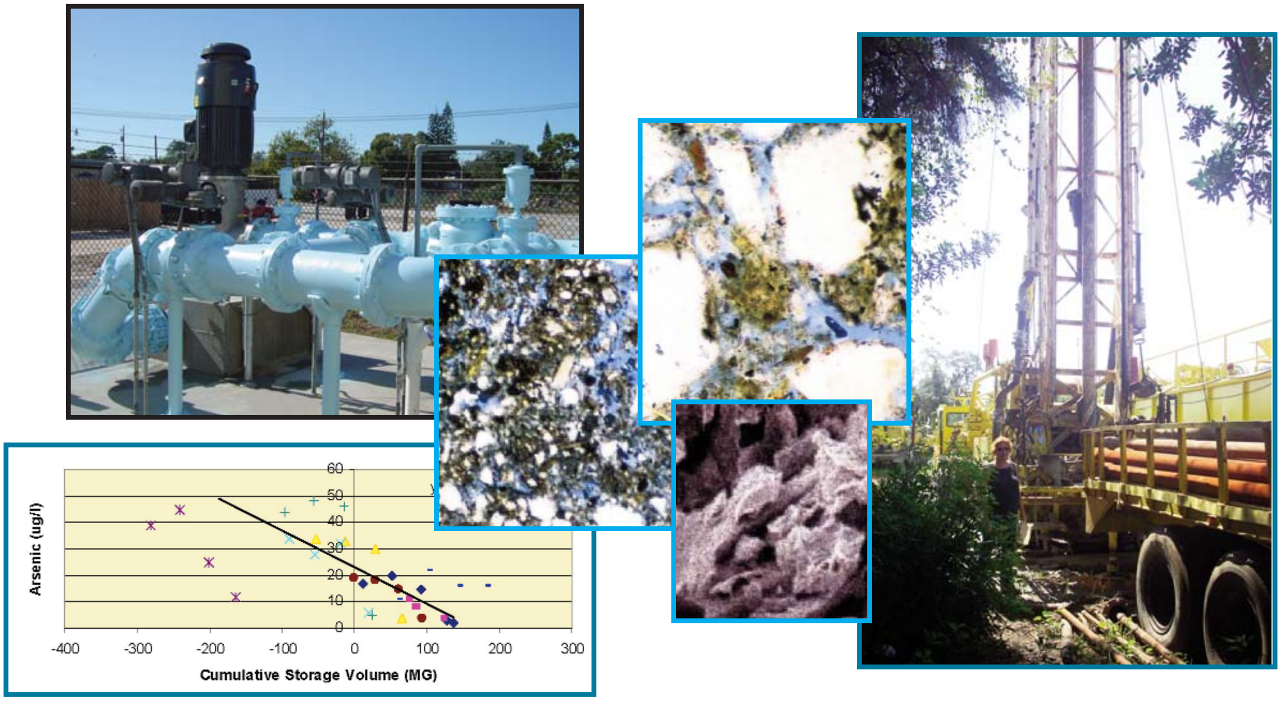
EVALUATION OF ARSENIC MOBILIZATION PROCESSES OCCURRING DURING AQUIFER STORAGE AND RECOVERY ACTIVITIES
(H046)

Prepared for

Southwest Florida Water Management District



November 15, 2007

Southwest Florida
Water Management District

ASR
SYSTEMS

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Southwest Florida Water Management District

ASR Systems LLC
Gainesville, Florida

November 15, 2007

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This final report is a compilation of the following Technical Memoranda:

Task 1 - Kickoff Meeting Minutes

Task 2 - Technical Memorandum: Literature Review: Arsenic Mobilization Processes During ASR Operations Including Capital, Operating and Life Cycle Cost Information

Task 3 - Technical Memorandum: Field Data Analysis

Task 4 - Technical Memorandum: Modeling

Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities

Southwest Florida Water Management District

ASR Systems LLC in association with Carollo Engineers PC

Task 1 - Kickoff Meeting Minutes
February 23, 2006

Attendees:

