

Investigation of the Mechanisms for Mobilization of Arsenic in

Two ASR Systems in Southwest Central Florida

by

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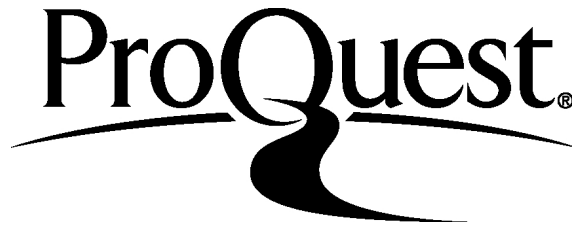
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DEDICATION

This dissertation is dedicated to my wife Judy who patiently calmed my worries and fears and offered unceasing encouragement through the full 18 years of this effort and to my mom and dad who never gave up hope I would finish.

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ABSTRACT

Aquifer storage and recovery (ASR) is a strategy in which water is injected into an aquifer when it is plentiful and pumped from the aquifer when water is scarce. An impediment to ASR in Florida is leaching of naturally-occurring arsenic from limestone of the Upper Floridan Aquifer System (UFAS) into stored water. The concentration of arsenic in surface water, which serves as the recharge water for many ASR systems, and native groundwater is usually much less than 3.0 $\mu\text{g/L}$. However, data from ASR wells in Florida show that arsenic in recovered water frequently exceeded the 10 $\mu\text{g/L}$ maximum contaminant level (MCL) established by the Environmental Protection Agency and were as high as 130.0 $\mu\text{g/L}$. The cause of elevated arsenic concentrations is displacement of reduced native groundwater with oxygenated surface water that dissolves arsenic-bearing pyrite in limestone. Although arsenic can be removed from recovered water during final treatment, mobilization of arsenic in the aquifer at levels that exceed the MCL is problematic under federal regulations.

This dissertation investigated a number of aspects of the ASR/arsenic problem to provide additional insights into the mechanisms of arsenic mobilization and measures that could be taken to avoid or reduce the release of arsenic during ASR operations.

Chapter 2, involved development of a geochemical model to simulate an ASR system's injection of oxygenated surface water into reduced groundwater to determine whether aquifer redox conditions could be altered to the degree of pyrite instability. Increasing amounts of

injection water were added to the storage-zone in a series of steps and resulting reaction paths were plotted on pyrite stability diagrams. Unmixed storage-zone water in wells plotted within the pyrite stability field indicating that redox conditions were sufficiently reducing to allow for pyrite stability. Thus arsenic is immobilized in pyrite and its concentration in groundwater should be low. During simulation, as the injection/storage-zone water ratio increased, redox conditions became less reducing and pyrite became unstable. The result would be release of arsenic from limestone into storage-zone water.

Chapter 3 examined the importance of maintaining a substantial volume of stored water around an ASR well to prevent recovery of reduced native groundwater to the vicinity of the well. Depleting the stored water and recovering reduced native groundwater would result in dissolution of arsenic-bearing hydrous ferric oxide (HFO) and release of arsenic into water recovered from the ASR well. Injection/recovery volumes for each cycle for each well were tracked to determine if a substantial volume of stored water was maintained for each cycle or if it was depleted so that reduced native groundwater was brought back to the well. Each well was assigned to either the “storage zone maintained group” where a zone of stored water was established in early cycles and largely maintained through the period of investigation, or the “storage-zone depleted group” where a zone of stored water was either established in later cycles and/or was depleted during the period of investigation. Graphical and statistical analyses verified that maximum arsenic concentrations for storage-zone maintained wells were nearly always lower in each cycle and declined below the MCL after fewer cycles than those of storage-zone depleted wells.

Chapter 4 was a mineralogical investigation of cores located at 20 m (ASR core 1), 152 m (ASR core 2), and 452 m (ASR core 3) from operating ASR wells to determine where

mobilized arsenic in limestone is precipitated during ASR. If arsenic is precipitated distally, reduced concentrations of elements in pyrite, (iron, sulfur, arsenic, etc.) would be expected in ASR core 1 relative to more distant cores and there would be noticeable changes in appearance of pyrite crystals due to enhanced oxidation. The results showed that mean concentrations of the elements were lowest in ASR core 2, which did not support distal precipitation. However, scanning electron microscopy identified well-defined pyrite framboids only in core 3 while framboids in ASR cores 1 and 2 were less clear and distinct, indicating pyrite oxidation in cores closest to ASR wells.

Statistical comparison of concentrations of iron, sulfur, and arsenic between the three ASR cores and 19 control cores not subject to ASR, showed that mean concentrations in ASR cores 1 and 2 were statistically similar to concentrations in control cores. This indicated that concentrations in ASR cores 1 and 2 had not been significantly reduced by ASR. The concentrations of elements were higher in ASR core 3 than in ASR cores 1 and 2 and control cores and statistically dissimilar to all but one control core. This indicated natural heterogeneity in core 3 rather than diminution of elements in ASR cores 1 and 2 due to ASR. The statistical analysis supported local precipitation. Once arsenic is mobilized from dissolved pyrite, it is rapidly complexed with precipitated HFO near the well. As long as all of the stored water is not removed during recovery so that reduced native groundwater is brought back to the well, HFO remains stable and complexed with arsenic. The concentration of elements would not have been lowest in ASR core 1 for this reason and because calculations showed that the mass of arsenic removed during recovery events prior to coring was minor compared to the total in limestone surrounding the well. The implications of this are that while large quantities of arsenic are present near the ASR well, only a small percentage may be available for dissolution. Most

arsenic occurs with pyrite in limestone, which may insulate it from exposure to oxidized injection water. Water recovered from ASR wells may continue to have low concentrations of arsenic indefinitely because as limestone is dissolved, more pyrite becomes exposed and available for dissolution.

The primary contribution of this dissertation to understanding and overcoming the arsenic problem in ASR systems is the empirical data developed to support or challenge important ASR/arsenic hypotheses. These data were used to 1) establish that background concentrations of arsenic in groundwater of the Suwannee Limestone were less than $1\mu\text{g/L}$, 2) demonstrate that redox conditions necessary for pyrite in limestone to become unstable and dissolve occur when oxygenated surface water is injected into the aquifer, 3) demonstrate that the concentration of pyrite in the Suwannee Limestone is spatially variable to a high degree, 4) support the hypothesis that following injection of oxygenated surface water, pyrite in limestone dissolves and releases arsenic into solution and HFO forms and complexes with the arsenic near the ASR well, 5) propose that only a small percentage of pyrite near an ASR well may be available for dissolution during each cycle because most occurs in the limestone matrix and is isolated from injection water, 6) propose that as a result of the previous conclusion, water recovered from ASR systems may continue to have low concentrations of arsenic indefinitely because as limestone that contains pyrite is dissolved with each cycle, additional pyrite is exposed and is available for dissolution, and 7) support the effectiveness of maintaining a zone of stored water in an ASR well as an effective means of minimizing arsenic in recovered water during ASR.

CHAPTER ONE:

INTRODUCTION

Aquifer storage and recovery (ASR) is a strategy in which water is injected into an aquifer when it is plentiful (e.g., during a wet season) and pumped from the aquifer when water is scarce (e.g., a dry season). An impediment to ASR development in Florida is the leaching of naturally-occurring arsenic from the limestone matrix of the Upper Floridan Aquifer System (UFAS) into the stored water. The concentration of arsenic in surface water, which serves as the recharge water for many ASR systems, and native groundwater is usually much less than 3.0 µg/L. However, data from cycle tests conducted at numerous ASR wells in Florida show that arsenic concentrations in recovered water frequently exceeded the 10 µg/L maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency and were as high as 130.0 µg/L (Arthur *et. al.*, 2003). The cause of the elevated arsenic concentrations is likely the displacement of reduced native groundwater in the storage zone with oxygenated injected surface water that dissolves arsenic-bearing pyrite in the limestone matrix (Arthur, *et. al.*, 2001). Although arsenic can be removed from recovered water during final treatment, mobilization of arsenic in the aquifer at levels that exceed the MCL of 10.0 µg/L is problematic under federal regulations (Code of Federal Regulations Title 40 Part 144).

The presence of arsenic in high concentrations in water recovered from ASR wells was unexpected and therefore, was neither recognized as a problem nor made a Class V Underground

Injection Control (UIC) permitting requirement until the early 2000s (Arthur *et.al.*, 2002). Analysis of geochemical data from early cycle tests at the City of Tampa's ASR wellfield showed that arsenic concentrations increased during storage and recovery (Arthur *et.al.*, 2002; Williams *et al.*, 2002). The MCL for Arsenic at the time was 50 µg/L and only one sample exceeded this level. However, numerous samples exceeded the current 10 µg/L MCL. Subsequent studies determined that arsenic concentrations decreased with successive cycles if the recharged volumes were approximately equal and that relatively high arsenic concentrations could occur if the recharged volume in a subsequent cycle increased. This would result from "new" aquifer volume being exposed to injected water (Arthur *et al.*, 2005; Pyne, 2005).

Price and Pichler (2005) conducted lithological, mineralogical, and geochemical analyses on core samples to determine the location and speciation of arsenic in the Suwannee limestone of the UFAS, the formation that encompasses the storage zone for most ASR systems in Florida. Analysis of over 300 core samples from 19 wells in their study area showed that the average arsenic concentration was 3.5 mg/kg concentrated in trace minerals, particularly framboidal pyrite, with framboidal pyrite containing arsenic at concentrations exceeding 1000 mg/kg and being most abundant in high porosity zones. Additional evidence to support mobilization of arsenic from pyrite included correlation of metals common to pyrite such as cobalt, iron, manganese, molybdenum, nickel, and vanadium with arsenic and iron in the limestone matrix, mobilization and correlation of arsenic and iron in recovered waters, and redox conditions conducive to pyrite oxidation. These findings were supported by the work of numerous researchers who have shown that pyrite, arsenopyrite, and/or unspecified sulfide minerals are often the primary source of arsenic in ground waters (Gotkowitz *et al.*, 2000; Nickson *et al.*,

2000; Peters *et al.*, 1999; Robinson *et al.*, 2000; Serfes *et al.*, 2000; Smedley and Kinniburgh, 2001).

Objectives and Organization

The objective of this dissertation is to investigate a number of aspects of the ASR/arsenic problem to provide additional insight into the mechanisms of arsenic mobilization and measures that could be taken to avoid or reduce the release of arsenic during ASR operations.

This dissertation is organized around three manuscripts with multiple coauthors. Chapter 2, “The Relationship between Pyrite Stability and Arsenic Mobility During Aquifer Storage and Recovery, Southwest Central Florida,” involved the development of a geochemical model to simulate an ASR system’s injection of oxygenated surface water into reduced groundwater to determine the conditions under which pyrite dissolves and releases its associated arsenic into solution. This study was published in the *Journal of Environmental Science and Technology* (Jones and Pichler, 2007). Chapter 3, “The Importance of Maintaining a Zone of Stored Water to Minimize Arsenic in Water Recovered from ASR Systems – Results of Long-Term Cycle Testing in Two ASR Wellfields,” examined the importance of maintaining a buffer of stored water in an ASR system to prevent reduced native groundwater from reaching the vicinity of the well. If the reduced native groundwater should reach the well, arsenic-rich hydrous ferric oxide (HFO) would dissolve, resulting in the release high concentrations of arsenic into stored water. Chapter 4, “A Mineralogical Investigation of Cores in an ASR Wellfield to Determine where Mobilized Arsenic is Precipitated,” was a detailed mineralogical investigation of three cores obtained at varying distances from operating ASR wells. The purpose was to test competing

hypotheses that when arsenic is mobilized it is flushed away from the ASR well to be precipitated distally or it is rapidly complexed with hydrous ferric oxide and precipitated locally.

Description of the Study Area

The three investigations described above were conducted within the 13,000 km² Southwest-Central Florida Groundwater Basin (SWCF Groundwater Basin) (Figure 1.1). The following is a description of the study area, its physiography, hydrology, geology and hydrogeology, the ASR wellfields that were included in the investigations, and the 19 Suwannee Limestone monitor wells distributed across the SWCF Groundwater Basin whose water and cores were used to provide background control for chemical and mineralogical comparisons with the ASR wellfield water chemistry and core mineralogy.

Physiography

The area within the SWCF Groundwater Basin has a diverse physiography. In southern Polk County and Hardee County, a broad, gently sloping plain is drained by the Peace River and its tributaries. Northern Polk County contains a portion of the Green Swamp, which is a mosaic of uplands and wetlands that forms the headwaters of four major rivers. The eastern side of the SWCF Groundwater Basin in Polk and Highlands Counties is defined by the Lake Wales Ridge, a northwest-southeast trending highland characterized by relatively high elevations, deep sands and sinkhole lakes. Land surface elevations within the SWCF Groundwater Basin gradually increase from sea level at the Gulf Coast to a high of 136 feet in northeastern Manatee County. This change in topography is evidence of former marine shorelines, called terraces. Each terrace consists of poorly-drained flatlands with many swamps, ponds, and lakes. Further to the east,

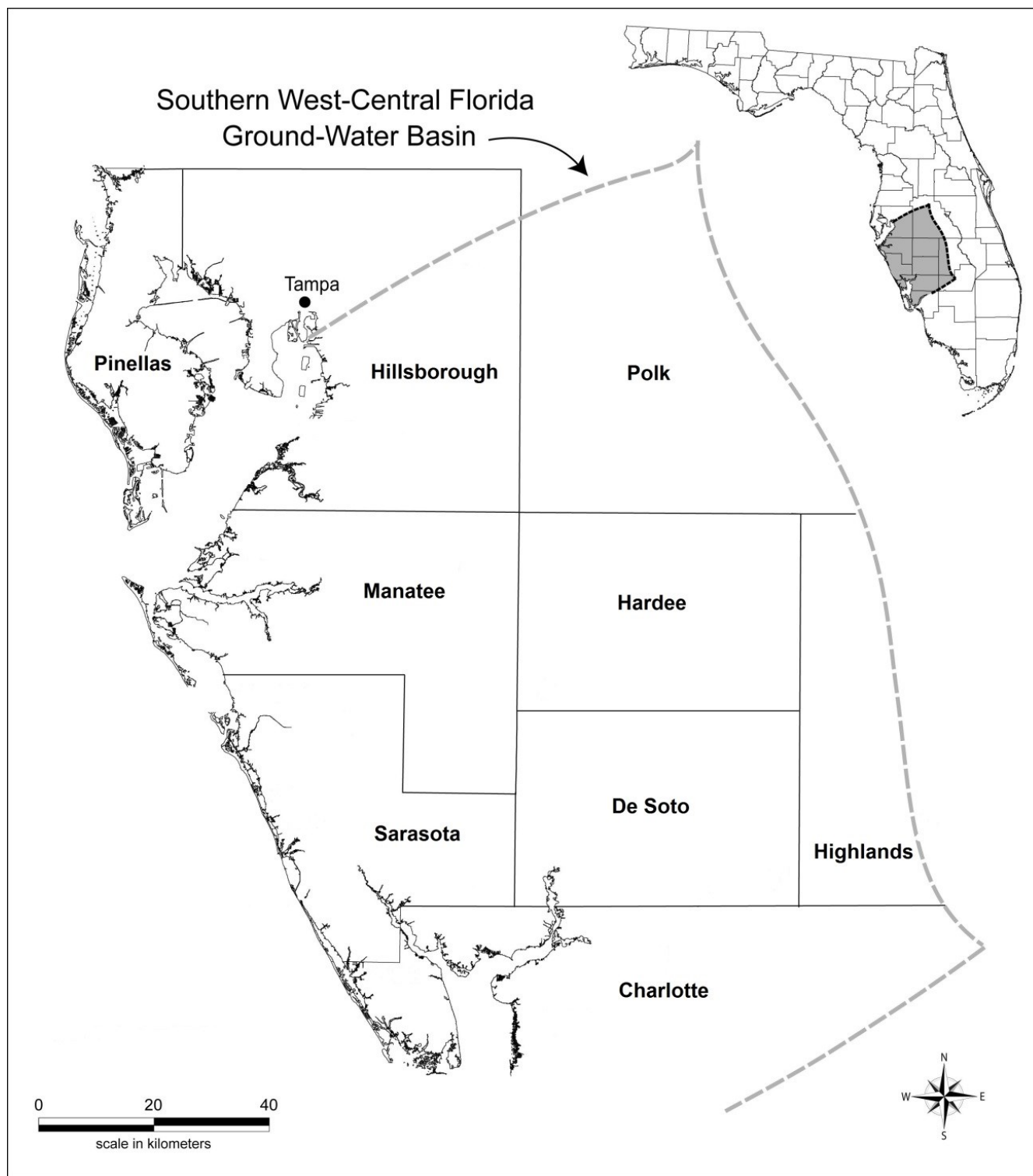


Figure 1.1. Location of the study area within the SWCF Groundwater Basin.

DeSoto County is topographically very similar to Charlotte and Manatee counties with poorly-drained marine terraces increasing in elevation to the east. The topography of the northwest portion of the SWCF Groundwater Basin in Hillsborough County is largely a result of limestone dissolution and sediment deposition. Numerous closed depressions and sinkholes throughout the area reflect active solution of the underlying limestone.

Hydrology

The SWCF Groundwater Basin contains all or part of seven major watersheds including the Hillsborough, Alafia, Little Manatee, Manatee, Braden, Myakka, and Peace Rivers. There are many smaller tributaries to these larger systems as well as several coastal watersheds drained by many small tidally-influenced or intermittent streams. The Hillsborough, Alafia, Braden, Manatee and Peace Rivers are utilized as public water supply sources.

Geology and Hydrogeology

Three principal aquifer systems; the surficial (SAS), intermediate (IAS), and UFAS, are present across much of the SWCF Groundwater Basin. Figure 1.2 is a generalized north-south cross section through the Southwest Florida Water Management District. The cross section shows that the UFAS dips to the south starting at the northern boundary of the SWCF Groundwater Basin. In addition, the IAS and its associated clay confining units appear at the boundary and thicken to the south, separating the SAS from the UFAS and confining the UFAS.

