.
- Makris, K.C., Harris, W.G., O’Conner, G.A., El-Shall, H., 2005. Long-term phosphorus effect on evolving physicochemical properties of iron and aluminum hydroxides. *J. Colloid. Interface Sci.* 287, 552-560.
- Manning, B.A., Fendorf, S.E., Goldberg, S., 1998. Surface structures and stability of As(III) on goethite: spectroscopic evidence for inner-sphere complexes. *Environ. Sci. Technol.* 32, 2383–2388.
- Manning, B.A., Goldberg, S., 1996. Modeling arsenate competitive adsorption on kaolinite, montmorillonite, and illite. *Clays Clay Mineral.* 44, 609-623.



- Manning, B.A., Goldberg, S., 1997. Adsorption and stability of arsenic (III) at the clay mineral–water interface. *Environ. Sci. Technol.* 31, 2005–5011.
- Manzoori, J.L., Sorouradin, M.H., Haji Shabani, A.M., 1999. Atomic absorption determination of cobalt after preconcentration by 1-(2-pyridylazo)-2-naphthol immobilized on surfactant-coated alumina. *Microchem. J.* 63, 295-301.
- McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem.* 19, 1255-1293.
- McArthur, J.M., Ravenscroft, P., Safiullah, D., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.* 37, 109-117.
- McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic (III/V) determinations: an evaluation of the literature and new analytical results. *Appl. Geochem.* 19, 995-1009
- Miller, J.A., 1986. Hydrogeological framework of the Floridan Aquifer system in Florida and in parts of Georgia, Alabama, and South Carolina. U.S. Geological Survey Prof. Paper 1403-B.
- Moore, D.M., Reynolds, R.C., 1989. X-ray diffraction and the identification and analysis of clay minerals. Oxford University press, Oxford, pp. 311–325.

- Moore, J.N., Ficklin, W.H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol.* 22, 432-437.
- Newman, D.K., Kennedy, E.K., Coates, J., Ahmann, D., Ellis, D., Lovely, D., Morel, F., 1997. Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp., *Nov. Arch. Microbiol.* 168, 380-388.
- Newman, D. K., Ahmann, D., Morel, F.M.M., 1998. A brief review of microbial arsenate reduction. *Geomicrobiol. J.* 15, 255-268.
- Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. *Nature* 395, 338.
- Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.* 15, 403-413.
- Nordstrom, D.K., 2002. Worldwide occurrences of arsenic in ground water, *Science* 296, 2143-2145.
- NRC, 1999. *Arsenic in Drinking Water*. National Academy Press, Washington, DC.
- NRC, 2001. *Arsenic in Drinking Water (2001 Update)*. National Academy Press, Washington, DC.
- Nriagu, J.O., 2002. Arsenic poisoning through the ages. In: *Environmental Chemistry of Arsenic* (W.T. Frankenberger, Editor), New York, Marcel Dekker, pp. 1-26.
- O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *PNAS* 101, 13703-13708.

- Oremland, R.S., Dowdle, P.R., Hoefft, S., Sharp, J.O., Schaefer, J.K., Miller, L.G., Blum, J.S., Smith, R.L., Bloom, N.S., Waluschilaeger, D., 2000. Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California. *Geochim. Cosmochim. Acta* 64, 3073-3084.
- Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. *Science* 300, 939-943.
- Oremland, R.S., Stolz, J.F., 2005. Arsenic, microbes and contaminated aquifers. *Trends Microbiol.* 13, 45-49.
- Page, R.A., 1957. The Questionable age of the Aquia Formation. *J. Paleontology* 33, 347-350.
- Pearson, Jr., F. J., White D. E., 1967. Carbon 14 ages and flow rates of water in Carrizo sand, Atascosa County, Texas. *Water Resour. Res.* 3, 251-261.
- Pedersen, H.D., Postma, D., Jakobsen, R., 2006. Release of arsenic associated with the reduction and transformation of iron oxides. *Geochim. Cosmochim. Acta* 70, 4116-4129.
- Pedersen, H.D., Postma, D., Jakobsen, R., Larsen, O., 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* 69, 3967-3977.
- Penn, R.L., Zhu, C., Xu, H., Veblen, D.R., 2001. Iron oxide coatings on sand grains from the Atlantic coastal plain: High-resolution transmission electron microscopy characterization. *Geology* 29, 843-846.
- Perkin ElmerSCIEX (2003) Elan DRC II. Expanding the capabilities of ICP-MS. Perkin ElmerSCIEX ICP Mass Spectrometry Instruments brochure and specifications.