Gregg Jones/ SWFWMD
Mark Barcelo/ SWFWMD
Don Ellison/ SWFWMD
Judy Richtar/ FDEP/ Tampa
Joe May/ FDEP/ West Palm Beach
Joe Haberfeld/ FDEP/ Tallahassee
Kathie Costello/ FDEP/ Tampa
Dr Jonathan Arthur/ FGS/ Tallahassee
Dr Pieter Stuyfzand/ KIWA/ Netherlands
Dr Thomas Pichler/ USF/ Tampa
Dr John Lisle/ USGS/ St Petersburg
Dr Joel Kostka/ FSU/ Tallahassee
Dr John Stolz/ Duquesne U./ Pittsburg
Dr Jess Brown/ Carollo Engineers/ Sarasota
Ash Vakharkar/ Carollo Engineers/ Sarasota
David Pyne/ ASR Systems/ Gainesville

The kickoff meeting was held at the SWFWMD Tampa Subdistrict Office, 10am to 4:15 pm. After introductions of all attendees, the project objectives and scope of work for each project task were reviewed, and also the Schedule and Project Deliverables. ASR Systems team members then made several presentations addressing geochemical and microbial processes for arsenic mobilization and attenuation. Copies of each powerpoint presentation are attached.

Dr Pieter Stuyfzand presentation

Pieter Stuyfzand then presented “Arsenic behavior during artificial recharge: the Dutch experience.” After a general introduction of the various dissolved As-species and As-containing rocks and minerals, the various processes that mobilize As were discussed.

A sampling bias was mentioned that is probably responsible for unexpected incidental As peaks, as reported in the data from several ASR sites. This relates to the lack of (anoxic) sample filtration in the field and subsequent acidification of the sample with nitric acid for conservation and analysis of total As. It is suspected that this procedure (without filtration) incidentally leads to the undesired dissolution of small pyrite grains which detach from the aquifer. These grains are probably not dissolved nor ingested by the drinking water consumer, as they are not exposed to nitric acid but deposited somewhere in the water distribution system and covered by protective ironhydroxide coatings. He suggested that, for a while, samples should be collected and analyzed both ways at affected sites: unfiltered and filtered.

Questions were raised regarding the importance of dissolved Si (as H_4SiO_4) in reducing As-adsorption to neoformed $Fe(OH)_3$. Strong evidence of its importance is put forward, however, by As water treatment studies (AWWARF reports 90903 and 90910), and As behavior in both exfiltrating hydrothermal systems (Swedlund & Webster, 1998) and ASTR-systems in low temperature aquifers in the Netherlands (Stuyfzand, 2001).

Another question was raised regarding the potential of SO_4 to oxidize arsenite to arsenate, and of H_2S to reduce arsenate to arsenite. Here, mediating bacteria may play a decisive role, which, for ASR wells, has not been studied to date.

The Dutch experience with native groundwater, ASTR (“Aquifer Storage Transfer Recovery”) systems and one recent ASR experiment yielded relevant information on water quality changes in general and As behaviour in particular, in these groundwater environments. Similar processes probably also operate in the Floridan ASR systems. Limitations were discussed because the Dutch boundary conditions deviate from the Floridan aquifer setting in various ways (slide 23).

A conceptual model of As peaking during ASR backpumping was drawn (slide 24) on the basis of (i) an earlier inventory of As behaviour at 13 ASR sites in Florida (Pyne et al., 2004), the Bradenton site in particular (Pyne, 2005), and (ii) the Dutch experience. The input of colloidal $Fe(OH)_3$ particles from the pretreatment plant and the transport of $Fe(OH)_3$ colloids deriving from pyrite oxidation constitute an intriguing research item for future consideration, rendering the surmised $Fe(OH)_3$-As roll front deposit and As sorption phenomena difficult to model.

Dr John Stolz presentation

Dr Stolz presented the "Microbial Transformation of Arsenic". The different metabolic processes relating to arsenic were described, i.e., assimilation (incorporation of arsenic into cell mass- i.e., arsenobetaine), detoxification (arsenite oxidation, methylation, arsenite reduction), and energy generation (arsenite oxidation, arsenate reduction). The diversity of arsenate respiring (bacteria that "breathe" arsenic), heterotrophic arsenite oxidizing, and chemoautotrophic arsenite oxidizing bacteria was shown. Focusing on arsenate respiring bacteria, the metabolic versatility was then discussed (these organisms use different carbon sources and may respire other substrates including nitrate, sulfate, and iron). An arsenic biogeochemical cycle in the anoxic bottom waters of Mono Lake CA, and the brines of Searles Lake CA were presented, stressing the point that arsenic is primarily biologically cycled between As3+ and As5+, even in the absence of oxygen. A simple model for arsenic mobilization from ferryoxyhydroxides was then shown. Iron reducing bacteria reduce the ferrioxyhydroxide, releasing Fe2+ and As5+. Arsenate respiring bacteria will only reduce the As5+ (bound to either ferrioxyhydroxide or aluminosilicates) resulting in the release of As3+. Bacteria capable of respiring both iron and As5+ release both Fe2+ and As3+. Lastly, functional probes now exist for the identification of arsenate metabolizing bacteria in natural populations.