The SAS is contained within near-surface deposits that mainly consist of undifferentiated sands, clayey sand, silt, shell, and marl. The aquifer produces relatively small quantities of water and is thin to absent in the northern portion of the SWCF Groundwater Basin to over 100 meters

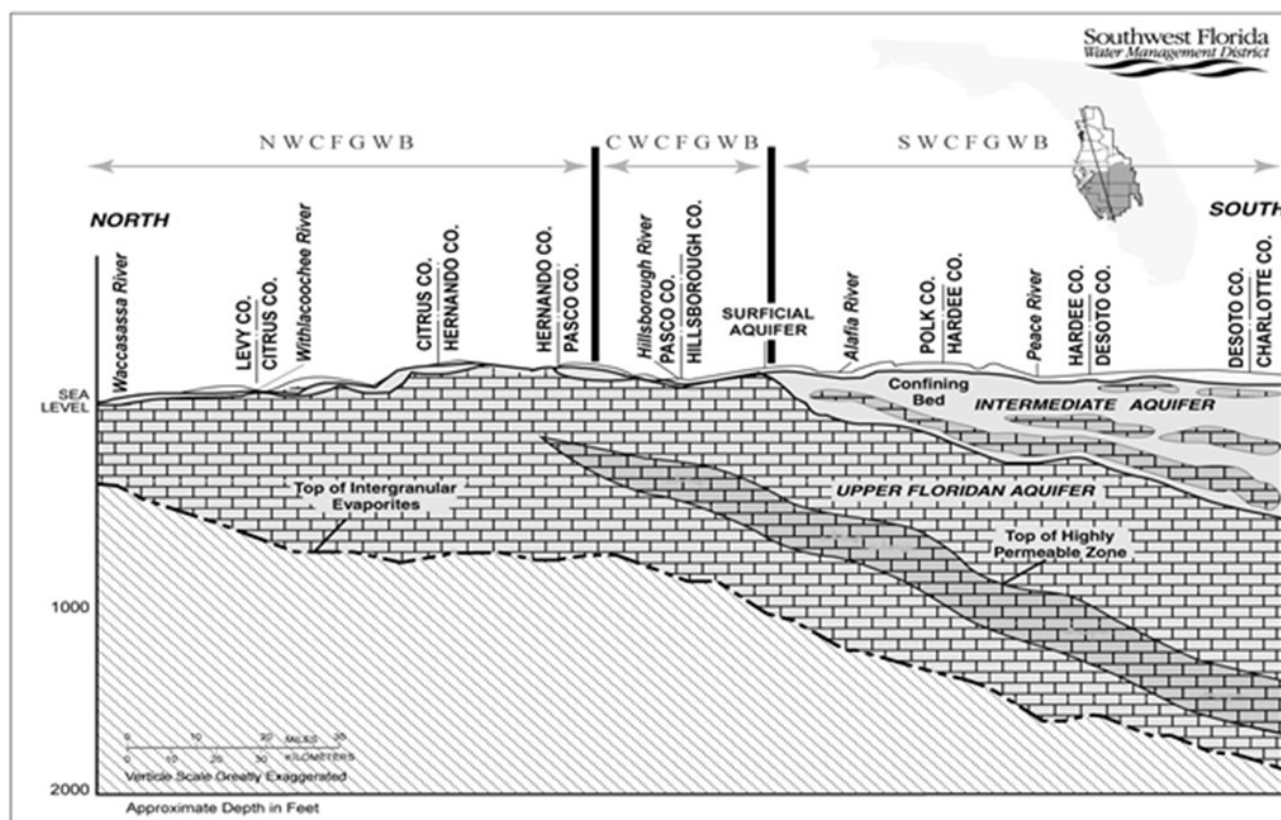


Figure 1.2. North-south geologic cross section through the Southwest Florida Water Management District showing the southward dip of the UFAS and increasing degree of confinement in the SWCF Groundwater Basin (after the Southwest Florida Water Management District).

in the southern portion. The aquifer produces relatively small quantities of water and is generally used for low-volume irrigation or domestic water supply. The aquifer ranges in thickness from a few feet in central Hillsborough County to greater than 100 meters in southern Highlands County within the Lake Wales Ridge (Yobbi, 1996).

The IAS underlies the SAS and consists of discontinuous sand, gravel, shell, limestone, and dolomite beds of the Hawthorn Group. The IAS may contain one or more distinct production zones (Wolansky, 1983) that are confined or semi-confined by low-permeability sandy clays, clays, and marls. Thickness of the IAS increases from north to south, varying from

thin to absent in the northern portion of the SWCF Groundwater Basin to over 100 meters in the southern portion.

Recharge to the IAS varies from low to moderate depending upon seasonal groundwater use in the area. Along the Lake Wales Ridge in Polk and Highlands Counties, the IAS and its confining units are extensively breached by karst features that are expressed on the surface as sinkhole lakes. In this region, the SAS and UFAS are locally connected through the karst features.

The UFAS, by far the most important source of water in the SWCF Groundwater Basin, is composed of a vertically continuous sequence of highly permeable carbonate rocks approximately 300 m thick (Miller, 1986). The UFAS includes the Suwannee Limestone of Oligocene age and the Ocala Limestone and Avon Park Formations of Eocene age. The Suwannee Limestone, the storage zone for ASR systems in the study area, is a wackestone mud to pelletal, foraminiferal grainstone (Gilboy, 2006; Hammes, 1992; Williams *et al.*, 2002; Green *et al.*, 1995) that contains minor phosphatic quartz sand and clay intermixed with limestone near the formation top, and a thin layer of dolostone in the lower third (Miller, 1986; Green, 1995). Chert nodules, organics and pyrite are present in minor amounts.

The UFAS can be separated into upper and lower flow zones. The Suwannee Limestone forms the upper flow zone. The lower zone is the highly transmissive portion of the Avon Park Formation. The two zones are separated by the lower permeability Ocala Limestone which acts as a semi-confining layer. The two flow zones are connected through the Ocala by diffuse leakage, vertical solution openings along fractures, or other zones of preferential flow (Menke *et al.*, 1961). The middle confining unit of the UFAS lies near the base of the Avon Park Formation. It is composed of evaporate minerals such as gypsum and anhydrite which occur as

thin beds or as nodules within dolomitic limestone that overall has very low permeability. The middle confining unit is generally considered to be the base of the freshwater production zone of the UFAS.

In much of the SWCF Groundwater Basin, recharge to the UFAS ranges from less than one inch to several inches per year (Sepulveda, 2002). This low recharge rate is due to the thick sequence of multiple clay confining layers of the IAS that overlie the UFAS. These clay layers restrict the vertical exchange of water from the SAS to the underlying UFAS. Recharge to the UFAS along the Lake Wales Ridge in the northern and eastern portions of Polk and Highlands Counties is much higher. In this area, the IAS is thinner or dissolution of limestone has resulted in the development of karst features that are expressed on the surface as a series of sinkhole lakes. Model-estimated recharge rates in the Lake Wales Ridge range from approximately six to 15 in/yr (SWFWMD, 1993).

ASR Wellfields

The ASR wellfields that were part of the studies described previously were the City of Tampa's Rome Avenue Park ASR Wellfield located in Hillsborough County and the Peace River Manasota Regional Water Supply Authority's (Peace River Authority) ASR Wellfield located in DeSoto County (Figure 1.3).

City of Tampa

The City of Tampa's Rome Avenue Park ASR wellfield has 8 ASR wells dispersed over a 0.75 square km area approximately 6 km north of downtown Tampa. The wellfield is designed to supply the city with 10 mgd of water during the region's March through May dry season. The

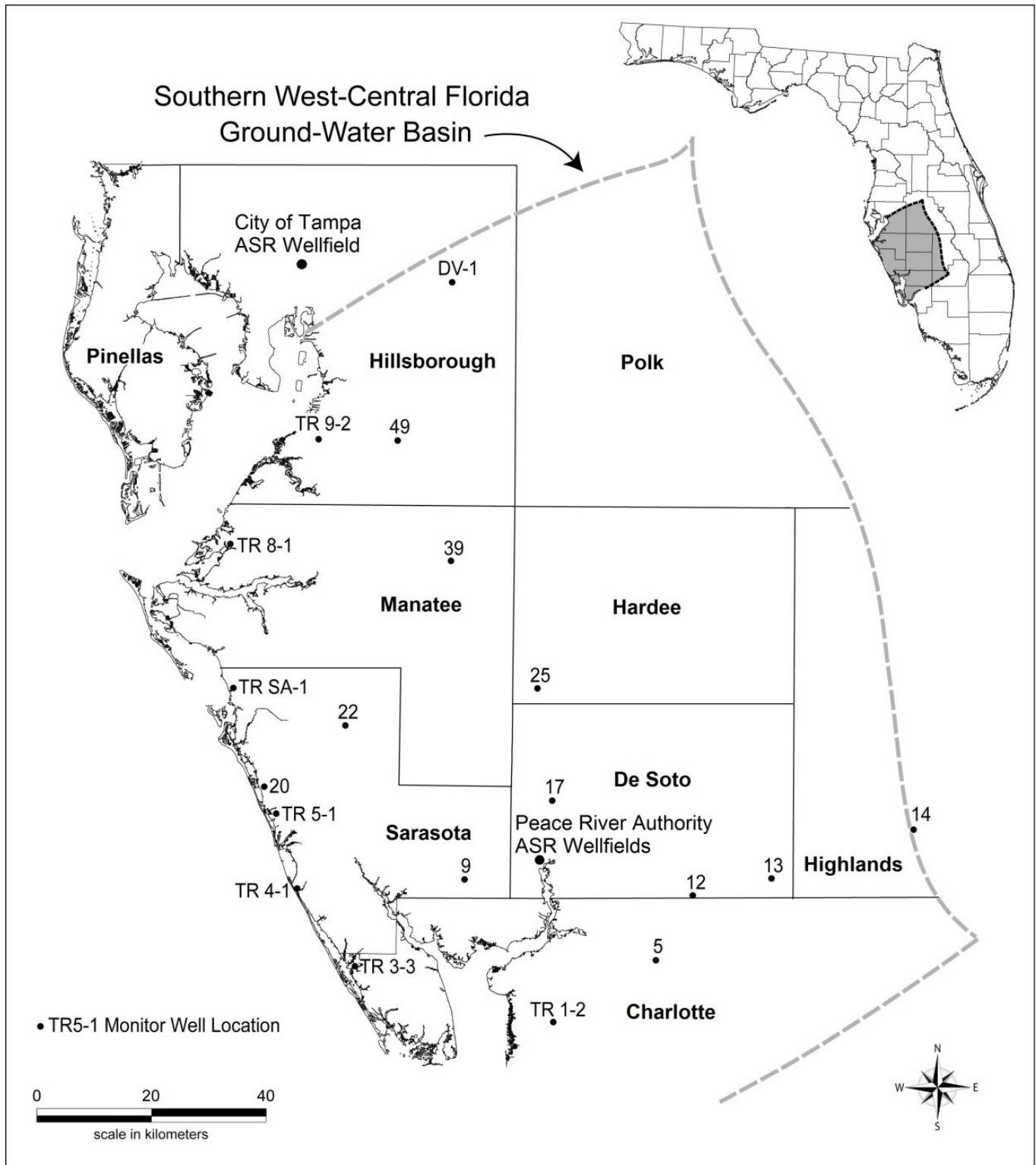


Figure 1.3. Location of the ASR wellfields and Suwannee Limestone control wells used in the investigation.

Hillsborough River is the source for ASR recharge and is also the City's primary source of potable supply. The ASR wells are recharged primarily during the June through September wet season when flow in the Hillsborough River is significantly elevated. The water is treated to drinking water standards and injected into the aquifer for storage. Water is withdrawn from the ASR wells during the dry season, subjected to additional treatment, and distributed to customers. The system has been characterized as a regulatory storage system in that injection allows the city to withdraw water during the dry season, which would not otherwise be allowed by the Southwest Florida Water Management District, the regional agency with water use permitting authority (Maliva and Missimer, 2010). The system was located in a freshwater aquifer to allow the city to achieve 100 percent or greater recovery of recharged water during the initial operational tests (McNeal and Bennet, 2003).

The Suwannee Limestone at the City of Tampa's ASR wellfield is approximately 76 m thick, occurring from 46 m below land surface (bls), to approximately 122 m bls. The lower 30 m of the Suwannee Limestone is the storage zone for the ASR system due to its moderate transmissivity, well defined confinement, and high quality water (CH2MHill, 2000). The wellfield's first ASR well, ASR 1, was constructed in 1995 and was drilled to a depth of 117 m bls with an open-hole interval that extended from 90 to 117 m. Although the well extends into the upper Ocala Limestone, most of the open-hole interval is within the lower Suwannee Limestone (Peer Consultants, CH2MHill, 1995, CH2MHill, 2000). Water within this zone, (storage zone) is fresh with a total dissolved solids concentration of 232 mg/L. The first cycle test was initiated in July of 1996 with approximately 18.2 million gallons recharged and recovered. The second cycle test was initiated in September of 1996 with approximately 99 million gallons recharged over 90 days. Storage occurred for another 90 days before recovery

began. Water levels recovered rapidly to the static level after both recharge and recovery. As expected in a regional confined aquifer, neither residual local pressure increased nor residual drawdowns occurred. Therefore, local storage was not being achieved because injection did not result in a persistent local increase in aquifer heads (Maliva and Missimer, 2010).

In 2000, the City of Tampa added an additional seven ASR wells to the wellfield. Depths of the wells range from 111 to 128 m bls, with final casing depths ranging from 87 m to 99 m bls (CH2MHill, 2011a). Cycle testing began at the wells in 2001 and has continued through the present time.

Peace River Authority

The Peace River Authority withdraws water from the Peace River primarily during the summer wet season and has the option of storing it in one of two off-stream reservoirs or its ASR system, distributing it directly to its customers, or doing some combination of storage and distribution. The Peace River Authority operates two ASR wellfields referred to as ASR Wellfield 1 and ASR Wellfield 2. Only data from ASR Wellfield 2 was included in the investigations that comprise this dissertation. ASR Wellfield 2 has a total of 12 wells that became operational in 2002 (Pyne, 1995, 2005). The wells were completed into the Suwannee Limestone and range in depth from 269 to 276 m bls, with final casing depths ranging from 173 to 189 m bls. Each well has the capacity to recharge and recover approximately 1 mgd. ASR wells in Wellfield 2 were constructed in close proximity to one another (no well is more than 60 m from its nearest neighbor) to ensure that the wellfield would function as a single system with the injected and recovered water coalescing among the wells (CH2MHill, 2011b). Two of these wells were not used in this investigation because their water quality data were skewed when the

wells were back plugged during the period of investigation to improve water quality.

Suwannee Limestone Control Wells

The water quality and cores from nineteen Suwannee Limestone monitor wells dispersed throughout the SWCF Groundwater Basin (Figure 1.3) were used to provide control for chemical and mineralogical comparisons with the ASR wellfield water chemistry and core mineralogy.

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CHAPTER TWO:
THE RELATIONSHIP BETWEEN PYRITE STABILITY AND ARSENIC
MOBILITY DURING AQUIFER STORAGE AND RECOVERY

Abstract

Elevated levels of arsenic are common in water recovered from ASR systems in west-central Florida that store surface water. Mineralogical investigations of the Suwannee Limestone of the UFAS, the preferred storage zone for ASR systems, have shown that the highest concentrations of arsenic are associated with pyrite in zones of high moldic porosity. This investigation employed geochemical modeling to examine pyrite stability in limestone during simulated injections of surface water. Nineteen control wells with open-hole intervals encompassing only the Suwannee Limestone with known mineralogy and water chemistry were included in the investigation. Injections were simulated for a subset of these wells that had representative water chemistry. The goal was to determine if aquifer redox conditions could be altered to the degree of pyrite instability. Increasing amounts of injection water were added to the storage-zone water in a series of steps and resulting reaction paths were plotted on pyrite stability diagrams. Unmixed storage-zone water in the wells plotted within the pyrite stability field indicating that redox conditions were sufficiently reducing to allow for pyrite stability. Thus arsenic is immobilized in pyrite and its concentration in ground water should be low. This was corroborated by analysis of water samples; none of the 19 wells sampled had arsenic concentrations above 0.036 $\mu\text{g/L}$. During simulation, however, as the injection/storage-zone

water ratio increased, redox conditions became less reducing and pyrite became unstable. The result would be the release of arsenic from the aquifer matrix into storage-zone water.

Introduction

The question arises as to whether dissolution of pyrite in the Suwannee limestone of the UFAS, the storage zone for ASR systems in Florida, could be responsible for elevated arsenic levels in groundwater during ASR operations. Building on the findings of Price and Pichler (Price and Pichler, 2002; Price and Pichler, 2005), the purpose of this investigation was to evaluate whether injection of surface water into the Suwannee Limestone storage zone would cause pyrite to become unstable. Components of this investigation included: a) analysis of water samples over a 30-month period from 19 Suwannee Limestone control wells dispersed throughout the SWCF Groundwater Basin to characterize water chemistry of the storage zone, b) analysis of variability of storage-zone water chemistry, c) delineation of a subset of wells with water chemistry representative of water types in west-central Florida, d) determination of background levels of arsenic in the storage zone using a method capable of quantifying arsenic at the low $\mu\text{g/L}$ range, and e) geochemical modeling of mixing of waters in the storage zone.

UFAS Flow System and Hydrochemistry

The UFAS in the SWCF Groundwater Basin is primarily recharged in the Lake Wales Ridge region of Polk and Highlands Counties. Groundwater in this area has a low total dissolved solids (TDS) content and is dominated by calcium, magnesium, and bicarbonate (Back and Hanshaw, 1970). As water moves westward and deeper into the aquifer, TDS increases and sulfate becomes dominant due to gypsum and anhydrite in the Avon Park Formation. Water

moves upward as it approaches the coast and becomes dominated by sodium and chloride as it interacts with seawater (Back and Hanshaw, 1970; Plummer, 1977; Plummer *et al.*, 1983).

Waters with different chemistries were used for geochemical modeling of the mixing of waters in the storage zone. The storage zone contained three distinct water types; a recharge end member, a discharge end member, and an intermediate stage. The injection water consisted of surface water used in the City of Tampa's public supply system. To characterize storage-zone water chemistry, samples were collected from 19 control wells open to the Suwannee Limestone in May 2002, 2003, and 2004; the end of the dry season and September 2002 and 2003; the end of the wet season to investigate possible seasonal variations. Locations of the wells are shown in Figure 1.3. Field parameters were measured and samples were collected in adherence to a quality assurance plan approved by the Florida Department of Environmental Protection. Temperature, dissolved oxygen (DO), conductivity, pH, and Eh were measured within wells using a YSI 600XLM probe. Samples were analyzed for bicarbonate, magnesium, calcium, sodium, potassium, chloride, sulfate, silicon, iron, strontium, and TDS by a state-certified laboratory using standard analytical methodology and QA/QC procedures, i.e. EPA Methods 200 and 300. Eh data showed an unacceptably high degree of variability and thus the sulfate/sulfide redox couple was used as a redox indicator. In June 2004, samples were collected specifically for sulfide, which was analyzed in accordance with EPA Method 376.1.

The concentration of arsenic was determined at the Center for Water Analysis at the University of South Florida by hydride generation-atomic fluorescence spectrometry using a PSA 10.055 Millennium Excalibur system. The sample was prepared by consuming it with concentrated, ultra-pure HCL, and a saturated potassium iodide solution, at a ratio of 68:30:2. This caused the reduction of arsenate (As^{5+}) to arsenite (As^{3+}) prior to formation of arsenic

hydride (AsH_3) via addition of sodium tetraborohydride (NaBH_4). EPA method 200.8 (Trace Elements in Natural Waters by ICP-MS) was not suitable for analysis of arsenic because concentrations in the Suwannee Limestone were generally below $1.4 \mu\text{g/L}$, the detection limit for that method.

Water for injection of the City of Tampa's ASR system is obtained from the Hillsborough River. The water is ozonated and chloraminated prior to injection. Water chemistry data were obtained from samples collected between January 2001 and May 2003. All analyses were conducted by the City's state certified laboratory.

Geochemical Modeling

Modeling was used to examine pyrite stability as a function of mixing injection and storage-zone waters where the injection/storage-zone water ratio was increased exponentially at each step. The modeling process was as follows.

Water Chemistry Variability

Storage-zone water chemistry was evaluated to determine whether significant variability existed between sampling events. If variability of the five values of each parameter was minor, the modeling could be simplified by inputting parameter means. For water quality data for each of the 19 control wells, means were calculated for the five values for each parameter. As stated above, sulfide had only one value. The percent each of the five values for each parameter varied from its mean was calculated and significance of the variation was determined.

Selection of Representative Wells for Modeling

An effort was undertaken to determine whether the water chemistry of a subset of the control wells could be representative of all 19 wells. To accomplish this, water chemistry for each well was plotted on a Piper diagram (Piper, 1944) (Figure 2.1). The resulting pattern was analyzed and the validity of selecting a subset of wells for modeling was determined.

Simulation of Injection of Water into Wells

Injection water was used as a reactant and titrated into the wells in a series of steps with the injection/storage-zone water ratio increasing exponentially at each step.

Reaction Paths

Because of the unacceptably high variability in Eh resulting from the difficulty of obtaining accurate measurements (Stumm and Morgan, 1981; Hostettler, 1984; Lindburg and Runnels, 1984; Runnels and Lindburg, 1990), the sulfate/sulfide redox couple was used as an indicator of the redox condition of storage-zone water and injection/storage-zone water mixtures. Sulfate/sulfide equilibrium was not assumed for mixtures because redox reactions in low temperature-systems proceed at such slow rates that equilibrium is seldom reached. However, equilibrium was assumed for storage-zone water, with the possible exception of recharge-area wells, because residence time of water is hundreds to thousands of years (Hanshaw *et al.*, 1965).