- Peters, S. C., Blum, J. D., 2003. The source and transport of arsenic in a bedrock aquifer, New Hampshire, USA. *Appl. Geochem.* 18, 1773-1787.
- Peters, S.C., Blum, J.D., Klaue, B., Karagas, M.R., 1999. Arsenic occurrence in New Hampshire drinking water. *Environ. Sci. Technol.* 33, 1328-1333.
- Phipotts, A.R., 1990. Principles of igneous and metamorphic petrology. Prentice Hall (New Jersey), pp. 5.
- Pierce, M.L., Moore, C.B., 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* 16, 1247-1253.
- Plummer, L.N., Parkhurst, D.L., Thorstenson, D.C., 1983. Development of reaction models for ground-water systems. *Geochim. Cosmochim. Acta.* 47, 665-686.
- Plummer, L.N., Sprinkle, C.L., 2001. Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Upper Floridan aquifer, Floridan, USA. *Hydrogeol J.* 9, 127-150.
- Purdy, C.B., 1991. Isotopic and chemical tracer studies of ground water in the Aquia Formation, southern Maryland: Including  $^{36}\text{Cl}$ ,  $^{14}\text{C}$ ,  $^{18}\text{O}$  and  $^3\text{H}$ . Ph.D. thesis, University of Maryland, College Park.
- Purdy, C.B., G.J. Burr, M. Rubin, G.R. Helz, Mignerey, A.C., 1992. Dissolved organic and inorganic  $^{14}\text{C}$  concentrations and ages for coastal plain aquifers in southern Maryland. *Radiocarbon* 34, 654-663.
- Purdy, C.B., Helz, G. R., Mignerey, A.C., 1996. Aquia aquifer dissolved Cl- and  $^{36}\text{Cl}/\text{Cl}$ : implications for flow velocities. *Water Resour. Res.* 32, 1163-1171.

- Raichur, A.M., Wang, X.H., Parekh, B.K., 2001. Estimation of surface free energy of pyrites by contact angle measurements. *Minerals Engineering*, 14, 65-75.
- Roden, E.E., Urrutia, M.M., 2002. Influence of biogenic Fe(II) on bacterial crystalline Fe(III) oxide reduction. *Geomicrobiol. J.*, 19, 209-251.
- Roden, E.E., Zachara, J.M., 1996. Microbial reduction of crystalline iron (III) oxides: Influence of oxide surface area and potential for cell growth. *Environ. Sci. Technol.* 30, 1618–1628.
- Ryder, P.D., 1985. Hydrology of the Floridan aquifer system in west-central Florida. Prof Pap 1403-F. USGS Washington, DC
- Rye, R.O., Back, W., Hanshaw, B.B., Rightmire, C.T., Pearson, F.J., 1981. The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas. *Geochim. Cosmochim. Acta.* 45, 1941-1950.
- Ryu, J-H., Gao, S., Dahlgren, R.A., Zierenberg, R.A., 2002. Arsenic distribution, speciation, and solubility in shallow groundwater of Owens Dry Lake, California. *Geochim. Cosmochim. Acta.* 66, 2981-2994.
- Sacks, L.A., Herman, J.S., Kauffman, S.J., 1995. Controls on high sulfate concentrations in the Upper Floridan aquifer in southwest Florida. *Water Resour. Res.* 31, 2541-2551.
- Saikat, S.Q., Selim. A.M., Kessi, J., Wehrli, E., Hanselmann, K.W., 2001. <http://www.microeco.unizh.ch/uni/kurs/mikoek/results/project2/arsen.html>
- Saxena, V.K., Kumar, S., Singh, V.S., 2004. Occurrence, behavior and speciation of arsenic in groundwater. *Current Sci.* 86, 281-284.