Dr Joel E. Kostka presentation

Dr. Joel Kostka presented "Subsurface microbiology and the microbial mediation of water-rock interactions." The focus was on the biogeochemical transformation of metals and sulfur in the subsurface. He outlined lessons learned from his many years of experience conducting research on the remediation of metal contaminants at the U.S. Department of Energy's Field Research Center, Oak Ridge, Tennessee. Dr. Kostka explained his ecological approach to subsurface contaminant remediation, including the biostimulation of indigenous microbial communities to catalyze the desired contaminant transformation reactions. He presented an overview on the microbial processes likely to be occurring in the Suwannee Limestone formation during ASR recharge, storage, and recovery. His presentation concluded with an overview of suggestions for refinement of the Phase I conceptual model from a microbiological perspective. In order to produce inputs for conceptual and quantitative models targeted to the fate/ transport of As in the subsurface, Dr. Kostka recommended the following emphases: 1) to identify geochemical and microbial mechanisms of contaminant transformation, and 2) determine controlling environmental parameters (redox) and their change over relevant spatial and temporal scales.

Dr John Lisle presentation

Dr Lisle presented “Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities: Microbial Processes.” This included a literature search of 13 databases addressing As mobilization and attenuation, including some aspect of microbially induced mobilization of one or more metals most likely to be present in geologic features associated with the regional aquifer systems of central and/or south Florida. Although over 2000 sources were considered, no papers were identified during this search. Two studies were identified that have addressed microbial processes in the Floridan aquifer, not specific to arsenic.

He presented microbial analyses of samples pumped from three monitor wells comprising part of the Comprehensive Everglades Restoration Program (CERP), noting the nutrients and other constituents in recharge water, favoring microbial metabolism. He also noted the changes in bacterial community diversity likely to occur during ASR storage. He then posed several questions and research needs.

Dr Thomas Pichler presentation

The last presentation, given by Dr. Pichler, addressed the modeling of arsenic behavior during ASR operations. He stated that the study of arsenic is not only difficult, but a subject matter that has to be taken very seriously because of the potential dangers associated with arsenic in the environment. He summarized the current knowledge about arsenic by presenting “the things we do know about arsenic” and “the things we do not know”. According to Dr. Pichler we know that (1) in the Suwannee Limestone arsenic is present in the mineral pyrite, (2) during ASR operation arsenic is most likely released due to the oxidation of pyrite, and (3) the distribution of arsenic in pyrite and the distribution of pyrite in the Suwannee Limestone is very heterogeneous. Things we do not know are (1) where is the arsenic released, (2) is it redistributed, (3) what is the role of microbes for pyrite dissolution, (4) what is the role of microbes for arsenic fate and transport and (5) what arsenic species are present. Since the unknowns are extremely important for meaningful modeling, Dr. Pichler concluded that modeling arsenic during ASR operations is premature. His recommendation was to delay the modeling until we will have a better conceptual understanding of arsenic release, transport and fate.

General Discussion

Questions and answers occurred throughout the presentations and also during a general discussion session following the presentations. A summary of these discussions and key findings is as follows.

A conceptual model for arsenic mobilization and attenuation that incorporates formation of a buffer zone is acceptable to FDEP. However the buffer zone should not be recovered during extended droughts since this may bring high As concentrations back to the well. This may require new regulatory and operational measures. The City of

Bradenton ASR data set and those from several other Floridan aquifer ASR wellfields suggests that building such a buffer zone accelerates attenuation of arsenic in the recovered water without causing As to extend laterally to adjacent monitor wells. Conversely eliminating formation of the buffer zone causes much slower attenuation of arsenic, as shown for the City of Tampa ASR wellfield which has been over-recovering water on each cycle. Application of such a conceptual model will need to be site-specific since property line constraints will apply at smaller sites.