Reaction paths were constructed by calculating the log activity of the sulfate/sulfide ratio from the model output and plotting this number versus the pH for storage-zone water and for injection/storage-zone water mixtures at ratios of 1×10^2 to 1, 1×10^5 to 1, 1×10^9 to 1, and 1×10^{15} to 1 on a stability diagram of the Fe - S system. Because mineral stability fields change as the

Results and Discussion

Water Chemistry

Analysis of water chemistry variability within each well between sampling events determined that variability was greatest in Eh, DO, iron, and arsenic. Eh was excluded from the analysis and not used for modeling because the high degree of variability indicated problems with the data. Variability in iron and arsenic resulted from the difficulty of accurately quantifying parameters that occur at low concentrations. Once DO, iron, and arsenic were isolated from the data set, 93 percent of the data for the remaining parameters varied less than 7 percent from their means. This small variation supported the assumption that conditions in the storage zone, i.e., slow travel times and isolation from the atmosphere, would prevent significant seasonal variation of the water chemistry within each well. The low degree of variability was verification that for each well, it was appropriate to use the mean of the five values for each parameter for modeling. Table 2.1 is a compilation of parameter means for the City of Tampa's water system and for the 19 control wells.

Determination of Representative Water Types

Plotting samples on a Piper Diagram revealed the pattern of chemical evolution in the flow system originally described by Back and Hanshaw (1970). Water enters the aquifer in the eastern portion of the SWCF Groundwater Basin, travels to the southwest, and discharges into the Gulf of Mexico. Water analyses from the 19 control wells that comprised this pattern can be characterized by wells at three points in the flow system that represent distinct water types; a recharge end member, a discharge end member, and an intermediate stage.

Table 2.1. Parameter means for City of Tampa injection water and five sampling events for the 19 control wells.

	T ^a	DO ^b	pH	SO ₄ ^b	S ^b	Cl ^b	Ca ^b	Mg ^b	Na ^b	K ^b	SiO ₂ (aq) ^b	Fe ^b	HCO ₃ ^b	Sr ^b	As ^c
City of Tampa Injection Water															
	25.8	15.4	7.6	114.0	nd	28.7	88.9	9.5	61.0	1.9	nd	0.10	81.9	nd	nd
Well ID	Monitor Well Water														
12	27.7	0.28	7.6	138.8	7.3	273.5	75.4	36.8	131.2	4.1	18.7	<0.012	124.4	27.9	<0.02
13	27.0	0.23	7.7	72.0	7.6	96.7	40.8	22.5	58.6	3.1	17.4	<0.012	124.3	15.0	<0.02
14	25.6	0.28	8.7	12.9	3.2	7.4	4.2	4.1	49.4	4.2	10.6	<0.012	115.9	1.4	<0.02
17	27.3	0.31	7.2	363.5	9.1	67.1	108.0	60.6	38.0	4.1	24.4	<0.012	157.8	16.8	<0.02
20	28.2	0.37	6.9	1676.7	5.0	278.7	486.6	175.0	142.8	7.2	22.9	0.05	133.5	15.0	<0.02
22	25.4	0.58	7.2	367.6	9.8	22.3	110.0	56.0	18.2	3.1	25.8	<0.012	161.1	16.7	0.022
25	28.1	0.20	7.2	555.3	8.2	17.1	151.0	70.7	14.3	3.5	26.5	0.06	140.4	21.1	0.029
39	27.1	0.28	7.4	128.8	4.9	13.8	62.2	27.4	10.3	2.1	21.3	<0.012	152.4	5.9	<0.02
49	25.9	0.22	7.5	58.1	1.9	14.1	48.1	20.5	10.7	1.3	24.7	<0.012	156.1	1.9	0.026
5	30.0	0.36	7.4	212.6	6.7	726.7	107.3	75.2	317.8	12.1	18.3	<0.012	98.3	48.6	<0.02
9	27.9	0.54	7.1	342.7	12.0	514.2	136.0	71.9	250.5	8.6	22.7	0.07	156.2	29.1	<0.02
TR 1-2	30.9	0.25	7.3	270.7	11.0	986.5	129.0	103.7	440.2	18.2	17.6	<0.012	122.8	27.9	<0.02
TR 4-1	28.5	0.53	6.9	623.7	8.6	3278.6	496.0	262.4	1382.0	18.7	23.1	0.04	154.9	37.9	0.035
TR 8-1	26.4	0.66	7.3	467.7	6.1	129.2	151.3	66.0	62.7	3.9	23.6	<0.012	144.1	11.8	0.036
TR 9-2	26.8	0.73	7.2	380.3	5.5	213.8	154.0	71.1	65.3	2.3	22.7	<0.012	142.9	6.8	<0.02
TR SA-1	27.8	0.55	7.1	1043.6	6.3	791.1	323.6	142.6	387.4	12.1	23.4	0.05	128.4	21.7	<0.02
DV-1	24.9	0.27	7.3	0.1	2.9	6.0	52.1	9.6	6.3	0.8	30.9	0.40	185.6	0.3	0.022
TR 5-1	26.4	0.32	7.0	1531.0	7.7	100.8	423.4	154.6	55.1	5.3	24.5	0.10	126.8	14.3	<0.02
TR 3-3	28.5	0.34	7.0	1228.0	6.1	8740.4	467.7	543.2	4428.2	139.3	19.7	0.06	153.0	61.8	<0.02

^a Degrees centigrade

^b mg/L.

^c µg/L.

The recharge end member, dominated by calcium and bicarbonate, had a low TDS concentration (212 mg/L) and entered the aquifer much more recently relative to the other water types. Control well DV-1 was chosen as being most representative of water chemistry in the recharge area.

The intermediate stage, dominated by calcium, magnesium, and sulfate, had a higher TDS concentration (2,500 mg/L) and had migrated westward and deep into the flow system and interacted with gypsum and anhydrite (Saks and Tihansky, 1996). Control well TR 5-1 was most representative of this portion of the flow system. Although this well is located only 2.4 km from

the coast, it is inland of the saltwater/freshwater interface and therefore, does not have the sodium/chloride dominance characteristic of the discharge end member.

The discharge end member, dominated by sodium and chloride, had the highest TDS concentration (15,877 mg/L). This water was mixing with seawater in the aquifer prior to discharging into the Gulf of Mexico. Control well TR 3-3 was most representative of this portion of the flow system.

Reaction Paths

The injection of surface water into the three representative wells was simulated. As stated above, data from the City of Tampa's public supply system was used to characterize injection water. Figures 2.2 through 2.4 are a series of stability diagrams of the Fe - S system for wells DV-1, TR 5-1, and TR 3-3, respectively. Each well has six diagrams. Diagram (A) depicts the mineral stability fields for the Fe-S system in the storage zone in contact with unmixed storage-zone water. The square shows where the log activity of the sulfate/sulfide ratio versus pH of the analyses for unmixed storage-zone water plots. Diagram (B) is unmixed storage-zone water but the scale for the y axis is magnified to focus on the pyrite stability field. The scale remains magnified for diagrams (C) through (F), which depict stability fields of minerals in contact with injection/storage-zone water mixtures with ratios of 1×10^2 to 1, 1×10^5 to 1, 1×10^9 to 1, and 1×10^{15} to 1, respectively. The log activity of the sulfate/sulfide ratio versus pH of storage-zone water and of the corresponding injection/storage-zone water mixture is plotted on each diagram.

pH was not relevant in determining pyrite stability because pH of the storage-zone water, injection water, and mixtures of the two, encompassed a narrow range that was within the pH

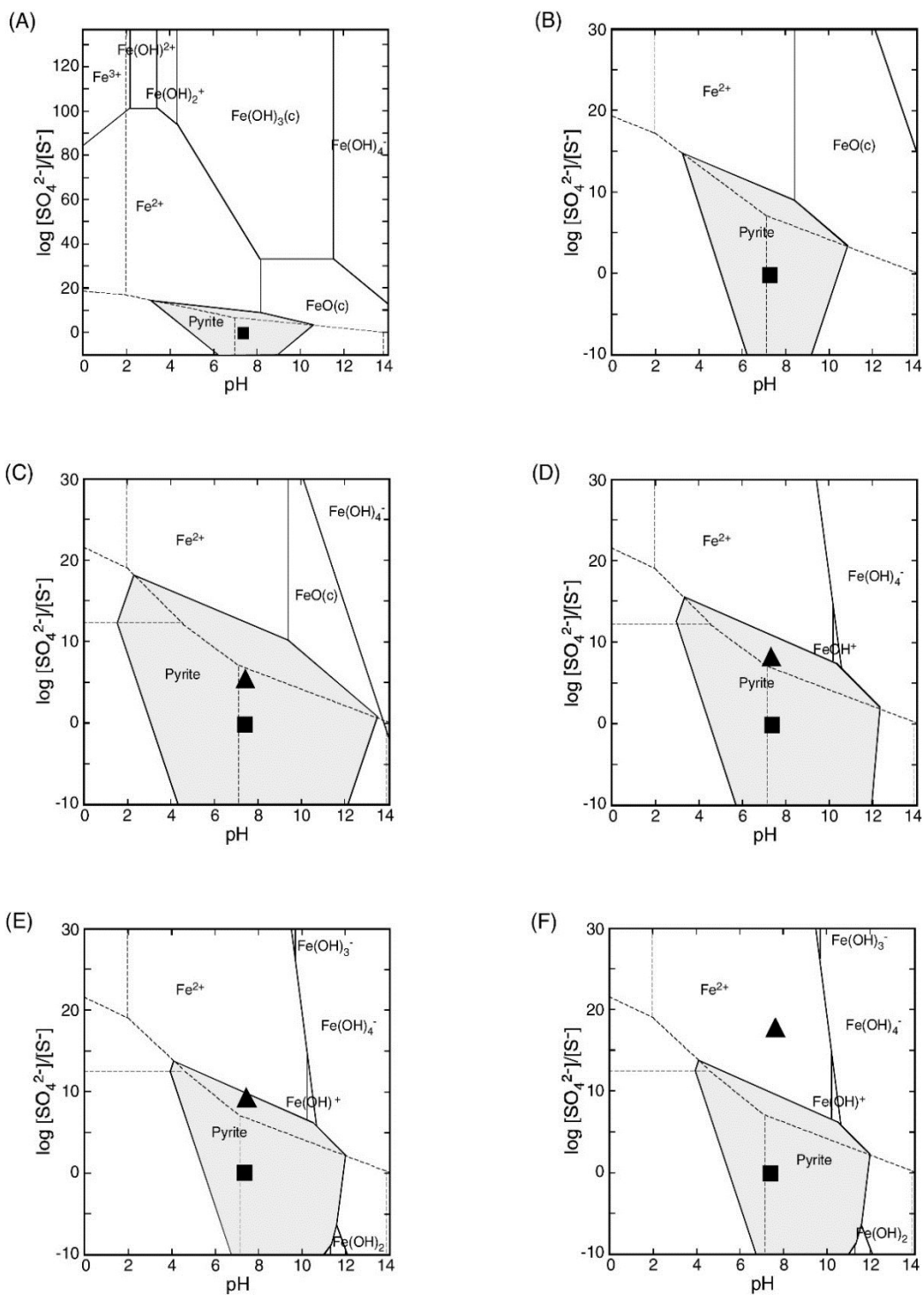


Figure 2.2. Fe-S stability diagrams showing pyrite stability during simulated injection of surface water into DV-1. The unmixed storage-zone water and the mixture of injection/storage-zone water plot as a square and a triangle, respectively. (A) Storage-zone water. (B) Magnification of the pyrite stability field in (A). (C), (D), (E), and (F) Injection/storage-zone water mixtures of 1X102 to 1, 1X105 to 1, 1X109 to 1, and 1X1015 to 1, respectively.

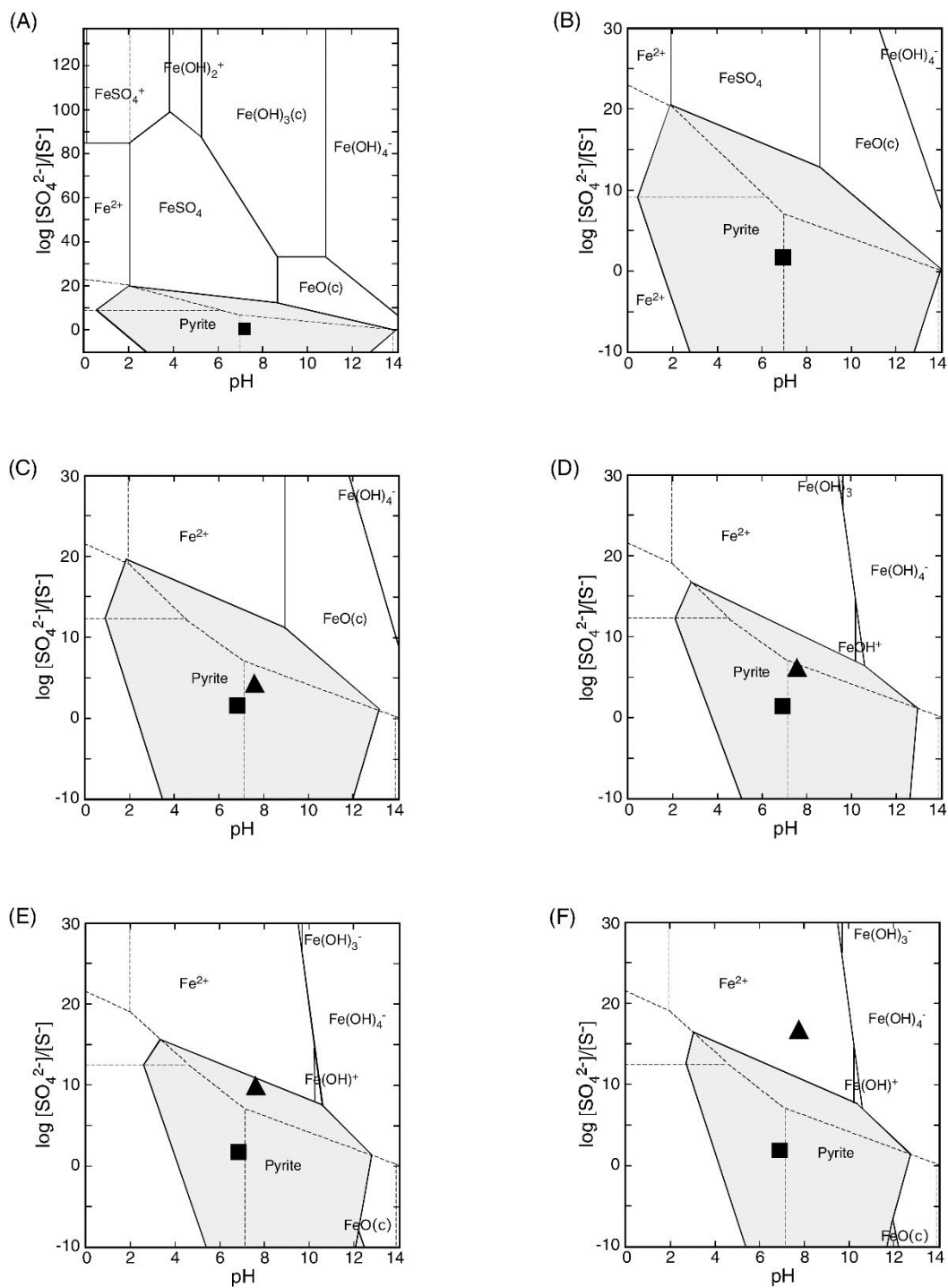


Figure 2.3. Fe-S stability diagrams showing pyrite stability during simulated injection of surface water into TR 5-1. See the caption for Figure 2.2 for an explanation of each diagram.

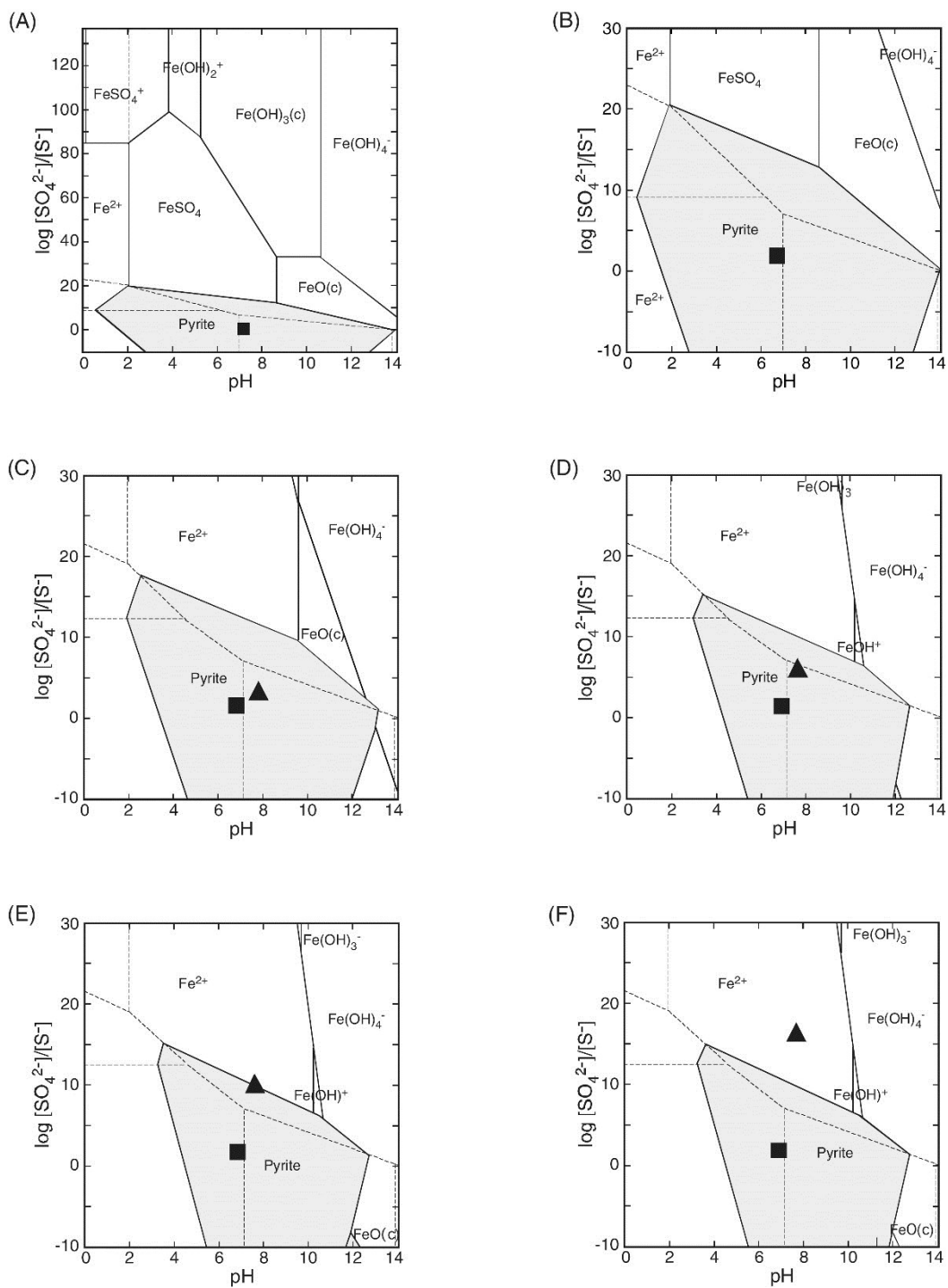


Figure 2.4. Fe-S stability diagrams showing pyrite stability during simulated injection of surface water into TR 3-3. See the caption for Figure 2.2 for an explanation of each diagram.

dimension of the pyrite stability field.