- Schelske, C.L., Eadie, B.J., Krausse, G.L., 1984. Measured and predicted fluxes of biogenic silica in lake Michigan. *Limnol. Oceanogr.* 29, 99-110.
- Sherman, D.M., Randall, S.R., 2003. Surface complexation of arsenic(V) to iron (III) oxides and oxide hydroxides: structural mechanism from *ab initio* molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* 67, 4223-4230.
- Smedley, P.L., 2003. Arsenic in Groundwater – South and East Asia. In: Welch A.H., Stollenwerk, K.G., (Eds), *Arsenic in Ground Water: Geochemistry and Occurrence*. Kluwer Academic Publishers, Massachusetts, USA, pp. 179–209.
- Smedley, P.L., Edmunds, W.M., 2002. Redox patterns and trace-element behavior in the East Midlands Triassic sandstone aquifer, U. K. *Ground Water* 40, 44-58.
- Smedley, P.L., Edmunds, W.M., Pelig-Ba, K.B., 1996. Mobility of arsenic in groundwater in the Obuasi gold-mining area of Ghana: some implications for human health. *Environmental Geochemistry and Health*. Geological Society. Special Pub. 113, 163-181.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.* 17, 527-568.
- Smith, A., Hopenhayn-Rich, C., Bates, M., Goeden, H., Hertz-Picciotto, I., Duggan, H., Wood, R., Kosnett, M., Smith, M., 1992. Cancer risks from arsenic in drinking water. *Environ. Health Perspect.* 97, 259-267.
- Solley, W.B., Pierce, R.R., Perlman, H.A., 1993. Estimated use of water in the United States in 1990. U. S. Geol. Surv. Circular 1081, 76 pp.

- Somasundaran, P., Agar, G.E., 1967. The zero point of charge of calcite. *J. Colloid Interface Sci.* 24, 433-440.
- Sracek, O., Bhattacharya P., Jacks G., Gustafsson J., Bromssen M., 2004. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. *Appl. Geochem.* 19, 169-180.
- Stolz, J.F., Oremland, R.S., 1999. Bacterial respiration of arsenic and selenium. *FEMS Microbio. Rev.* 23, 615-627.
- Stookey, L., 1970. Ferrozine - a new spectrophotometric reagent for iron. *Anal. Chem.* 42, 779-781.
- Stringfield, V.T., 1966. Artesian water in Tertiary limestone in the southeastern States. U.S. Geological Survey Prof Paper. 517.
- Stringfield, V.T., 1936. Artesian water in the Florida Peninsula. U.S. Geological Survey Water-supply Paper. 773-C.
- Stumm, W., Morgan, J.J., 1996, *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3rd edn. John Wiley & Sons. pp. 537.
- Stute, M., Schlosser, P., Clark, J.F., Broecker, W.S., 1992. Paleotemperatures in the Southwestern United States derived from Noble gases in ground water. *Science* 256, 1000-1003.
- Tang, J., Johannesson, K.H., 2005a. Rare earth element concentrations, speciation, and fractionation along groundwater flow paths: The Carrizo sand (Texas) and Upper Floridan aquifers. In: Johannesson K.H. (Ed.) *Rare Earth Elements in Groundwater Flow Systems*. Springer (Dordrecht), pp. 223-251.

- Tang, J., Johannesson, K.H., 2005b. Adsorption of rare earth elements onto Carrizo sand: Experimental investigations and modeling with surface complexation. *Geochem. Cosmochim. Acta.* 69, 5247-2561.
- Tang, J., Whittecar, G.R., Johannesson, K.H., Daniels, W.L., 2004. Potential contaminants at a dredged spoil placement site, Charles City County, Virginia, as revealed by sequential extraction. *Geochem. Transactions* 5, 49- 60.
- Tani, Y., Miyata, N., Ohashi, M., Ohnuki, T., Seyama, H., Iwahori, K., Soma, M., 2004. Interaction of inorganic arsenic with biogenic manganese oxide produced by a Mn-oxidizing fungus strain KR21-2. *Environ. Sci. Technol.* 38, 6618-6624.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particular trace metals. *Anal. Chem.* 51, 844-851.
- Tipping, E., Hetherington, N.B., Hilton, J., Thompson, D.W., Bowles, E., Hamilton-Taylor, J., 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. *Anal. Chem.* 57, 1944-1946.
- Thompson, G.R., Hower, J., 1975. The mineralogy of glauconite. *Clay Clay Minerals* 23, 289-300.
- Tye, A.M., Young, D., Crout, N.M., Zhang, H., Preston, S., Bailey, E.H., Davison, W., McGrath, S.P., Paton, G.I., Kilham, K., 2002. Predicting arsenic solubility in contaminated soils using isotopic dilution techniques. *Environ. Sci. Technol.* 36, 982-988.