The conceptual model should include, among other factors, consideration of electron donors and electron acceptors; variability in source water quality constituent concentrations, and variability in well clogging. As cycling can occur with or without dissolved oxygen, so removal of oxygen in the recharge water may not be sufficient to prevent As mobilization. Some microbes may be sensitive to changes in salinity that occur during ASR recharge and recovery operations at some brackish water sites, but other microbes may not be that sensitive.

More data sets are needed in which samples are collected every few minutes during the first few hours of ASR recovery, to document variations in pH, Eh, As speciation, NO_3, SO_4, Fe and other key constituents along the recovery flowpath, and thereby better define gradients of these constituents near the well. It would be helpful for the Project Team to define constituents of interest for such tests. The best, high precision analytical methods are needed for some of these tests, to achieve the needed level of resolution. Some of these analytical methods may not yet be EPA-approved, however for research purposes this would be considered acceptable. EPA-approved tests would subsequently be used for regulatory purposes. Colloidal Fe needs to be measured in the recharge water, requiring large sample volumes.

Characteristics of a suggested ASR test site to obtain such data were discussed. The advantages of having a new site with no prior ASR activities was suggested, however this may require several years of monitoring. Such an approach would not preclude obtaining data from one or more long term operational ASR wells around which geochemical and microbial systems may have reached closer to an equilibrium. From analysis of cores it would be necessary to learn the microbe distribution in the aquifer. Consideration should also be given to developing two sites, one for potable water storage and one for reclaimed water storage, considering the substantial differences between these two source water qualities.

There is a concern regarding the potential for internal vertical movement within the open hole sections of monitor wells. FDEP has tightened up acceptable open hole intervals, generally not exceeding 100 ft at each site. Concern was also expressed regarding the reliability of nested cluster monitor wells, which are deemed to be problematic due to short-circuiting through the aquifer between the monitoring intervals.

We do not know for sure where the “hot zone” for arsenic occurs within the ASR bubble. Indications are that this occurs close to the ASR well, probably within a few tens of feet, and generally less than 150 ft. A “sponge” effect may occur, trapping As during recharge as the velocity drops with increasing distance from the ASR well, and with increasing opportunity for adsorption along the flow path during recharge. That the trapped As does not seem to remobilize during recovery once a buffer zone has formed suggests that perhaps microbial processes are contributing to the attenuation process.

Engineering pretreatment options that may inhibit or prevent As mobilization are particularly needed for those situations where ASR wells are located very close to property lines. SWFWMD wants to get a list of suggestions regarding what to do next, not necessarily all the answers at this stage. Potential new ASR sites would then be screened according to such a list, prior to SWFWMD funding.

FDEP questioned whether the bacterial die-off occurring during ASR storage is, in fact, a die-off or just an inactivation, the key issue being their culturability. However the use of cultures for such purposes is considered old-fashioned so better methods should be suggested. The use of a rock chamber was discussed favorably, so that formation of biofilms could be monitored during ASR storage. We should maximize the use and biostimulation of indigenous microbes rather than introducing new ones to the subsurface. FDEP was open to this suggestion so long as the biostimulation does not transgress UIC recharge water quality criteria. The possible use of parallel filters above ground was also discussed, following procedures already in use in the Netherlands.

Some discussion occurred regarding aquifer heterogeneity, particularly around the ASR well. This will need to be addressed in any conceptual model of As mobilization and attenuation.

Not every pyrite contains As. The range is zero to 12,000 mg/kg with a mean of 0.2 mg/kg. Arsenic stability fields neglect complexation, therefore they are not totally accurate. As thermodynamics are therefore not totally accurate on all processes. Concerns exist regarding surface effects on pyrite, particularly the reduction in As mobilization resulting from coating of pyrite with ferric hydroxide precipitate.

Some possibility exists that increased storage time is associated with increasing As concentration, in the absence of other variables such as successive cycles at the same volume of storage.

Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities

Task 2 - Technical Memorandum
Literature Review: Arsenic Mobilization Processes During ASR Operations

Prepared for

Southwest Florida Water Management District

ASR Systems LLC
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May 4, 2006

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Task 2 - Literature Review: Arsenic Mobilization Processes Occurring During ASR Operations

This literature review is presented in two parts. The first part is a review of approximately 50 selected papers pertaining to arsenic mobilization and attenuation to ascertain the most likely processes occurring during ASR storage under the hydrogeologic conditions representative of southwest Florida. The second part is a review of engineering experience, literature and information supplied by manufacturers regarding available pretreatment processes that may prevent arsenic mobilization during ASR storage.