The reaction paths for all three wells were fairly similar. Pyrite was stable in contact with the storage-zone water in all three wells (Figures 2.2 A, B through 2.4 A, B). Between injection/storage-zone water mixing ratios of 1×10^2 to 1 and 1×10^5 to 1, the waters plotted higher in the pyrite stability field due to increasing proportions of oxygenated injection water (Figures 2.2 C, D through 2.4 C, D). At a mixing ratio of 1×10^9 to 1, the limit of pyrite stability was approached and beyond this, pyrite became unstable (Figures 2.2 E, F through 2.4 E, F). Regarding variation in pyrite stability field size, the low sulfate concentration for storage-zone water in DV-1 (0.13 mg/L) (Figure 2.2 B) resulted in a smaller field than that of TR 5-1 (Figure 2.3 B) and TR 3-3 (Figure 2.4 B) with sulfate concentrations of 1,531 mg/L and 1,228 mg/L respectively. For DV-1, the field increased in size from storage-zone water to water with a mixing ratio of 1×10^2 to 1 (Figure 2.2 C), as low sulfate storage-zone water was mixed with injection water with a sulfate concentration of 114 mg/L. Between mixing ratios of 1×10^2 to 1 and 1×10^5 to 1, the field size decreased for DV-1 (Figures 2.2 C, D). Although the sulfate concentration had stabilized, the iron concentration declined as storage-zone water, with an iron concentration of 0.4 mg/L, was mixed with injection water with an iron concentration of 0.1 mg/L. Beyond a mixing ratio of 1×10^5 to 1, field size did not change because sulfate and iron concentrations stabilized (Figures 2.2 E, F).

For TR 5-1 (Figure 2.3) and TR 3-3 (Figure 2.4), pyrite stability field size decreased from the unmixed storage-zone water to a point at or before the 1×10^9 to 1 mixture because the high sulfate concentration of the storage zone waters (1,531 mg/L and 1,228 mg/L respectively) was diluted by larger volumes of lower sulfate injection water.

Iron did not have a significant impact on pyrite stability field size for these wells because

the iron concentrations of injection and TR 5-1 storage-zone water were equal (0.10 mg/L).

Although the iron concentration of TR 3-3 storage zone water (0.06 mg/L) was lower than that of injection water (0.1 mg/L), the much greater magnitude of changes in sulfate concentrations as storage-zone and injection waters were mixed, overshadowed the effect of changes in iron concentrations.

Reaction Paths and Arsenic Occurrence

That pyrite in limestone was stable in contact with storage-zone water for all three wells indicated that redox conditions in the Suwannee Limestone were reducing. As stated previously, arsenic in the Suwannee Limestone is concentrated in framboidal pyrite (Arthur *et al.*, 2003; Price and Pichler, 2002; Arthur *et al.*, 2002). Because modeling shows that pyrite is stable in limestone in contact with unmixed storage-zone water for all three wells, the arsenic concentration in water in the wells should be very low. This was verified by the analysis of arsenic in samples from the wells, which indicated arsenic concentrations less than or equal to 0.036 µg/L (Table 2.1).

As the injection/storage-zone water ratio increased, redox conditions became more oxidizing, and the mixtures plotted higher in the pyrite stability field. At injection/storage zone water mixing ratios above 1×10^9 to 1, pyrite became unstable and dissolved. The result of dissolution is thought to be the release of arsenic immobilized in pyrite into solution. The reaction for pyrite oxidation is: $\text{FeS}_2 + 7/\text{O}_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$. When this occurs, ferrous iron, sulfate, and arsenic associated with the pyrite are released from limestone into storage-zone water. While increases in arsenic and ferrous iron have been observed in water recovered from ASR systems, along with a subsequent decrease in DO (Saks and Tihansky, 1996; Arthur *et al.*,

2002), an increase in sulfate is difficult to detect because of high background concentrations.

Hydrous Ferric Oxides and Arsenic Occurrence

Iron can precipitate from solution to form colloidal and suspended oxide, hydroxide, and oxyhydroxide phases known as HFO (HFOs, $\text{FeOOH} \cdot n\text{H}_2\text{O}$). HFO are highly soluble under acidic conditions but nearly insoluble at near-neutral pH (Mirecki, 2002). Due to large specific surface areas, they readily adsorb metals from solution (Bethke, 1996). Ferrihydrite for example, can have arsenic concentrations greater than 5 wt. % (Dzombak and Morel, 1990). A mineralogical investigation of the Suwannee Limestone found HFOs in only three core samples out of over 300 analyzed (Price and Pichler, 2002). These occurred as oxidation halos around framboidal pyrite and could have resulted from pyrite oxidation during the drilling process. HFO would not be common in the reducing conditions of the storage zone because they are generally stable only in oxidizing environments (Pichler *et al.*, 1999). This is apparent in Figures 2.2A through 2.4A where HFO stability fields are in the portion of the diagrams that is significantly more oxidized than the pyrite stability field.

It has been suggested that when pyrite is oxidized and arsenic is released, arsenic could complex with HFO which would remove it from solution, and under the appropriate conditions, HFO could dissolve and release arsenic to solution. Figures 2.2 through 2.4 show that HFO is not stable in the full range of waters from unmixed storage-zone water to nearly pure injection water. This indicates that arsenic could not be removed from solution by HFO because it is not stable in oxidized mixtures where dissolved arsenic is present.

Investigations by a number of researchers including Stuyfzand (2001), Pyne (2005), Mirecki (2006), and others support a hypothesis where the complexation of arsenic by HFO

during injection of oxygenated surface water and dissolution of HFO and release of arsenic into solution upon recovery of stored water is central to explaining arsenic mobilization during ASR. This hypothesis has gained widespread acceptance and is a cornerstone of the investigations in Chapters 3 and 4 of this dissertation. There are a number of explanations for the contradictions regarding HFO stability between the results of this investigation and the work of the other investigators. An important possibility is that the focus of geochemical modeling in this investigation was on demonstrating that pyrite in the vicinity of the ASR well would dissolve as oxygenated surface water replaced native groundwater in the storage zone. The role of HFO in complexing with and releasing arsenic during injection and recovery was outside the scope of the investigation. As a result, studies of the stability of HFO during the geochemical modeling that could have resulted in refinements of the HFO stability fields that may have supported their role in complexation and release of arsenic, were not conducted.

Microbiological Activity and Pyrite Stability

It is difficult to determine whether microbes have a significant role in pyrite oxidation during surface water injection. The authors speculate that the role of microbes would not be important in the immediate vicinity of an ASR well. This is because the pyrite oxidation potential of the ozonated and chloraminated injection water as well as its toxicity to microbes would be high when it initially contacts storage-zone limestone. As the injection water moves further into the storage zone, its potential to oxidize pyrite and its toxicity to microbes would probably diminish rapidly. How rapidly depends on the injection water's initial concentration of chloramines and degree of ozonation. At some distance from the injection well, the reduced toxicity of the injection water and the presence of nutrients in the injection water could stimulate

microbes that would be capable of oxidizing pyrite.

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CHAPTER THREE:

**THE IMPORTANCE OF MAINTAINING A ZONE OF STORED WATER TO
MINIMIZE ARSENIC IN WATER RECOVERED FROM ASR SYSTEMS -
RESULTS FROM LONG-TERM CYCLE TESTING IN TWO ASR WELLFIELDS**

Abstract

Pyne (2005) proposed that creating a zone of stored water of substantial volume in ASR wells early in the cycle-testing process and maintaining it through each subsequent cycle, will cause arsenic concentrations in recovered water to decline with each cycle and eventually fall below the 10 µg/L arsenic MCL within a relatively small number of cycles. Pyne (2005) also predicted that if wells are over-recovered so that stored water is depleted and water consisting of mixed stored water and native groundwater is brought to the vicinity of the well, arsenic concentrations in recovered water are likely to increase significantly. The objective of this study was to determine the validity of these predictions through the analysis of long-term cycle test data from wells in two ASR wellfields in west-central Florida. The wellfields are owned and operated by the City of Tampa and the Peace River Manasota Regional Water Supply Authority (Peace River Authority) and consist of eight and 12 wells, respectively. The City of Tampa and Peace River Authority's ASR wells had undergone 11 cycles and 10 cycles, respectively, through the end of the period of investigation in 2011.

Injection/recovery volumes for each cycle for each well were tracked to determine whether a substantial zone of stored water was maintained for each cycle or if it was depleted so that mixed stored water and native groundwater was brought back to the well. From this analysis, each well was assigned to one of two groups: the “storage zone maintained group” where substantial volumes of stored water were established in early cycles and maintained through the period of investigation, or the “storage-zone depleted group” where volumes of stored water were either established in later cycles and/or were depleted then re-established during the period of investigation

Water samples collected during each recovery event were analyzed for arsenic. Graphs were constructed for each wellfield that showed the maximum arsenic concentrations that occurred during recovery for each cycle for the storage-zone maintained group vs the storage-zone depleted group. For each cycle, means of the combined maximum arsenic concentrations were calculated for each group and exponential trendlines were fitted for comparison through successive cycles. Means of the maximum arsenic concentration means for all cycles for the storage-zone maintained and storage-zone depleted groups were compared using a two-tailed t -test with unequal variances to determine whether the means represented different populations.

Results of these analyses verified original predictions demonstrating that maximum arsenic concentrations for storage-zone maintained wells were nearly always considerably lower in each cycle and declined below the MCL after fewer cycles than those of storage-zone depleted wells. Results of two-tailed t -tests showed that means of the maximum arsenic concentration means for the two groups of wells for each wellfield were of different populations.

Introduction

Pyne (2005) has proposed that establishing a zone of stored water and replacing native groundwater in the vicinity of an ASR well by injecting a substantial volume of water early in the cycle-testing process and maintaining it through each subsequent cycle, will cause arsenic concentrations in recovered water to decline with each cycle and eventually fall below the arsenic 10 mg/L MCL. Pyne (2005) also predicted that if the well is over-recovered to the degree that the stored water is depleted and water consisting of mixed stored water and native groundwater is brought to the vicinity of the well, arsenic concentrations are likely to substantially increase.

The objective of this study was to use long-term cycle test data from wells in the City of Tampa and Peace River Authority ASR wellfields (Figure 3.3) to show that if a zone of stored water is established and maintained in ASR wells through successive cycles, arsenic concentrations generally decline faster and decline to lower levels than if a zone of stored water is not established or is established then depleted. An additional objective is to show that if the well is over-recovered to the degree that the zone of stored water is depleted and mixed stored water and native groundwater is brought back to the well, arsenic concentrations are likely to substantially increase. Detailed information on the ASR wellfields is provided in Chapter 1.

Current Conceptualization of Arsenic Mobilization

Contributions to the current conceptualization of arsenic behavior throughout ASR recharge, storage, and recovery phases have been made by a number of investigators (Stuyfzand, 2001; Mirecki 2006; Pyne (2005); SWFWMD 2007b). Pyne (2005) provided a conceptual geochemical and hydrogeological model of the processes that occur around an ASR well during

recharge, storage, and recovery. The basis of the model is the division of the storage zone into three distinct sub-zones; the proximal zone, storage zone, and buffer zone (Figure 3.1). The proximal zone encompasses an area of up to roughly 10 m from the ASR well. It is an area of high geochemical and microbial reactivity, potentially driven by a high oxidation/reduction potential (ORP). Water quality gradients are potentially steep, with ORP typically dropping from positive to negative in a relatively short period of time. Geochemical and microbial reactivity also decline exponentially with distance. Consequently, the reactivity of the storage zone is greatest near the well, diminishing with increasing distance.

Beyond the proximal zone is the storage zone where geochemical and hydraulic gradients are reduced and water quality changes are less pronounced. The stored water volume typically extends several hundred feet from the ASR well. During the initial ASR cycle, water quality changes are at a maximum. With successive cycles at approximately the same storage and recovery volumes, the zone of stored water around the well gradually becomes purged of native groundwater. At the edge of the storage zone is the beginning of the buffer zone surrounding the well, typically at a radial distance of several hundred feet. The buffer zone separates the stored water from the surrounding water in the aquifer and is comprised of a mixture of stored water and surrounding native groundwater. Depending upon differences in quality between the stored water and native groundwater, water quality changes in the buffer zone may be substantial. Water quality deterioration may occur rapidly if the buffer zone is brought back to the ASR well.

According to Mirecki (2006) and Pyne (2005), when oxygenated surface water is injected into the proximal zone, the elevated dissolved oxygen reacts with available arsenic-bearing pyrite in voids and fractures along flow paths. This results in the oxidation of pyrite, which releases iron, sulfur, and arsenic into solution. In addition, dissolved iron in the injection water

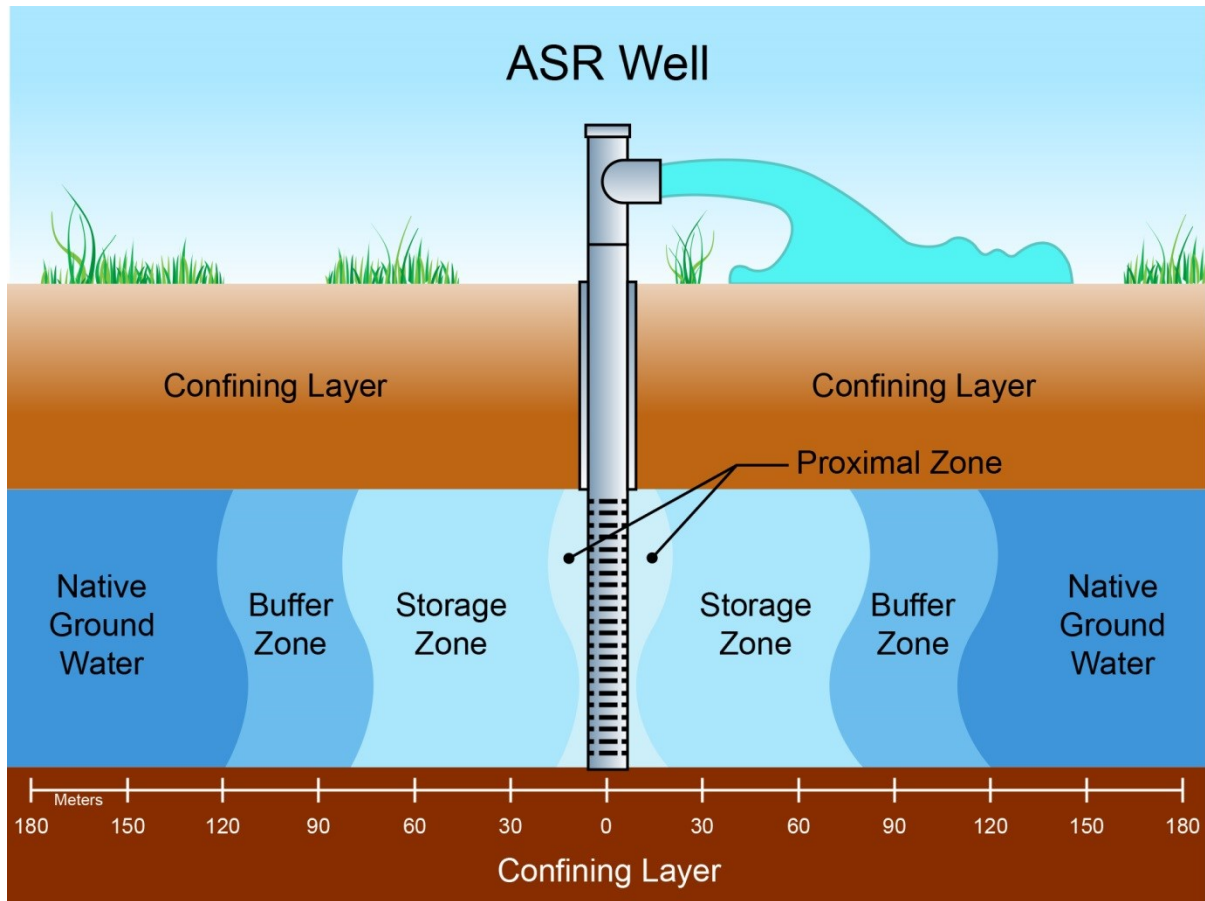
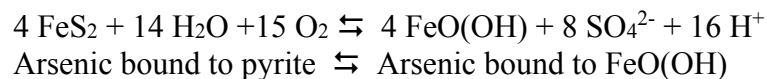


Figure 3.1. The proximal, storage, and buffer zones within an ASR system (modified from Pyne, 2005).

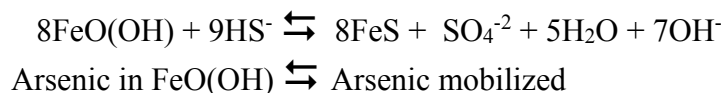
and iron released during pyrite oxidation re-precipitate locally as amorphous hydrous ferric oxide (HFO) as depicted in the reaction:



The HFO serve as complexation sites, which sequester all dissolved arsenic species, thereby reducing the concentration of arsenic in groundwater in the proximal zone (Vanderzalam *et al.*, 2011).

According to Mirecki (2006) and SWFWMD (2007b), during storage and recovery, the aquifer redox environment in the storage zone evolves from oxic, through anoxic, to sulfate

reducing conditions (approximately -200 mV) where dissolved hydrogen sulfide is present. HFO are not stable in this redox environment. The HFO undergo reductive dissolution and the complexed arsenic is released into solution, according to the reaction:



The arsenic in solution is then captured by the ASR well and brought to the surface in the recovered water. These findings are consistent with bench-scale studies conducted by Arthur et al. (2005a; 2005b) and field studies by Vanderzalm et al. (2007).

Methods and Results

The volume of water recharged and recovered for each well for each cycle was obtained from the Florida Department of Environmental Protection (FDEP) Oculus Electronic Document Management System and the 2010 annual reports for each of the wellfields (CH2MHILL, 2011a; 2011b). In total, there were data for 10 cycles for the wells at the City of Tampa ASR Wellfield and 9 cycles for the wells at the Peace River Authority's ASR wellfield. Injection/recovery volumes for each well were carefully tracked to determine whether the volume of stored water was maintained for each cycle or if it was depleted so that the buffer zone was brought back to proximal zone surrounding the well. From this analysis, each well was assigned to one of two groups: the "storage-zone maintained group" where a substantial volume of stored water was established in early cycles and largely maintained through the period of investigation, or the "storage-zone depleted group" where a substantial volume of stored water was either established in later cycles and/or was depleted and re-established during the period of investigation.

Arsenic concentration data from water samples obtained from each well during the recovery periods of each cycle were obtained from the FDEP Oculus Electronic Document

Management System and the 2010 annual reports for the wellfields (CH2MHILL 2011a, CH2MHILL 2011b). Arsenic data were not available for wells in either wellfield for the first cycle. Graphs were constructed for each wellfield that showed the maximum arsenic concentration that occurred during recovery for each cycle for the storage-zone maintained group vs the storage-zone depleted group. For each cycle, the mean of the combined maximum arsenic concentrations was calculated for each group and exponential trendlines were fitted for comparison through successive cycles.

The means of the maximum arsenic concentration means for all cycles for the storage-zone maintained and storage-zone depleted groups were compared using a two-tailed *t*-test with unequal variances to determine whether the means represented different populations.

Stored-Water Volume

Tables 3.1 and 3.2 show the volume of stored water maintained in each ASR well for each cycle. A positive value, for example 20 million gallons, indicates that the volume of stored water at the end of that cycle was 20 million gallons. A value of zero indicates that there was no stored water at the end of the cycle because it had been completely recovered. A negative value, for example -20 million gallons, indicates that all the stored water was completely recovered and an additional 20 million gallons of mixed stored water and/or native groundwater in the buffer zone was recovered.