- USGS, 2003. In: Fahlquist, L. Ground-water quality of the southern high plains aquifer, Texas and New Mexico, 2001. Open-file report 03-345, Texas, USA.
- Vahter, M., 2002. Mechanisms of arsenic biotransformation. *Toxicol.* 181-182, 211-217.
- van Geen, A., Rose, J., Thoraj, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations *Geochim. Cosmochim. Acta* 68, 3475-3486.
- Vessely, M.M., 2004. Chromium along groundwater Flow Paths: The Carrizo Sand and Upper Floridan aquifers, Texas and Florida, USA. Master's thesis, The University of Texas at Arlington, Arlington, Texas.
- Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A., 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* 57, 2251–2270.
- Welch, A.H., Lico, M.S., Hughes, J.L., 1988. Arsenic in groundwater of the western United States. *Ground Water* 26, 333-347.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in groundwater of the United States - occurrence and geochemistry. *Ground Water* 38, 589-604.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* 436, 309–323.
- Whitfield, M.S., 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnol. Oceanogr.* 19, 857–865.

- Wicks, C.M., Herman, J.S., 1994. The effect of confining unit on the geochemical evolution of ground water in the Upper Floridan aquifer system. *J. Hydrol.* 153, 139-155.
- Wilkie, J.A., Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids and Surfaces: Physicochemical and Engineering Aspects* 107, 97-110.
- Wilkie, J.A., Hering, J.G., 1998. Rapid oxidation of geothermal as(III) in streamwaters of the eastern Sierra Nevada. *Environ. Sci. Technol.* 32, 657-662.
- Wilkin, R.T., Wallschläger, D., Ford, R.G., 2003. Speciation of arsenic in sulfidic waters. *Geochemical Transactions* 4, 1-7.
- Wilson, W.E., Gerhart, J.M., 1979. Simulated changes in potentiometric levels resulting from groundwater development for phosphate mines, west-central Florida. *J. Hydrol.* 43, 491-515.
- Wolff, R.G., 1967. X-ray and chemical study of weathering glauconite. *Am. Mineralogist* 52, 1129-1138.
- Zachara, J.M., Kukkadapu, R.K., Fredrickson, J.K., Gorby, Y.A., Smith, S.C., 2002. Biomineralization of poorly crystalline Fe(III) oxides by dissimilatory metal reducing bacteria (DMRB). *Geomicrobiol. J.* 19, 179-207.
- Zheng, Y., Stute, M., van Geen, A., Gavrieli, I., Dhar, R., Simpsom, H.J., Schlosser, P., Ahmed, K.M., 2004. Redox control of arsenic mobilization in Bangladesh groundwater. *Appl. Geochem.* 19, 201-214.

Zobrist, J., Dowdle, P.R., Davise, J.A., Oremland, R.S., 2000. Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate. *Environ. Sci. Technol.* 34, 4747-4753.

Zouboulis, A.I., Kydros, K.A., Matis, K.A., 1993. Arsenic (III) and arsenic (V) removal from solutions by pyrite fines. *Sep. Sci. Technol.* 28, 2449-2463.

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Shama Emy Haque, born in Dhaka, Bangladesh, earned a Bachelor's Degree in Civil Engineering from The University of Texas at Austin in 1995. In 2002, before beginning her Doctoral studies in Environmental Science and Engineering at The University of Texas at Arlington, she spent four years working as a Civil Engineer in Bangladesh.

Shama's dissertation research work, which addresses the evolution of arsenic in groundwater aquifer systems, is of great importance because of its relevance to human health. Elevated levels of arsenic in groundwater systems are a concern for human health in portions of the US, and even more so in her motherland of Bangladesh. Upon completion of her PhD in 2007, Shama plans to join the Department of Geological Sciences, University of Saskatchewan in Canada as a Post Doctoral Fellow, where she will continue her research in regional groundwater geochemistry.