1.0 BACKGROUND ON ASR OPERATIONS IN FLORIDA GEOLOGICAL SETTINGS

Aquifer storage recovery (ASR) is a method by which treated drinking water, treated surface water, groundwater or highly treated wastewater is injected into unconfined, confined or semi-confined aquifers through a well, for subsequent withdrawal from the same well as needed. Large volumes of water can be stored underground, thereby reducing or eliminating the need to construct large, expensive surface reservoirs. ASR systems have been in development and operation in Florida since the early 1980s (Pyne, 2005) and Florida ASR activity has increased substantially during the past 10 to 15 years (Reese, 2004).

ASR wells have been drilled in the carbonate-based Floridan aquifer at 30 sites in Florida, mostly by municipalities or counties in coastal regions (Figure 1). The Upper Floridan Aquifer is being used or is planned for use at 29 of the 30 sites (Reese, 2004). Of the 30 sites in Florida, 13 are fully permitted. The total number of active ASR wells in Florida is at least 65. Most of these sites are storing treated drinking water in brackish aquifers containing total dissolved solids (TDS) concentrations from 700 to 20,000 mg/L. Water is typically stored during wet months (June-October) when water demand is low and is recovered during dry months (December-May) to help meet peak demands. A single well is used for both storage and recovery.

Water supply economics is the main driver for ASR implementation in Florida. ASR systems can usually meet water management needs at less than half the capital cost of other water supply/storage alternatives (Pyne, 2005). Due to its success as a water management tool in Florida, ASR has been accepted by many utilities and regulatory agencies as a viable regional water management tool (SJRWMD, 2004). In fact, ASR is a critical component of the Southwest Florida Water Management District's (SWFWMD's) long-term water supply plan. However, the viability of ASR as a safe and cost-effective water resource alternative to meet projected water demands in Southwest Florida is now being questioned due to the occurrence of arsenic in stored and recovered water at some ASR wells at concentrations exceeding the national arsenic maximum contaminant level (MCL) of 10 µg/L. Prior to January 2006 the national primary drinking water standard for arsenic was 50 µg/l.