City of Tampa ASR Wellfield Table 3.1 shows the volume of stored water at the end of each cycle for the 8 wells in the City of Tampa ASR wellfield during the period of investigation. The storage-zone maintained group included wells 1, 2, 6, and 8. A substantial volume of stored water was established in cycles 2 or 3 for wells 1, 2, and 8 and cycle 5 for well 6, then

Table 3.1. Storage-zone volume for each well for each cycle. City of Tampa ASR Wellfield (million gallons).

Cycle	Storage-Zone Maintained				Storage-Zone Depleted			
	Well 1	Well 2	Well 6	Well 8	Well 3	Well 4	Well 5	Well 7
Cycle 1 ¹								
Cycle 2	23	-25	46	96	-4	-59	-83	-57
Cycle 3	73	49	-14	44	38	162	-91	140
Cycle 4	6	53	-6	56	0	12	-25	1
Cycle 5	21	120	29	76	-10	0	-66	3
Cycle 6	34	114	31	107	11	-7	-47	-14
Cycle 7	40	121	33	112	13	4	-37	6
Cycle 8	74	133	32	117	39	1	34	17
Cycle 9	85	149	28	100	39	-1	35	30
Cycle 10	157	235	86	182	127	72	106	95
Cycle 11	92	185	13	137	71	19	50	31

¹Data were not available for Cycle 1

maintained through cycle 11. The storage-zone depleted group included wells 3, 4, 5, and 7. A substantial volume of stored water was not established and maintained in these wells until cycle 6 for well 3, cycle 7 for well 7, cycle 8 for well 5, and cycle 10 for well 4.

Peace River Authority ASR Wellfield. Table 3.2 shows the volume of stored water at the end of each cycle for 10 wells in the Peace River Authority's ASR Wellfield during the period of investigation. Data from two additional wells in the wellfield were not used because they were backplugged during the period of investigation. The storage-zone maintained group included only well S-19. A substantial volume of stored water was established no later than cycle 2 in this well and was maintained through cycle 10. The storage-zone depleted group consisted of the remaining 9 wells. A substantial volume of stored water was established and maintained in the early cycles in these wells. However, in cycle 5 all of the wells were over-recovered and the volume of stored water was reduced significantly. The wells were again over-recovered in cycle 6, which completely depleted the stored water for all wells. Substantial volumes of stored water were not re-established in all of the wells until cycle 9. The volume of stored water increased significantly for all the wells in cycle 10.

Table 3.2. Storage-zone volume for each well for each cycle. Peace River Authority ASR Wellfield (million gallons).

Cycle	Storage-Zone Maintained	Storage-Zone Depleted								
		Well S-4	Well S-10	Well S-12	Well S-13	Well S-14	Well S-15	Well S-16	Well S-18	Well S-20
Cycle 1 ¹										
Cycle 2	73	30	21	4	15	17	-25	-10	5	60
Cycle 3	95	43	44	26	37	39	18	24	28	83
Cycle 4	112	9	60	44	53	54	66	43	45	99
Cycle 5	82	-42	30	18	23	23	36	13	14	68
Cycle 6	54	-13	-24	-92	-79	-95	-71	-110	-94	-50
Cycle 7	120	-23	-9	-14	-4	-16	-21	-17	4	-9
Cycle 8	137	27	-26	-45	-15	-94	-46	-95	-46	-46
Cycle 9	188	67	28	27	44	37	6	4	16	43
Cycle 10	229		69	52	83	63	30	29	41	85

¹Data were not available for Cycle 1

Comparing Arsenic Concentrations for the Storage-Zone Maintained and Storage Zone Depleted Groups

Tables 3.3 and 3.4 show the maximum arsenic concentrations that occurred during recovery for each cycle for each well and Figures 3.1 and 3.2 are graphs of those concentrations. In the figures, the maximum arsenic concentrations for the storage-zone maintained group are identified by green shades and those of the storage-zone depleted group are identified by red and brown shades. The mean of the maximum arsenic concentrations for each well for each cycle was calculated for each group and exponential trendlines were fitted for comparison through successive cycles.

City of Tampa ASR Wellfield. Table 3.3 and Figure 3.2 show that the maximum arsenic concentrations for each cycle for the storage-zone maintained wells 1, 2, and 8 were considerably lower and had much less variability through successive cycles than those of the storage-zone depleted wells. In addition, their maximum arsenic concentrations remained lower through successive cycles than those of the storage-zone depleted wells. Although well 6 is included in the storage-zone maintained group, its maximum arsenic concentration for each cycle was higher and showed a greater degree of variability than those of the other storage-zone

Table 3.3. Maximum arsenic concentrations during recovery events for each well for storage-zone maintained and storage-zone depleted wells. City of Tampa's ASR Wellfield ($\mu\text{g/L}$).

Cycle	Storage-Zone Maintained					Storage-Zone Depleted				
	Well 1	Well 2	Well 6	Well 8	Mean	Well 3	Well 4	Well 5	Well 7	Mean
Cycle 1 ¹										
Cycle 2	15	39	45	28	32	151	40	53	116	90
Cycle 3	45	27	66	49	47	83	25	70	-	59
Cycle 4	39	32	51	31	38	61	58	144	101	91
Cycle 5	20	11	25	22	19	34	37	48	52	43
Cycle 6	17	9	26	17	17	31	31	38	37	34
Cycle 7	17	9	38	15	20	24	35	35	34	32
Cycle 8	13	9	26	20	17	21	27	27	30	26
Cycle 9	11	11	22	13	14	19	21	28	29	24
Cycle 10	10	6	13	12	10	17	31	25	27	25
Cycle 11	13	6	15	26	15	22	24	30	26	25

¹Data were not available for Cycle 1

maintained wells. However, by cycles 10 and 11, maximum arsenic concentrations for well 6 were clustered with those of wells 1, 2, and 8.

Figure 3.2 shows that the exponential trend line of the means of the maximum arsenic concentrations for each cycle for the storage-zone maintained group was considerably lower than that of the storage-zone depleted group throughout the period of investigation. Although the distance between the trend lines decreased through successive cycles, the trend line of the storage-zone maintained wells was approximately 10 $\mu\text{g/L}$ lower than that of the storage-zone depleted wells in cycle 11.

Peace River Authority ASR Wellfield. Table 3.4 and Figure 3.3 show that the maximum arsenic concentrations for the only storage-zone maintained well, S-19, were considerably lower and had much less variability through successive cycles than those of the storage-zone depleted wells. For the storage-zone depleted wells, there was a marked spike in maximum arsenic concentrations in cycles 5 and 6. For the storage-zone maintained well S-19, the spike did not occur.

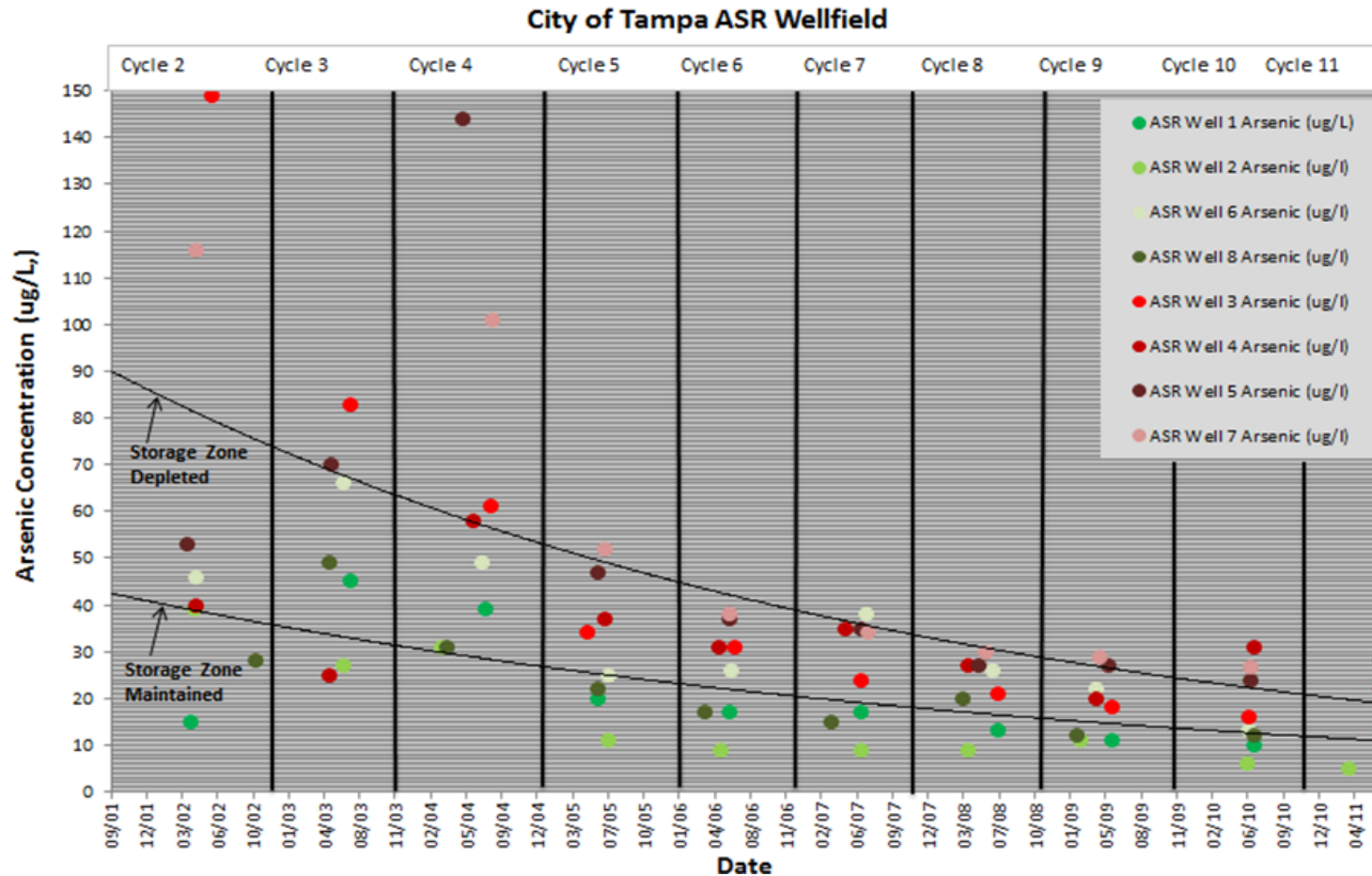


Figure 3.2. City of Tampa ASR Wellfield. Graph of maximum arsenic concentrations during recovery for each cycle for the storage-zone maintained wells (green shades) vs the storage-zone depleted wells (red and brown shades). An exponential trend line has been fitted to the mean of the maximum arsenic concentrations for each cycle for each group.

Table 3.4. Maximum arsenic concentrations during recovery events for each well for storage-zone maintained and storage-zone depleted wells. Peace River Authority ASR Wellfield 2 ($\mu\text{g/L}$).

Cycle	Storage-Zone Maintained		Storage-Zone Depleted									
	Well S-19	Mean	Well S-4	Well S-10	Well S-12	Well S-13	Well S-14	Well S-15	Well S-16	Well S-18	Well S-20	Mean
Cycle 1 ¹												
Cycle 2	53	53	48	96	55	51	114	66	108	88	39	74
Cycle 3	23	23	45	82	49	31	78	89	52	39	24	54
Cycle 4	19	19	32	62	42	32	59	32	31	29	24	39
Cycle 5	29	29	85	107	94	79	111	130	131	87	31	95
Cycle 6	18	18	75	57	51	54	61	115	109	87	22	70
Cycle 7	18	18	41	51	41	35	49	48	65	32	21	43
Cycle 8	8	8	35	24	25	21	19	31	32	36	15	27
Cycle 9	6	6	24	29	19	23	19	17	38	18	17	23
Cycle 10	3	3	19	14	12	11	11	10	10	11	11	12

¹Data were not available for Cycle 1

Figure 3.3 shows that the exponential trend line of the maximum arsenic concentration for each cycle for the storage-zone maintained well S-19 was considerably lower than the exponential trend line of the means of the maximum arsenic concentrations for each cycle for the storage-zone depleted group throughout the period of investigation. Although the distance between the trend lines decreased through successive cycles, the trend line for the storage-zone maintained well S-19 was approximately 10 $\mu\text{g/L}$ lower than that for the storage-zone depleted group in cycle 10.

Statistical Comparison of Arsenic Concentrations for the Storage-Zone Maintained vs Storage-Zone Depleted Groups. Table 3.5 shows the results of the comparison of the means of the maximum arsenic concentration means for all cycles for the storage-zone maintained and storage-zone depleted groups using a two-tailed t test with unequal variance. The results indicate that the means of the maximum arsenic concentration means for the two groups of wells for each wellfield were of different populations.

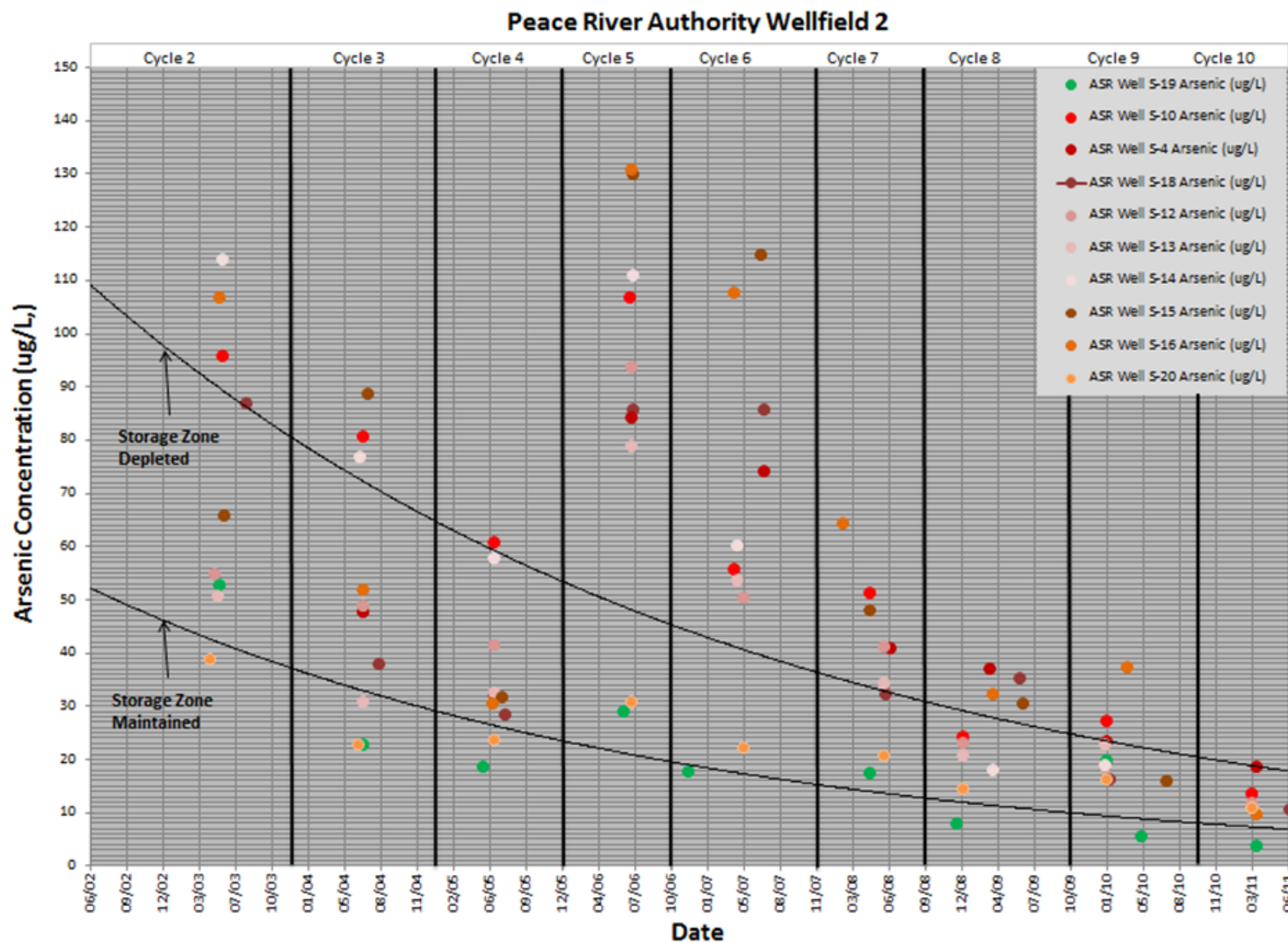


Figure 3.3. Peace River Authority ASR Wellfield 2. Graph of maximum arsenic concentrations during recovery for each cycle for the sole storage-zone maintained well (green shade) vs each of the storage-zone depleted wells (red and brown shades). An exponential trend line has been fitted to the mean of the maximum arsenic concentrations for each cycle for each group.

Table 3.5. Comparison of the means of the maximum arsenic concentration means for all cycles for the storage-zone maintained and storage-zone depleted groups using a two-tailed t-test with unequal variances.

ASR Wellfield	As Concentration (µg/L) Storage-Zone Maintained Group		As Concentration (µg/L) Storage-Zone Depleted Group		<i>p</i> -value
	Mean	SD	Mean	SD	
City of Tampa	19.2	10.3	42.3	22.7	0.009
Peace River Authority	20.0	15.0	50.1	25.1	0.006

Discussion

The results of this investigation verify the hypothesis that if a substantial volume of stored water is established and maintained in an ASR well, arsenic concentrations in recovered water generally decline with each cycle and decline more rapidly and to lower levels than for wells where a substantial volume of stored water is not established or if the well is over-recovered during a cycle to the degree that the stored water is completely depleted. This is because during injection of oxygenated water, when arsenic-bearing pyrite dissolves and releases arsenic into solution, HFO form in the proximal zone near the well and complex with available arsenic. As discussed previously, Mirecki (2006) states that during storage and recovery, the aquifer redox environment in the storage zone evolves from oxic, through anoxic, to sulfate reducing conditions (approximately -200 mV) where dissolved hydrogen sulfide is present. HFOs are not stable in this redox environment. The HFO undergo reductive dissolution and the complexed arsenic is released into solution, whereupon they are captured by the ASR well and brought to the surface in the recovered water.

The following modification to the recovery phase of this hypothesis is proposed based on the results of this investigation. During recovery, as water in the proximal and storage zones, which probably is less reduced than water in the buffer zone, is drawn toward the ASR well, only

a portion of the arsenic-bearing HFO in the proximal zone dissolves and releases arsenic into solution. Some of the HFO remains stable and retains its arsenic. As long as all of the stored water is not recovered and the more reduced water in the buffer zone is brought back to the proximal zone, it is unlikely that all of the HFO in the proximal zone dissolves. If all of the HFO did dissolve during recovery of only a portion of the stored water, there would be a major spike in arsenic concentrations in recovered water. Results from the storage-zone maintained groups for both wellfields show this does not happen.

If all the stored water in the proximal and storage zones is recovered, more of the reduced mixture of stored and native groundwater in the buffer zone will be brought to the proximal zone and most if not all of the HFO will dissolve and release arsenic into solution. This was demonstrated by the Peace River Authority's storage-zone depleted wells when a marked spike in maximum arsenic concentrations occurred due to the complete recovery of all the stored water and recovery of their buffer zones in cycle 6.

With each subsequent cycle as this process is repeated, more of the arsenic-bearing pyrite in the proximal zone that is exposed to injected water is removed as it dissolves and releases its arsenic to complex with HFO. Eventually, most of the exposed pyrite is dissolved from the proximal zone and arsenic concentrations in recovered water are likely to be near or below the MCL. However, arsenic concentrations may remain at this level indefinitely because as the limestone matrix is dissolved with each additional cycle, additional arsenic-bearing pyrite apparently becomes exposed and available for dissolution.

If a substantial volume of stored water is not established or if the well is over-recovered during a cycle to the degree that the stored water is completely depleted, arsenic concentrations may not decline with each cycle and can spike to very high levels. In addition, they will not

decline as rapidly or to levels as low as wells where a substantial volume of stored water is established and maintained. This is because when the mixture of stored water and native groundwater in the buffer zone, which is probably considerably more reduced than water in the storage zone, is brought into the proximal zone during recovery, it is likely that most or all of the arsenic-bearing HFO dissolves and releases arsenic into solution. Arsenic concentrations in storage-zone depleted wells will also eventually be in the range of the MCL. However, this is likely to happen after several more cycles than what was required for this to occur in the storage-zone maintained wells. The data presented below supports the conclusions stated above.

City of Tampa ASR Wellfield

Storage-Zone Maintained Wells. Substantial volumes of stored water for the storage-zone maintained wells 1, 2, and 8 were established in cycle 2 or 3 and maintained through cycle 11 and the maximum arsenic concentrations for these wells generally declined through cycle 10. Although well 6 was classified as a storage-zone maintained well, maximum arsenic concentrations for each cycle for this well were considerably elevated over those of the other wells, possibly because a substantial volume of stored water in this well was not established until cycle 5 and because the volume of stored water in this well was significantly lower than that of the other 3 wells. However, the maximum arsenic concentrations in this well reached 13 mg/L by cycle 10.

The maximum arsenic concentrations for each well increased in cycle 11 by anywhere from 3 µg/L to 12 µg/L, with the exception of well 2, which remained at 6 µg/L. It is likely that the increase occurred because the volumes of their storage zones were reduced by anywhere from 21 to 84 percent. This resulted in stored water that was probably more reduced being

brought into the proximal zone, which caused enhanced dissolution of HFO. Maximum arsenic concentrations declined to levels that were at or near the 10 µg/L MCL relatively rapidly. Well 2 dropped below the MCL by cycle 6, well 1 reached the MCL by cycle 10, and wells 6 and 8 came close to the MCL in cycle 10 with concentrations of 13 µg/L and 12 µg/L, respectively.

Storage-Zone Depleted Wells. For the storage-zone depleted wells 3, 4, 5, and 7, volumes of stored water between cycles 2 through 7 went through various combinations of not being established, being established then depleted, and being established at very low volumes, then depleted. As a result, maximum arsenic concentrations were highly variable in cycles 2 through 4 and spiked to high levels in wells 4, 5, and 7. Maximum arsenic concentrations were elevated over those of the storage-zone maintained wells (with the exception of well 6) in all cycles. Except for well 3, which had a maximum arsenic concentration of 17 µg/L in cycle 10, maximum arsenic concentrations for these wells never fell below 20 µg/L.

Statistical comparison of the maximum arsenic concentration means using a two-tailed *t*-test with unequal variance provided additional data that demonstrated the difference between the storage-zone maintained vs. storage-zone depleted wells. The results showed that the means of the maximum arsenic concentration means for each cycle for the two groups were of different populations

Peace River Authority ASR Wellfield

Storage-Zone Maintained Well. For the only Peace River Authority storage-zone maintained well, well S-19, a substantial volume of stored water was established in cycle 2 and except for cycles 5 and 9, maximum arsenic concentrations generally declined with each cycle, reaching 8 µg/L by cycle 8. The increase in the maximum arsenic concentration in cycle 5

probably occurred because the well was over-recovered and the volume of stored water was reduced by approximately 37 percent. However, the volume of stored water remained large at 82 million gallons.

Storage-Zone Depleted Wells. For the storage zone-depleted wells, the volume of stored water was depleted by a range of 31 to 85 percent in cycle 5, then completely depleted in cycle 6. This brought the more reduced water in the buffer zone into the proximal zone which caused enhanced dissolution of HFO. As a result, a very large spike in maximum arsenic concentrations occurred for all wells, with the exception of well S-4, which continued to decline. Although the wells continued to be over-recovered in cycles 7 and 8, arsenic concentrations declined rapidly. This may have been because so much of the arsenic that was exposed to injected water (as opposed to arsenic that is within the limestone matrix and probably isolated from injected water) had been dissolved and removed from the proximal zone in cycles 5 and 6 that very little remained for removal in the later cycles. Substantial volumes of stored water were re-established in all wells by cycle 9 and their volumes were increased considerably in cycle 10. In cycle 10, maximum arsenic concentrations declined to levels below, at, or slightly above the 10 µg/L MCL except for wells 4 and 10, which had concentrations of 19 µg/L and 14 µg/L, respectively.

Statistical comparison of the maximum arsenic concentration means using a two-tailed t test with unequal variance demonstrated the difference between the storage-zone maintained vs. storage-zone depleted wells. The results showed that the means of the maximum arsenic concentration means for each cycle for the two groups were of different populations

Operational Considerations

It may not be practical for operators of ASR wells to always maintain large-volumes of

stored water at the end of each recovery cycle. This is clear from an analysis of the operation of the Peace River Authority's ASR wells during the period of investigation. Prior to completion of an off-stream reservoir in 2010 with a storage capacity of 6 billion gallons, the quantity of water that was injected and recovered from the Peace River Authority ASR wells was directly dependent on the volume of flow in the Peace River. The majority of ASR recharge occurs during south and central Florida's June through September wet season, while recovery mainly occurs during the March through May dry season. During the period from 2006 through 2009, the region experienced a drought that resulted in a cumulative rainfall deficit of over 27 inches (SWFWMD Web Site, Hydrologic Data). Consequently, wet season withdrawals from the river for aquifer storage were curtailed because flow in the Peace River dropped below minimum regulatory levels. To meet regional demand, the ASR wells were over-recovered during these years and their stored water was depleted as shown in Table 3.2 for cycles 6, 7, and 8. The depletion of the stored water resulted in the spikes in arsenic concentrations that are apparent in Table 3.4 and Figure 3.3 in cycles 5 and 6.

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CHAPTER FOUR:
A MINERALOGICAL INVESTIGATION OF CORES IN AN ASR WELLFIELD
TO DETERMINE WHERE MOBILIZED ARSENIC IS PRECIPITATED

Abstract

A mineralogical investigation was conducted on cores obtained at 20 m (ASR core 1), 152 m (ASR core 2), and 452 m (ASR core 3) from operating ASR wells in Florida to determine where mobilized arsenic in limestone is precipitated during ASR. As arsenic-bearing pyrite dissolves during injection and arsenic is mobilized, the prevailing hypotheses are that it is either flushed away from the well to be precipitated distally, or rapidly complexed with hydrous ferric oxide (HFO) and precipitated locally. If arsenic is precipitated distally, reduced concentrations of elements found in pyrite, (iron, sulfur, arsenic, etc.) would be expected in ASR core 1 relative to more distant cores and there would be noticeable changes in the appearance of pyrite crystals in ASR core 1 due to enhanced oxidation. The results showed that the mean concentration of the elements was lowest in ASR core 2, which did not support distal precipitation. However, scanning electron microscopy identified well-defined pyrite framboids only in ASR core 3 while framboids in ASR cores 1 and 2 were less clear and distinct, indicating pyrite oxidation in cores closest to ASR wells.

Statistical comparison of concentrations of iron, sulfur, and arsenic between the ASR cores and 19 control cores not subject to ASR, showed that mean concentrations in ASR cores 1

and 2 were statistically similar to concentrations in control cores. This indicated that concentrations in ASR cores 1 and 2 had not been significantly reduced by ASR. The concentrations of elements were higher in ASR core 3 than in ASR cores 1 and 2 and control cores and statistically dissimilar to all but one control core. This indicated natural heterogeneity in ASR core 3 rather than diminution of concentrations in ASR cores 1 and 2 due to ASR. The statistical analysis supported local precipitation. Once arsenic is mobilized from dissolved pyrite, it is rapidly complexed with precipitated HFO near the well. As long as all stored water is not removed during recovery so that reduced native groundwater is brought back to the well, HFO remains stable and complexed with arsenic. The concentration of elements would not have been lowest in ASR core 1 for this reason and because calculations showed that the mass of arsenic removed during recovery events prior to coring was minor compared to the total in limestone surrounding the well.

The implications of this are that while large quantities of arsenic are present near the ASR well, only a small percentage may be available for dissolution. Most arsenic occurs with pyrite in limestone, which may insulate it from exposure to oxidized injection water. Water recovered from ASR wells may continue to have low concentrations of arsenic indefinitely because as limestone is dissolved, more pyrite is exposed and available for dissolution.

Introduction

A mineralogical investigation was conducted on three cores obtained at varying distances from operating ASR wells at the City of Tampa's ASR wellfield to determine where mobilized arsenic in limestone is precipitated during ASR. It has been widely accepted that the source of elevated concentrations of arsenic in water recovered from ASR wells is the dissolution of

framboidal pyrite in the limestone matrix (Arthur *et al.*, 2003; Price and Pichler, 2002; Price and Pichler, 2005).

As arsenic-bearing pyrite dissolves during ASR injection and arsenic is mobilized, the prevailing hypotheses are that it is either flushed away to be precipitated distally or it is rapidly complexed with hydrous ferric oxide and precipitated locally. If arsenic is precipitated distally, reduced concentrations of elements found in pyrite (iron, sulfur, arsenic, etc.) would be expected in cores closest to ASR wells relative to more distant cores and there would be noticeable changes in the appearance of pyrite crystals due to enhanced oxidation. If arsenic is precipitated locally, concentrations of iron, sulfur, and arsenic would not be reduced in cores closest to ASR wells relative to more distant cores. However, changes in the appearance of pyrite crystals might still be more pronounced relative to more distant cores due to enhanced oxidation.

Description of the Study Area

The study area encompasses an operational ASR wellfield within the City of Tampa as shown in Figure 1.2 and described in detail in Chapter 1. Figure 4.1 shows the locations of ASR wells and cores in the City of Tampa's ASR wellfield.

Conceptualization of Arsenic Mobilization

It was originally hypothesized that mechanical and chemical leaching from repeated injection and recovery of water in an ASR system would result in reductions in the concentration of elements found in pyrite (iron, sulfur, arsenic, etc.) and detectable changes in the appearance of pyrite crystals in the limestone matrix in close proximity to ASR wells (SWFWMD, 2007). The closer the matrix was to an ASR well, the more pronounced the effects would be. It was thought that when oxygenated water was injected into the reducing environment around the ASR

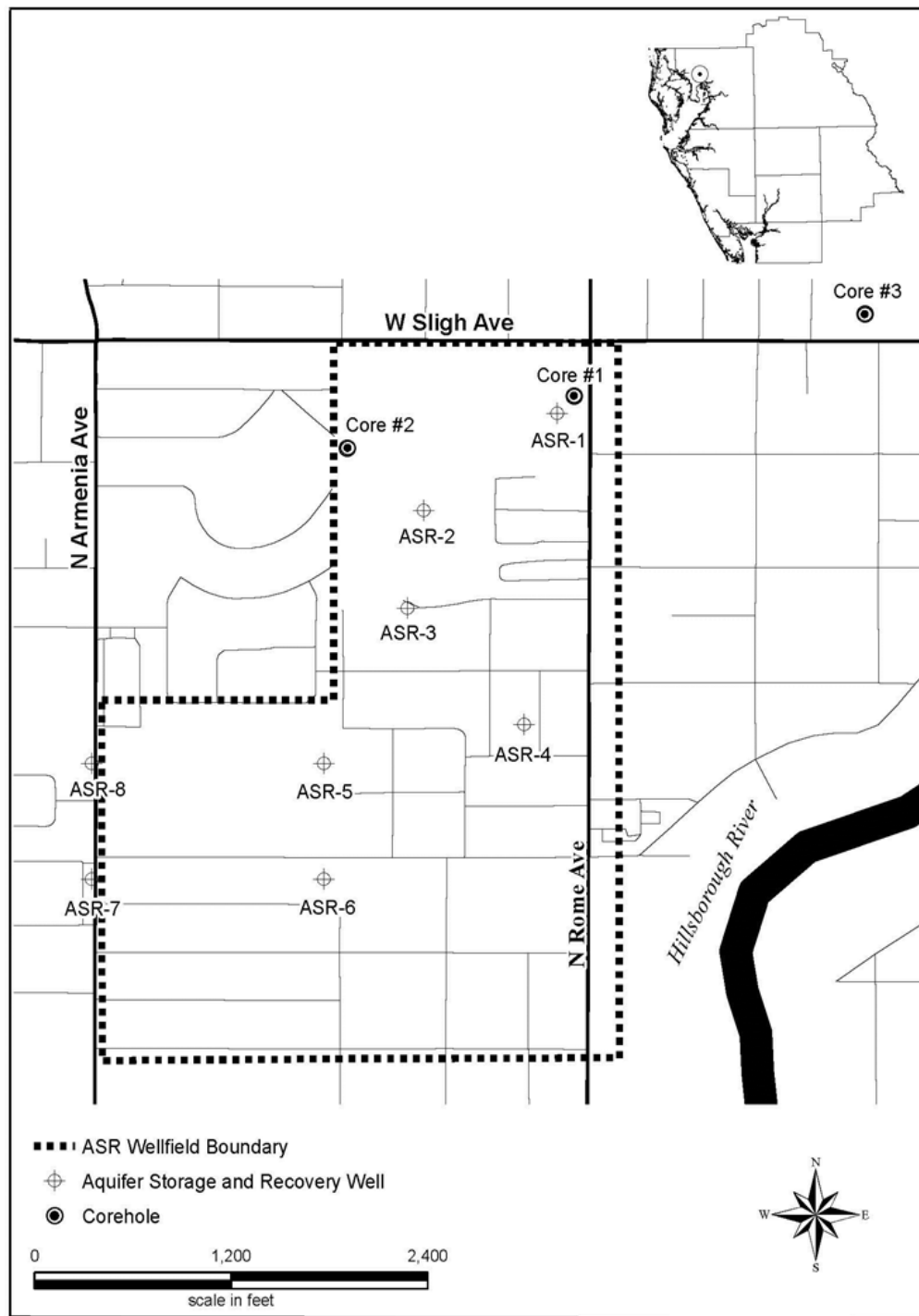


Figure 4.1. Location of ASR wells and core holes within the City of Tampa's ASR wellfield.

well, arsenic-bearing pyrite would dissolve and release arsenic into solution. The mobilized arsenic would be flushed laterally away from the well and would precipitate at some distance from it. Any dissolved arsenic near the well would be slowly purged from the aquifer during ASR operations as long as injection and recovery volumes of successive cycles remained relatively constant (SWFWMD, 2007a).

An updated conceptualization of arsenic behavior throughout ASR recharge, storage, and recovery phases has been developed by a number of investigators including Stuyfzand (2001), Mirecki (2006), and Pyne (2005). Pyne (2005) provided a conceptual geochemical and hydrogeological model of the processes that occur around an ASR well during recharge, storage, and recovery. The basis of the model is the division of the storage zone into three distinct sub-zones; the proximal zone, the main storage zone, and the buffer zone (Figure 3.1) as explained in detail in Chapter 3.

During injection of oxygenated surface water, the redox environment in the vicinity of the well (proximal zone) is altered from reducing to oxidizing and iron, sulfur and arsenic are released into solution as pyrite becomes unstable and dissolves. The iron re-precipitates locally as amorphous hydrous ferric oxides (HFO), which serve as complexation sites to sequester all dissolved arsenic species. During recovery, HFO undergoes reductive dissolution and the complexed arsenic is released into solution, which leads to an increase in the concentration of arsenic in recovered water. Additional detail on this process is provided in Chapter 3.

Methods and Results

Determining Core Hole Locations.

The initial design for the core locations was to locate them near a single ASR well and extend them along a radius from the well at increasing distances. This would avoid the effects of adjacent ASR wells, which would complicate the analysis. Both the radial design for the core locations and avoiding the effects of adjacent ASR wells proved not to be possible because the cores had to be focused around ASR well 1, which was the initial test well in the wellfield that had experienced the most injection/recovery cycles. Because ASR well 1 had to be included and the difficulty of obtaining permission at sites to obtain cores, the potential effects from ASR well 2 could not be eliminated from the analysis.

To increase the probability of identifying significant differences between cores, it was decided to obtain a core from an area strongly affected by injection water, an area completely unaffected by injection water, and an area that might be affected to a minimal degree. To determine these locations, an analysis was done to estimate the volume of the aquifer around ASR wells 1 and 2 that would be occupied by and therefore affected by the injected water stored in the aquifer. The radius of the distance from the ASR well to the edge of this zone was calculated using the formula for the volume of a cylinder. The maximum volume of injected water for a cycle at the time was 190 million gallons for ASR well 1 and 150 million gallons for ASR well 2. Porosity was estimated at 25 percent and thickness of the storage zone was 33 m. The assumption was made that the aquifer was homogeneous with no vertical movement of injected fluid. The regional potentiometric surface was also analyzed to ensure that the unaffected well would be upgradient of the ASR wellfield. The calculation suggested that the

distances from ASR wells 1 and 2 to the edge of the zone of stored water for the injection event with the largest volume, were 167 m and 148 m, respectively. The analysis of the regional potentiometric surface showed that the hydraulic gradient across the ASR wellfield is relatively flat; sloping to the southwest at approximately 0.57 m/km. Based on this information, locations for the three core holes were chosen (Figure 4.1). The location of ASR core 1 was chosen to be strongly affected and was within 20 m of ASR well 1. The location of ASR core 3 was chosen to be completely unaffected and was approximately 454 m up-gradient of ASR well 1. The location of ASR core 2 was to be minimally affected and was approximately 384 m down-gradient from ASR well 1 and 152 m down-gradient of ASR well 2. The next closest ASR well in the wellfield, ASR well 3, was located down gradient of all three core holes; approximately 457 m from ASR core 1, 335 m from ASR core 2, and 823 m from ASR core 3. All three cores were considered to be well outside of the area where they would be affected by water recharged from ASR well 3. The remaining five ASR wells were located down gradient of ASR well 3 and much further away from the cores.

Construction Specifications and Injection/Recovery History for ASR Wells 1 and 2

ASR well 1 was constructed in 1995 and was drilled to a depth of 117 m bls with an open-hole interval that extended from 90 to 117 m. Although the well extends into the upper Ocala Limestone (late Eocene), most of the open hole interval is within the lower Suwannee Limestone (early Oligocene) (Peer Consultants, CH2MHill, 1995), which is the storage zone for most ASR wells in Florida. ASR well 2 was constructed in 2000 and was drilled to a depth of 111 m bls with an open hole interval that extended from 91 to 111 m. Most of the open-hole interval is within the Suwannee Limestone. Water within the Suwannee Limestone in these wells

is fresh with a total dissolved solids concentration of approximately 232 mg/L. Table 4.1 shows the recharge/recovery history of ASR wells 1 and 2 up to the drilling of the cores in 2004. The data were obtained from a number of sources including Arthur, *et al.*, 2000, the Florida Department of Environmental Protection's Oculus data base, and CH2MHill (2011a).

For ASR well 1, the cycles labeled A, B, and C were initial test cycles completed following construction of the well in 1995. Cycles 1 through 4 were conducted for all 8 ASR wells after the other 7 wells were constructed in 2000. Although the data are incomplete, for ASR well 1, at least 452 mg was injected and at least 538 mg was recovered prior to drilling of the cores. For ASR well 2, at least 415 mg was injected and at least 387 mg was recovered prior to drilling of the cores.

Table 4.1. Injection/recovery history of ASR wells 1 and 2 prior to drilling of the cores.