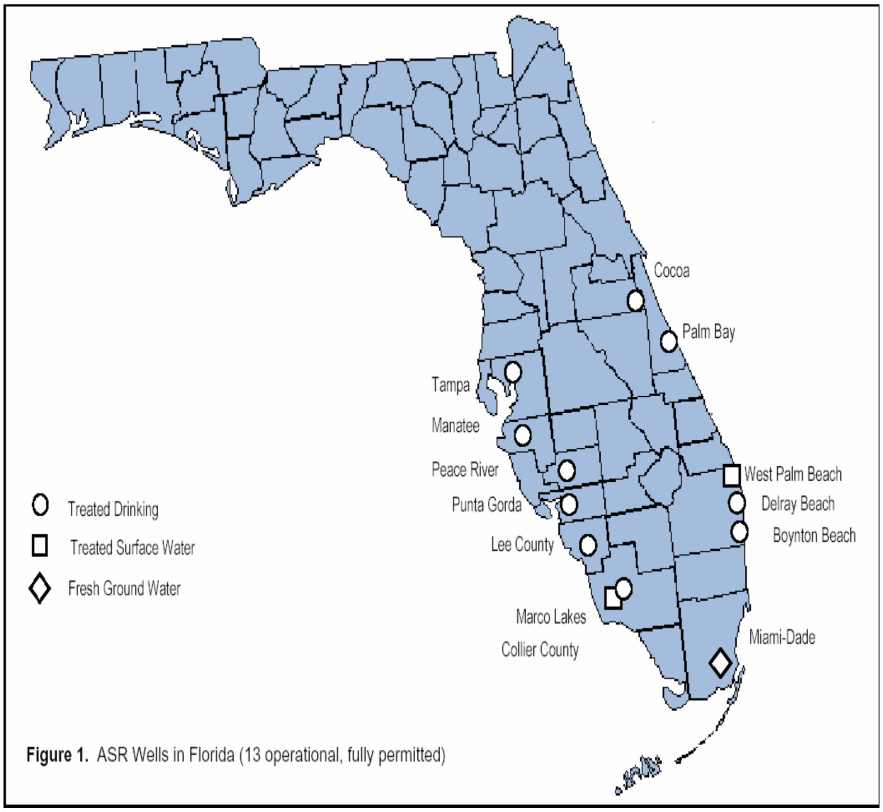
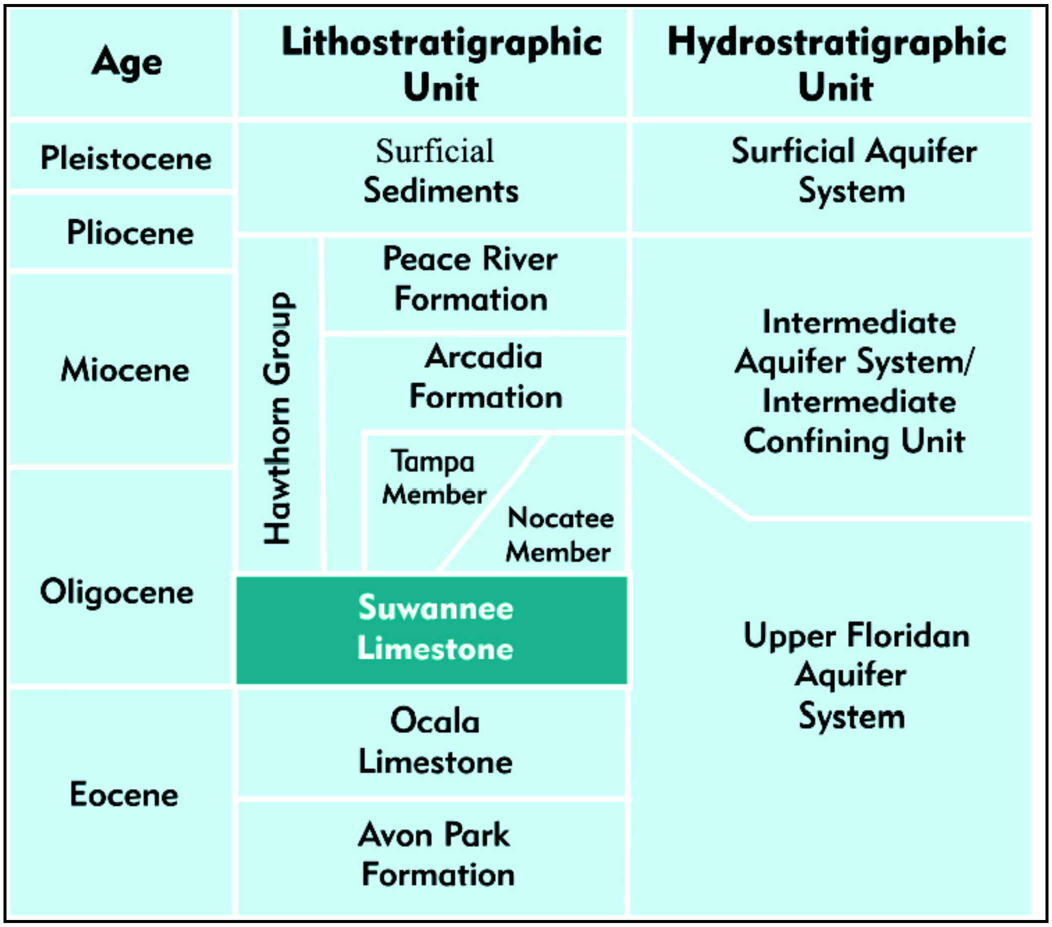


Figure 1. Active ASR Wellfields in Florida (Figure adapted from SJRWMD 2004)

1.1 THE FLORIDAN AQUIFER SYSTEM

The Floridan Aquifer System (FAS), one of the most productive aquifer systems in the world, consists of a vertically continuous sequence of highly permeable carbonate rocks (limestone and dolomite) that are hydraulically connected to varying degrees. The FAS is broadly divided into the Upper Floridan Aquifer, the Middle confining unit and the Lower Floridan Aquifer (Miller, 1986). A detailed lithographic and hydrostratigraphic cross-section of the FAS for Southwest Florida is provided in Figure 2 along with the associated approximate ages of formation. The vast majority of ASR productivity in Southwest Florida relies on the Suwannee Limestone Unit, which has been shown by Price and Pichler (2006) to contain abundant concentrations of pyrite (FeS_2). This same study also showed that arsenic concentrations in Suwannee Limestone (relative to the bulk rock composition) ranged from 0.01 to 54.1 mg/kg with a mean concentration of 3.5 mg/kg. The heterogenous distribution of arsenic illustrates the potential for recovery of high arsenic concentrations, despite a reasonably low average concentration within the limestone matrix. The arsenic distribution was shown to be concentrated in minor mineral phases, such as pseudo-framboidal pyrite (a *framboid* is a spheroidal aggregate of microcrystals with a diameter of up to 150 μm), which is shown in Figure 3. Furthermore, pyrite was predominantly associated with secondary calcite in high porosity zones.