Cycle	Injection Initiated	Recovery Initiated	Injection Volume (million gal)	Recovery Volume (million gal)
ASR 1				
A	July 1996	July 1996	18	18
B	Sept. 1996	March 1997	99	92
C	August 1998	Dec 1997	?	?
1	?	Oct 2000	?	?
2	Sept. 2001	March 2002	38	144
3	June 2002	April 2003	154	104
4	August 2003	Feb 2004	143	210
Total			452+	568+
ASR 2				
1	?	?	?	?
2	Sept 2001	March 2002	121	146
3	June 2002	April 2003	153	104
4	August 2003	February 2004	141	137
Total			415+	387+

Drilling of Core holes and Collection of Cores

ASR cores 1 and 2 were drilled in February 2004 and ASR core 3 was drilled in December of 2004. The entire ASR storage zone within the Suwannee Limestone, which is approximately 33 m thick, was cored at each location. Cores were collected through a 7.6 cm

diameter NQ wireline system on 1.5 m intervals. The rotary drilling operation uses direct circulation of clean water to advance the drill pipe, which produces a core that is retrieved from the bottom of the pipe with a wireline cable winch.

Selection of Samples

A sample was collected from each core at intervals of approximately 3 m, to ensure representation of the entire Suwannee Limestone interval. Twelve samples were collected from each core. However, because Price and Pichler (2005) determined that pyrite in the Suwannee limestone is not uniformly distributed but is concentrated along fracture surfaces, it was concluded that the collection of samples only at 3 m intervals could result in significantly underestimating the pyrite and arsenic content of the cores. To avoid this problem, special interest (SI) samples were collected from portions of the cores that had the potential for high arsenic concentrations, i.e., organic layers, areas with abundant visible pyrite, areas that were clearly oxidized, and fracture surfaces. The number of SI samples collected from the cores was eight for core 1, two for core 2, and eight for core 3. A total of 54 samples were collected from all three cores.

Determination of Arsenic, Iron and Sulfur Concentration of the Cores

The total arsenic content of the core samples was determined for all samples through Hydride Generation-Atomic Fluorescence Spectrometry (AFS) and the total iron and sulfur content was determined using an Inductively Coupled Plasma-Optical Emission Spectrometry system. Table 4.2 is a summary the arsenic, iron, and sulfur concentrations for all of the samples. The mean of the values is provided for each element. ASR core 2, located 384 m from

Table 4.2. Arsenic, iron, and sulfur concentrations of samples from ASR cores 1, 2, and 3 (mg/kg).

Sample Depth (m)	ASR Core 1			ASR Core 2			ASR Core 3		
	As	Fe	S	As	Fe	S	As	Fe	S
88.4	0.64	900	5300	1.96	5400	6200	7.78	3700	9300
89.3 (SI)							2.89	1100	6100
89.6 (SI)				2.87	1100	5800			
90.2 (SI)	1.86	1300	6800						
91.4	1.54	900	6800	2.06	1000	5400	3.89	1700	6600
93.3 (SI)	1.5	1400	8400						
94.2 (SI)	15.98	4200	13200						
94.5	6.21	1600	8200	2.75	900	3700	5.94	1000	6300
96.0 (SI)							15.23	3600	11000
96.3 (SI)							19.07	3100	9400
96.6 (SI)	4.32	1000	6900				8.43	1700	10800
96.9 (SI)	6.99	1000	6200						
97.5	6.55	800	6000	1.37	1200	4900	4.6	100	3600
100.6	6.21	2300	6600	3.46	1400	5500	36.12	3400	9600
102.1(SI)							17.82	2400	7300
103.6	0.57	1000	4000	1.15	700	5100	1.33	700	4700
105.2 (SI)	0.24	800	3500						
106.4 (SI)	0.67	800	4200						
106.7	0.01	19700	3000	1.77	1200	8200	1.82	100	4600
108.2 (SI)							1.48	900	3400
109.7	0.44	3400	2900	1.75	300	3800	6.39	6000	14500
112.5 (SI)	2.97	12400	18900						
112.8	11.24	6300	11900	0.38	100	2800	1.32	600	3800
114.3 (SI)							1.53	1100	4000
115.8	1.35	500	4400	0.65	2300	5600	0.71	900	8500
116.1 (SI)				1.39	600	5300			
118.9	0.76	700	6000	2.23	700	5200	0.77	600	6000
120.7 (SI)							128.81	46700	76100
122.0	9.23	600	5900	0.95	500	4300	1.11	500	4900
Mean	3.96	3080	6950	1.77	1240	5100	13.4	4000	10500

SI - Special Interest Sample

ASR well 1 and 152 m from ASR well 2, had the lowest mean concentration of the elements while ASR core 3, located 454 m from ASR well 1, had the highest mean concentration. The mean concentration of the elements in ASR core 1, located within 25 m of ASR well 1, was

higher than that of ASR core 2 and lower than that of ASR core 3.

Stereo and Scanning Electron Microscopy

The samples from the cores selected at 3 m intervals and the special interest samples were independently examined by the author and the Florida Geological Survey (Arthur and Fischler, 2006) using stereo and scanning electron microscopy (SEM). Each sample selected from the cores was broken up into gravel-size pieces and first examined with a Leica Zoom Stereo Microscope with 10.5x to 45x magnification. The objective was to identify samples that had a high potential of containing pyrite, i.e., an obvious abundance of pyrite crystals, dark metallic minerals, organic layers, and reddish areas that could indicate pyrite oxidation, for subsequent analysis with the SEM. For ASR core 1, the author and the Florida Geological Survey observed what appeared to be oxidized framboidal pyrite and HFO (reddish oxidation halos around dull metallic pyrite framboids and reddish minerals) (Figure 4.2). These features were also observed in ASR core 2 (Figure 4.3) but less frequently than in ASR core 1. Metallic patches, dark minerals, and organic layers were also observed. Pieces from samples that contained an abundance of these features were selected for examination with the SEM. In ASR core 3, the author and the Florida Geological Survey observed abundant framboidal and euhedral pyrite crystals that were shiny and golden, particularly in samples obtained from the 91, 114, 119, 121, and 122 m intervals (Figure 4.4).

The author examined the selected samples for the presence of pyrite using a Hitachi S-3500N variable pressure scanning electron microscope located at the College of Marine Science, University of South Florida. Samples were coated with carbon, taped onto carbon mounts, then examined for the presence of pyrite. The SEM investigation by the author and the Florida

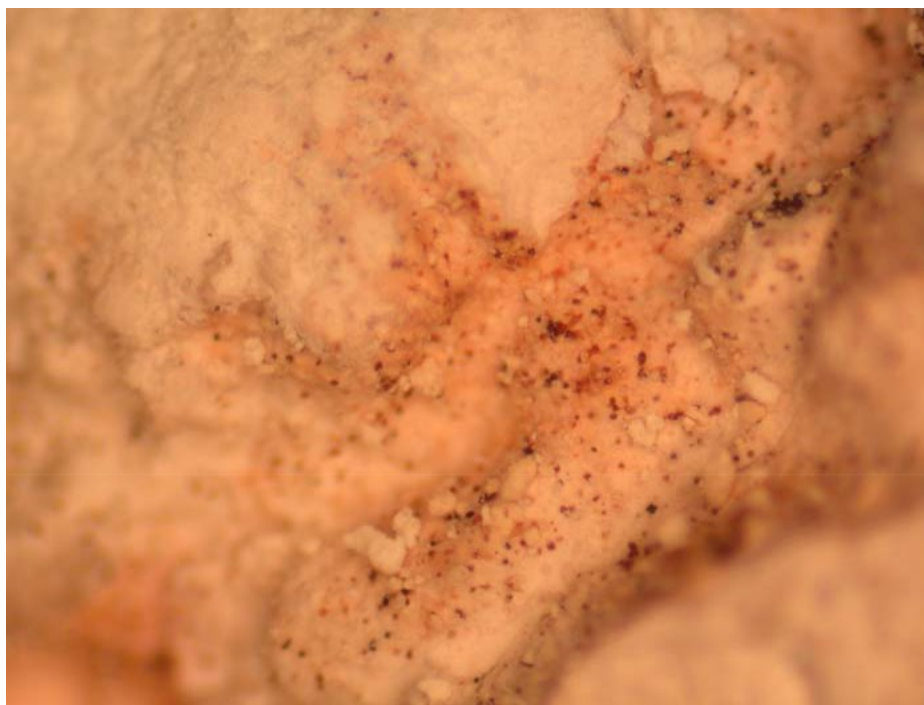


Figure 4.2. Photograph of oxidized framboidal pyrite in ASR core 1 (Florida Geological Survey, 2005).



Figure 4.3. Photograph of pure and oxidized framboidal pyrite in ASR core 2 (Florida Geological Survey, 2005).

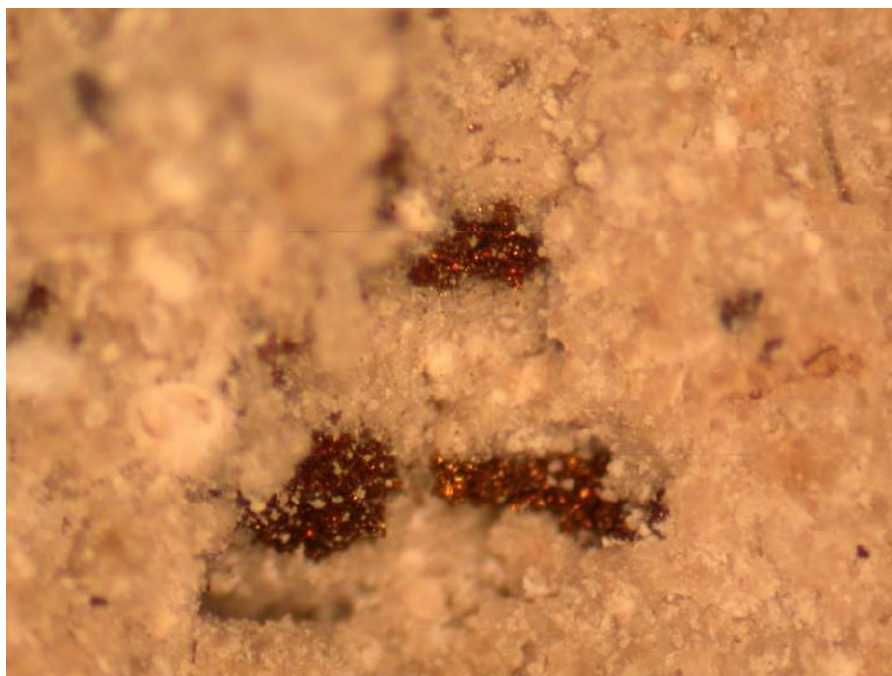


Figure 4.4. Photograph of pure and shiny framboidal pyrite in ASR core 3 (Florida Geological Survey, 2005).

Geological Survey of selected samples from the cores led to the observation that framboidal pyrite crystals appeared to be melted and indistinct in ASR core 1 (Figure 4.5) and ASR core 2 (Figure 4.6). This may have indicated that a higher level of oxidation of pyrite was occurring in ASR core 1 that was directly adjacent to ASR well 1 and that ASR core 2 may also have experienced enhanced oxidation but possibly to a lesser degree. Well-defined euhedral framboidal pyrite crystals were only identified in ASR core 3 (Figure 4.7)

Control Core Comparisons

Arsenic, iron, and sulfur concentration data were obtained from Price and Pichler's (2005) mineralogical investigation of 19 Suwannee Limestone control cores, the locations of which are shown in Figure 4.3. This was done to create a control data set of element

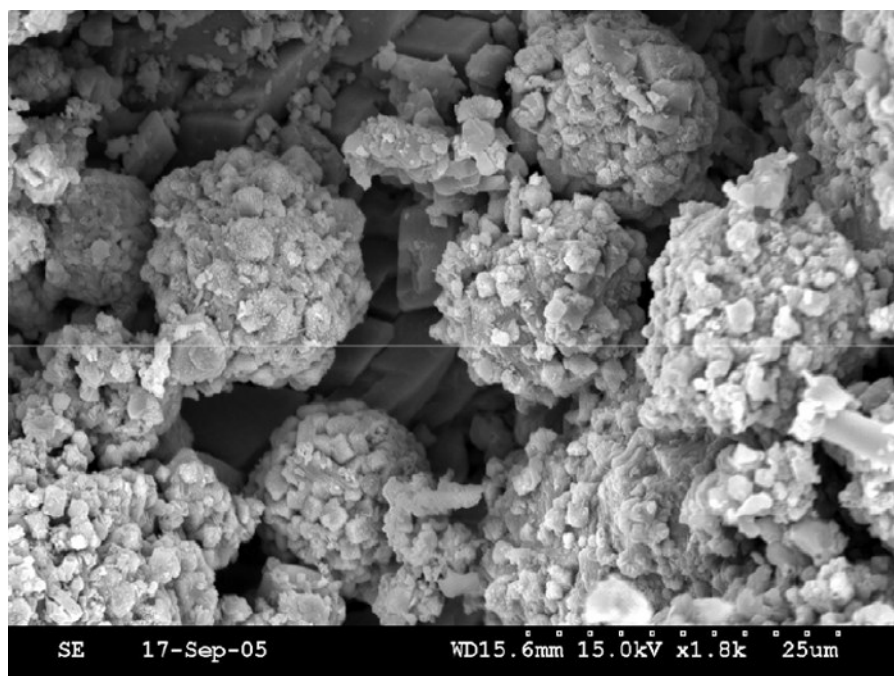


Figure 4.5. SEM image of framboidal pyrite in ASR core 1 with a melted, indistinct appearance (Florida Geological Survey, 2005).

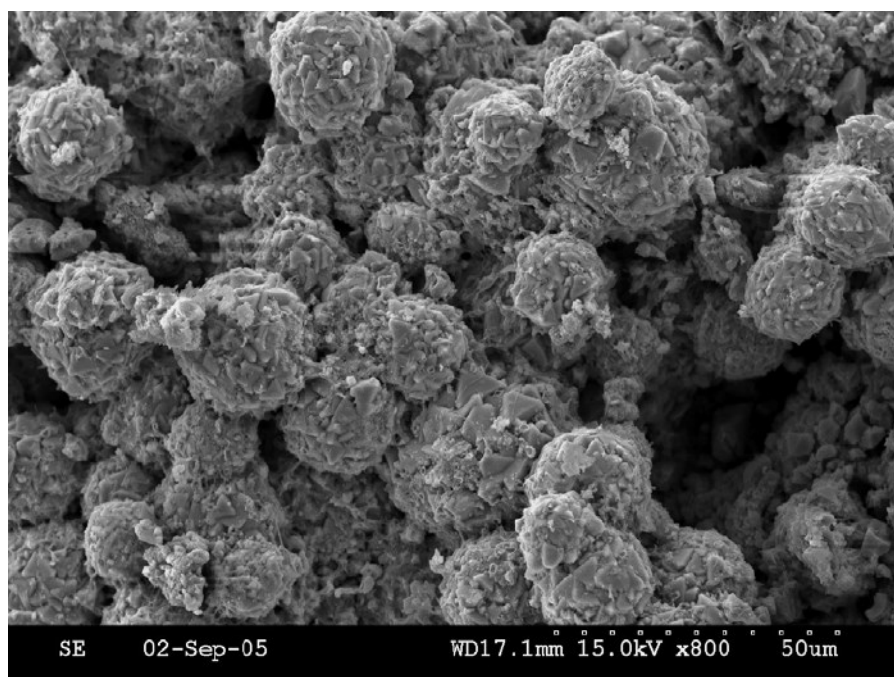


Figure 4.6. SEM image of framboidal pyrite in ASR core 2 with a melted, indistinct appearance (Florida Geological Survey, 2005).

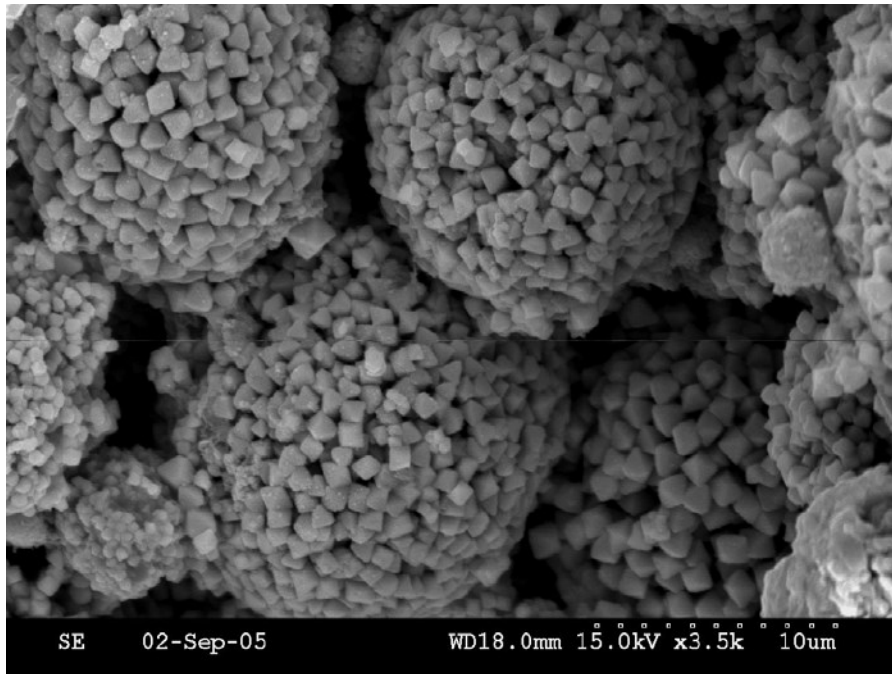


Figure 4.7. SEM image of framboidal pyrite in ASR core 3 with distinct, euhedral crystals (Florida Geological Survey, 2005).

concentrations in cores that were not affected by ASR operations to compare statistically to concentrations of elements in ASR cores that were potentially affected. Table 4.3 is a summary of the mean concentration of the elements for all samples for each ASR and control core. The mean of the values is provided for each element. If the control core had less than five analyses for iron and sulfur, they were not used for statistical analyses (shaded rows).

Statistical Comparison of the Element Concentrations of ASR Wellfield and Control Cores. Figures 4.8 through 4.10 are plots of means diamonds of arsenic, iron, and sulfur concentrations for ASR cores and control cores. Because control cores that had fewer than 5 samples for a given element were not included in the analysis, only 12 cores were used for the iron statistical comparison and 11 cores were used for the sulfur comparison. In the figures,

Table 4.3. The mean concentrations of arsenic, iron, and sulfur for ASR wellfield and control cores (mg/kg).

Core #	Distance from nearest ASR well (m)	As	Fe	S
ASR Wellfield Cores				
Core 1	25 m	4.0	3080	6,950
Core 2	152 m	1.8	1,240	5,100
Core 3	454 m	13.4	4,000	10,500
Control Cores				
9	n/a	10.4	1,280	1,374
1-2	n/a	6.2	3,965	4,890
DV-1	n/a	5.5	670	725
9-2	n/a	4.9		
5	n/a	4.4	1,164	1,400
4-1	n/a	4.1		
8-1	n/a	3.8		
25	n/a	3.7		
5-1	n/a	3.5		
20	n/a	3.1	878	1,834
3-3	n/a	2.8		
17	n/a	2.6	450	1,029
39	n/a	2.5	556	839
28	n/a	2.4		
49	n/a	2.2		
14	n/a	2.2		
SA-1	n/a	1.7	240	460
12	n/a	1.7	344	
13	n/a	1.1		
22	n/a	0.6		

means of the concentrations of arsenic, iron, and sulfur for each core are represented by a means diamond. The diamonds are ordered by the magnitude of their mean element concentration, with the lowest on the left and highest on the right. The width of each diamond is proportional to sample size. A narrow diamond is taller because fewer data points yield a less precise estimate of the mean of the element concentration. The line across the middle of the diamond is the mean of the element concentration for the core and the vertical span of each diamond represents the 95 percent confidence interval for the data. The horizontal line extending across the entire graph is the global mean of the element concentrations for all cores. Overlap marks above and below the means for each diamond are used to compare means of the element concentrations between cores. If the global mean is between the overlap marks of a diamond, that diamond's mean is statistically similar to the global mean.

Figure 4.8 displays means diamonds for arsenic concentrations of the cores. The figure shows that means of all the cores are statistically similar with the exception of control core 9 and ASR core 3. The figure also shows that the mean of the arsenic concentration of ASR core 2 is close to the lowest of all the cores.

Figure 4.9 displays means diamonds for iron concentrations of the cores. The figure shows that the means of all the cores are statistically similar with the exception of ASR core 3. In addition, the mean iron concentration of ASR core 2, while considerably higher than that of most control cores, is considerably lower than the other ASR cores. ASR Core 3 has the highest mean iron concentration of all cores.

Figure 4.10 displays means diamonds for sulfur concentrations of the cores. The figure shows that the means of all the cores are statistically similar with the exception of ASR cores 1 and 3, which also have the highest mean sulfur concentrations.

The following is a summary of the statistical comparison of the means of the element concentrations:

- The mean concentration of arsenic in ASR cores 1 and 2 was statistically similar to that of all but one of the control cores (control core 9) and ASR core 3.
- The mean concentration of iron in ASR cores 1 and 2 was statistically similar to that of all of the cores with the exception of ASR core 3.
- The mean concentration of sulfur in ASR core 2 was statistically similar to that of all the cores with the exception of ASR cores 1 and 3.

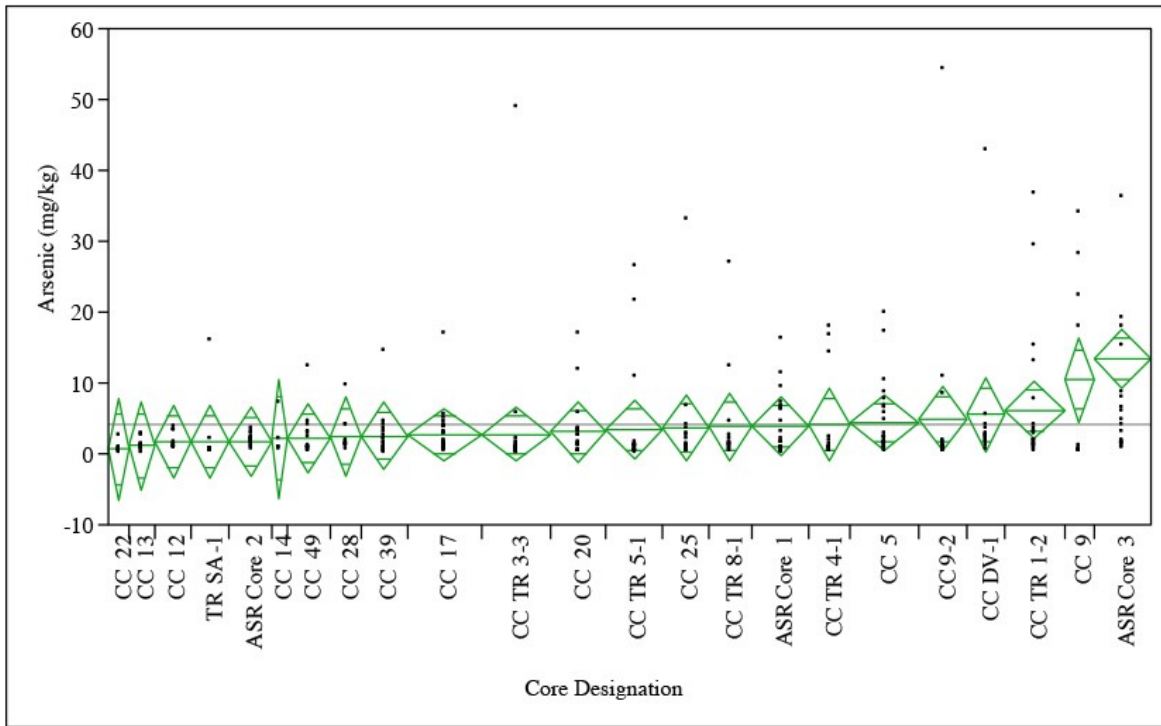


Figure 4.8. Mean arsenic concentrations of ASR and control cores. The means of all cores, with the exception of control core 9 and ASR core 3, are statistically similar at the 95 percent confidence level.

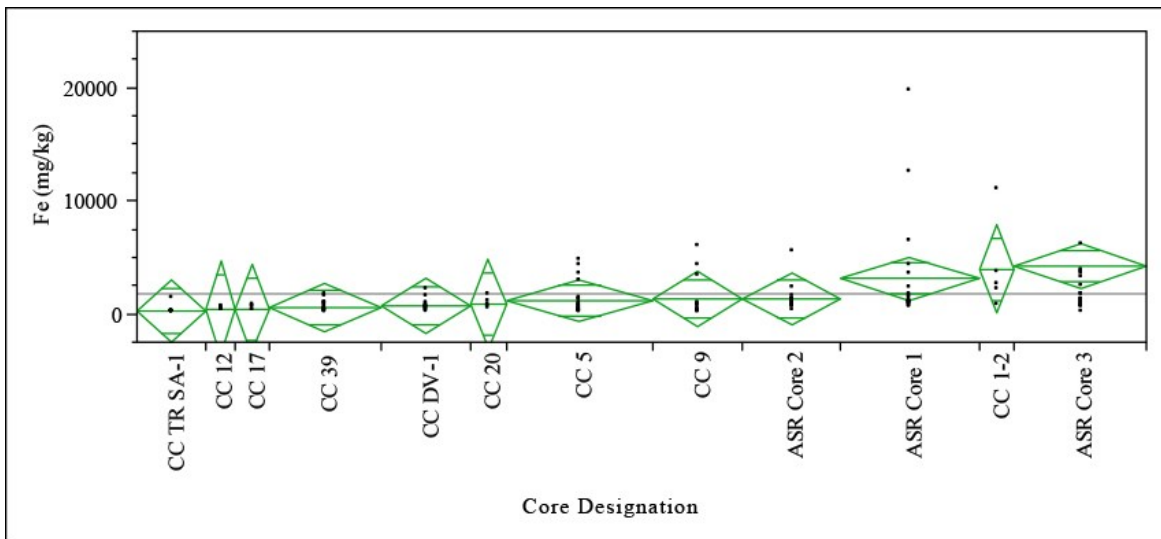


Figure 4.9. Mean iron concentrations of ASR and control cores. The means of all cores, with the exception of ASR core 3, are statistically similar at the 95 percent confidence level.

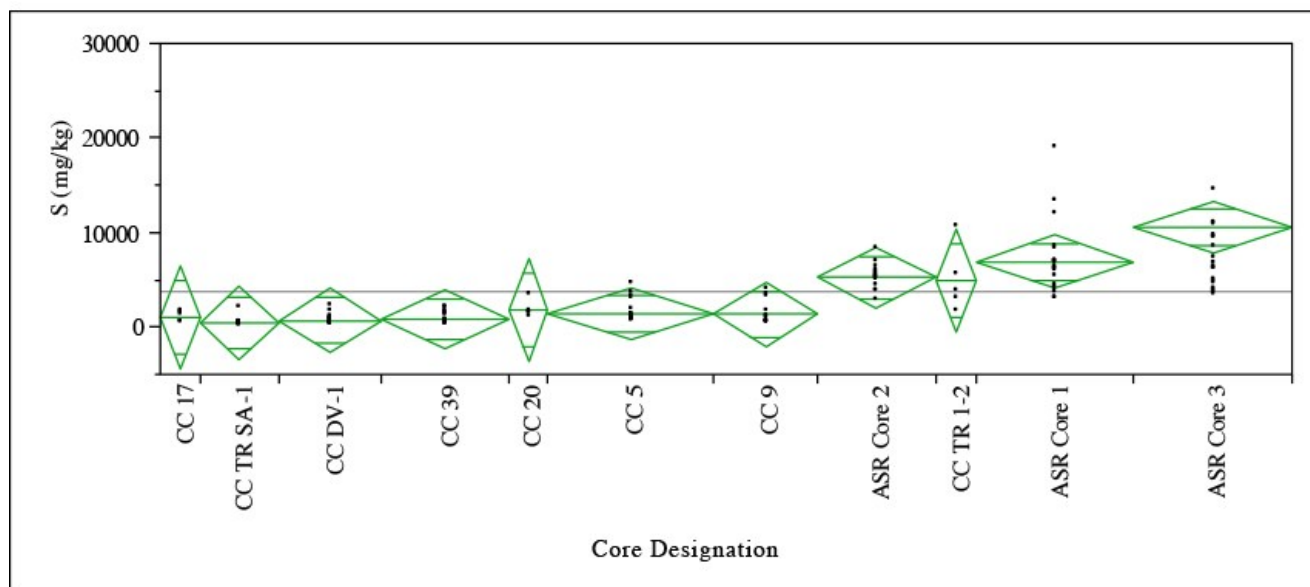


Figure 4.10. Mean sulfur concentrations of ASR and control cores. The means of all cores with the exception of ASR cores 1 and 3, are statistically similar at the 95 percent confidence level.

Estimation of the Quantity of Arsenic Removed During Recovery

An important aspect of determining how the mineralogy of the cores was affected by ASR injection/recovery was to develop an estimate of the quantity of arsenic that was removed from the aquifer matrix prior to the drilling of the cores. Although ASR core 1 may have experienced as many as 5 cycles prior to drilling of the cores as shown in Table 4.1, the injection and recovery volume data could not be used in the calculation because the recovered water for the initial cycles was not analyzed for arsenic. Instead, as part of the investigation conducted in Chapter 3, injection/recovery volume data and arsenic concentration data for ASR well 1 were obtained from the Florida Department of Environmental Protection's Oculus Electronic Document Management System and the annual report for the ASR wellfield (CH2MHILL, 2011a). The data covered 10 full cycles from 2001 through 2011 and were used to develop an estimate of the quantity of arsenic removed from the aquifer matrix in the vicinity of ASR well 1

during each cycle as shown in Table 4.4. The calculations show that the 5 cycles that occurred prior to the drilling of the cores removed only 4.0 percent of the arsenic in the volume of the proximal zone occupied by recovered water.

Table 4.4. Calculation of the Quantity of Arsenic Removed During Each Cycle from the Aquifer Matrix Surrounding ASR Well 1.

Calculation	Result
Mean recovery volume of the 10 cycles = 119.5 mgd or 15.9 million ft ³	119.5 mgd or 15.9 million ft ³
Volume of aquifer occupied by 15.9 million ft ³ of recovered water	63.8 million ft ³
Weight of aquifer occupied by 63.8 million ft ³ assuming 2.5 g/cm ³ for density of limestone	3.4 X 10 ⁹ kg
Weight of arsenic in the mass of aquifer calculated above, assuming 3.96 mg arsenic/kg (Price and Pichler, 2005) of aquifer matrix	1.33 X10 ⁴ kg
Weight of Arsenic in the mass of aquifer in the proximal zone ¹	1,330 kg
Total weight of arsenic recovered from ASR 1 for 10 cycles	71.4 kg
Total weight of arsenic recovered for 5 cycles prior to drilling of cores	53.1 kg
Percent of arsenic recovered after 5 cycles vs total weight of arsenic in the portion of the proximal zone occupied by recovered water	4 %

¹Because the proximal zone is the zone of greatest geochemical reactivity where the majority of the process of pyrite dissolution/arsenic mobilization and HFO/arsenic complexation during injection and HFO dissolution/arsenic mobilization during recovery is likely to occur, it can be assumed that most of the arsenic in water recovered during each cycle originates in the proximal zone. If it is assumed that the proximal zone comprises 10 percent of the volume of aquifer occupied by the recovered water, then the weight of arsenic in the volume of the proximal zone occupied by recovered water is 1,330 kg.

Discussion

As arsenic-bearing pyrite dissolves during injection and arsenic is mobilized, the prevailing hypotheses are that it is either flushed away to be precipitated distally or rapidly complexed with hydrous ferric oxide and precipitated locally.

According to the distal hypothesis, concentrations of the elements found in pyrite (iron, sulfur, arsenic, etc.) in ASR core 1 should have been lower than concentrations in ASR cores 2 and 3 and in the control cores as a result of the chemical leaching core 1 would experience during repeated injection/recovery cycles. This was because it was thought that when oxygenated water was injected into the reducing environment around the ASR well, arsenic-

bearing pyrite would dissolve and release arsenic into solution. The mobilized arsenic would be flushed laterally away from the well and would precipitate at some distance from the well (SWFWMD, 2007a). Any dissolved arsenic in the storage zone would be slowly purged from the aquifer during ASR operations as long as injection/recovery volumes of successive cycles remained relatively constant.

Results of the analyses of the ASR cores did not support the hypothesis because the concentration of the elements was considerably lower in ASR core 2 than in ASR core 1 and the mean concentrations in ASR cores 1 and 2 were statistically similar to those of the control cores. This indicated that the concentration of the elements in ASR core 1 had not been affected by the operation of ASR well 1. This result is in agreement with the local precipitation hypothesis, which proposes that as arsenic is mobilized from dissolved pyrite during injection, it is not flushed away from the ASR well but is removed from solution as it complexes with precipitated HFO in close proximity to the well. This would maintain the concentration of arsenic in the limestone matrix of the proximal zone at pre-ASR levels. Furthermore, the weight of arsenic removed from the aquifer during the cycles that occurred prior to the drilling of the cores as a percentage of the total arsenic in the proximal zone was only 4.0 percent, which is a minimal degree of arsenic depletion. For these reasons, the distal hypothesis was not valid.

An important implication of these results is that although large quantities of arsenic-bearing pyrite are present in the proximal zone, only a small percentage, probably the portion that is concentrated in voids, fractures, or organic lenses (SWFWMD, 2007b), is actually available for dissolution during each cycle. It is possible that most of the pyrite is within the limestone matrix and isolated from injection water to some degree. As shown in Chapter 3, arsenic concentrations in recovered water decrease with each cycle as this readily available

pyrite is dissolved until eventually, arsenic concentrations in recovered water decrease below the MCL. It is possible that recovered water may continue to have these low concentrations of arsenic indefinitely because as the limestone matrix that surrounds the arsenic-bearing pyrite is dissolved and additional pyrite is exposed, it becomes available for dissolution.

According to the distal hypothesis, ASR core 3, the furthest core from ASR well 1, would have the highest concentrations of the pyrite elements and associated arsenic because it would not be subject to the effects of ASR injection/recovery due to its distance from the ASR well. While the results of the investigation did indeed show that the concentration of the elements was the highest in ASR core 3, the discussion above makes it clear that it was not because ASR injection/recovery reduced the concentration of the elements in ASR cores 1 and 2. This was further supported by the fact that the concentration of the elements in ASR core 3 was considerably higher than and statistically dissimilar to that of the control cores. This probably indicates that the concentration of the elements in ASR core 3 was naturally elevated over that of the ASR cores and control cores. Arthur and Fischler (2006) stated that statistical evidence exists to support heterogeneous arsenic concentrations within the Suwannee Limestone in the region.

That the appearance of pyrite crystals would be altered to a greater degree in ASR core 1 over the more distant cores, as specified in the distal hypothesis, may have been valid to some degree. Results of the SEM analysis provided evidence that pyrite crystals appeared to be less clear and distinct in ASR core 2 than in ASR core 3 and even less distinct in core 1. This may have indicated that a higher level of pyrite oxidation was occurring in ASR core 1 as a result of its proximity to ASR well 1. Pyrite exposed to injected water in ASR core 1 could have dissolved or been in the process of dissolving. It is also possible that the appearance of pyrite

crystals in ASR core 2 was affected by ASR injection/recovery because the data showed that ASR core 2 was at the distal end of the portion of the aquifer that was exposed to injected water from ASR well 2.

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CHAPTER FIVE:

CONCLUSIONS

The principal contribution of this dissertation to understanding and overcoming the arsenic problem in ASR systems in Florida is the empirical data that was developed to support a number of important ASR/arsenic hypotheses and predictions that had been developed previous to or during the course of this research. In Chapter 2, “The Relationship between Pyrite Stability and Arsenic Mobility During Aquifer Storage and Recovery,” previous work that determined that pyrite dissolution was the most important source of elevated arsenic in water recovered from ASR systems was supported. Water samples from the 19 control wells in the study area open to the Suwannee Limestone were analyzed for arsenic at the low $\mu\text{g/L}$ level for the first time to establish background concentrations. Arsenic concentrations did not exceed $0.036 \mu\text{g/L}$, thus verifying that only a very small fraction of the elevated concentrations in water recovered from ASR systems could result from natural processes. In addition, this investigation demonstrated through geochemical modeling that redox conditions necessary for pyrite in the limestone matrix to become unstable and dissolve do indeed occur when oxygenated surface water is injected into the aquifer. The result is the dissolution of arsenic-bearing pyrite and the release of arsenic into groundwater in the vicinity of the well.

In Chapter 3, “The Importance of Maintaining a Zone of Stored Water to Minimize Arsenic in Water Recovered from ASR Systems, Results from Long-Term Cycle Testing in Two ASR Wellfields,” predictions that establishing a substantial quantity of stored water by replacing

native groundwater early in the cycle-testing process and maintaining it through each subsequent cycle, will cause arsenic concentrations in recovered water to decline with each cycle and eventually fall below the arsenic MCL of 10 µg/L, were supported. Furthermore, if the well is over-recovered to the degree that the stored water is depleted and mixed stored water and native groundwater is brought to into the proximal zone, arsenic concentrations in recovered water are likely to increase significantly.

The results of this investigation verified predictions of a number of investigators by demonstrating that maximum arsenic concentrations for wells where a substantial volume of stored water zone was maintained were nearly always considerably lower in each cycle and declined below the MCL after fewer cycles than those of wells where stored water was depleted.

The third investigation “a Mineralogical Investigation of Cores in an ASR Wellfield to Determine where Mobilized Arsenic is Precipitated,” was a detailed mineralogical examination of three cores from the Suwannee Limestone located at distances of 25 m (core 1), 152 m (core 2), and 452 m (core 3), respectively from operating ASR wells. Results of the analyses showed that the concentration of elements in pyrite (iron, sulfide, arsenic) was not lowest in ASR core 1, the core closest to the ASR well, but in ASR core 2. This result supported the hypothesis that when arsenic-bearing pyrite dissolves near an ASR well, it is not flushed laterally to precipitate at some distance from the well, but is rapidly complexed in the vicinity of the well by newly formed HFO that is stable in oxygenated environments.

The results also showed that the concentration of the elements in ASR core 1 would not have been lower than the concentration in more distant cores because the mass of arsenic removed through the ASR well during each recovery event was very small compared to the total arsenic present in the limestone matrix. Calculations show that cycles that occurred prior to

drilling of the cores would have removed only 4.0 percent of the total arsenic in limestone in the portion of the proximal zone occupied by recovered water. The implications of this result are that while significant quantities of arsenic-bearing pyrite are present in the limestone matrix in the proximal zone, the pyrite that is most available for dissolution is probably concentrated in voids and fractures and is a small percentage of the total amount present. Assuming that a zone of stored water is maintained, arsenic concentrations in recovered water decrease with each cycle as this readily available pyrite is dissolved until arsenic levels reach the 5 µg/L to 15 µg/L range. Recovered water may continue to have these low concentrations of arsenic indefinitely because as the pyrite that is within the limestone is dissolved, additional pyrite becomes exposed. It then goes through the process of dissolution, arsenic release, arsenic complexation with HFO during injection, and dissolution of HFO, arsenic release, and recovery through the ASR well during recovery.

Finally, the results showed that the concentration of the iron, sulfur, and arsenic in ASR core 3 was higher than and statistically dissimilar to concentrations not only in ASR cores 1 and 2, but in all but one of the control cores for which the elements had been analyzed. This may indicate that the degree of spatial heterogeneity of the pyrite content of the Suwannee limestone can be very high.