Age	Lithostratigraphic Unit		Hydrostratigraphic Unit
Pleistocene	Surficial Sediments		Surficial Aquifer System
Pliocene			
Miocene	Hawthorn Group	Peace River Formation	Intermediate Aquifer System/ Intermediate Confining Unit
		Arcadia Formation	
Oligocene		Tampa Member Nocatee Member	Upper Floridan Aquifer System
	Suwannee Limestone		
Eocene	Ocala Limestone		
	Avon Park Formation		

Figure 2. Lithographic and hydrostratigraphic column of the Floridan Aquifer System (Price and Pichler, 2006)

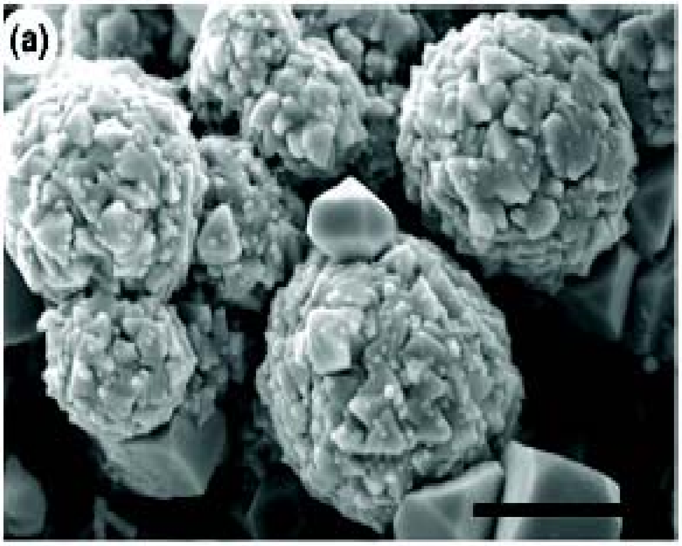


Figure 3. Scanning Electron Photograph of framboidal pyrite found in Suwannee Limestone (Price and Pichler, 2006)

1.2 OVERVIEW OF ARSENIC HYDROGEOCHEMISTRY

The chemical characteristics of arsenic are, in many aspects, more complicated than those of other elements. Environmental arsenic can exist in a solid phase (e.g., $FeAsS$, As_2S_2, trace species in FeS_2), an aqueous phase (e.g., H_3AsO_3, H_3AsO_4), or an adsorbed phase (e.g., $H_3AsO_3 \bullet Fe\ (OH)_3$). Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements in its sensitivity to mobilize at the pH values found in groundwaters (pH 6.5-8.5), under both oxidizing and reducing conditions. In natural waters arsenic is mostly found in inorganic form as oxyanions of trivalent arsenite (As (III)) or pentavalent arsenate (As (V)). Both As (V) and As (III) are, at elevated concentrations, deadly toxins; however, the latter is much more soluble and 60 times more toxic.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, $HAsO_4^{2-}$ is dominant at higher pH, $H_2AsO_4^-$ predominates at pH less than 6.9, and H_3AsO_4 is dominant in extremely acidic conditions (Shih, 2005). Under anoxic conditions, arsenite is stable, with nonionic (H_3AsO_3) and anionic ($H_2AsO_3^{-1}$) species dominant below and above pH 9.2, respectively. Almost no data has been obtained in Florida ASR wells to determine arsenic speciation. Figure 4 shows a representative Eh – pH diagram for arsenic. Most Florida ASR wells would typically operate between +400 and -400 mv and between pH 6.5 to 8.5. Figure 4 does not account for the presence of high concentrations of sulfate and sulfide in the aquifers of southwest Florida. The presence of these constituents would tend to alter the simple Eh-pH diagram shown in Figure 4.

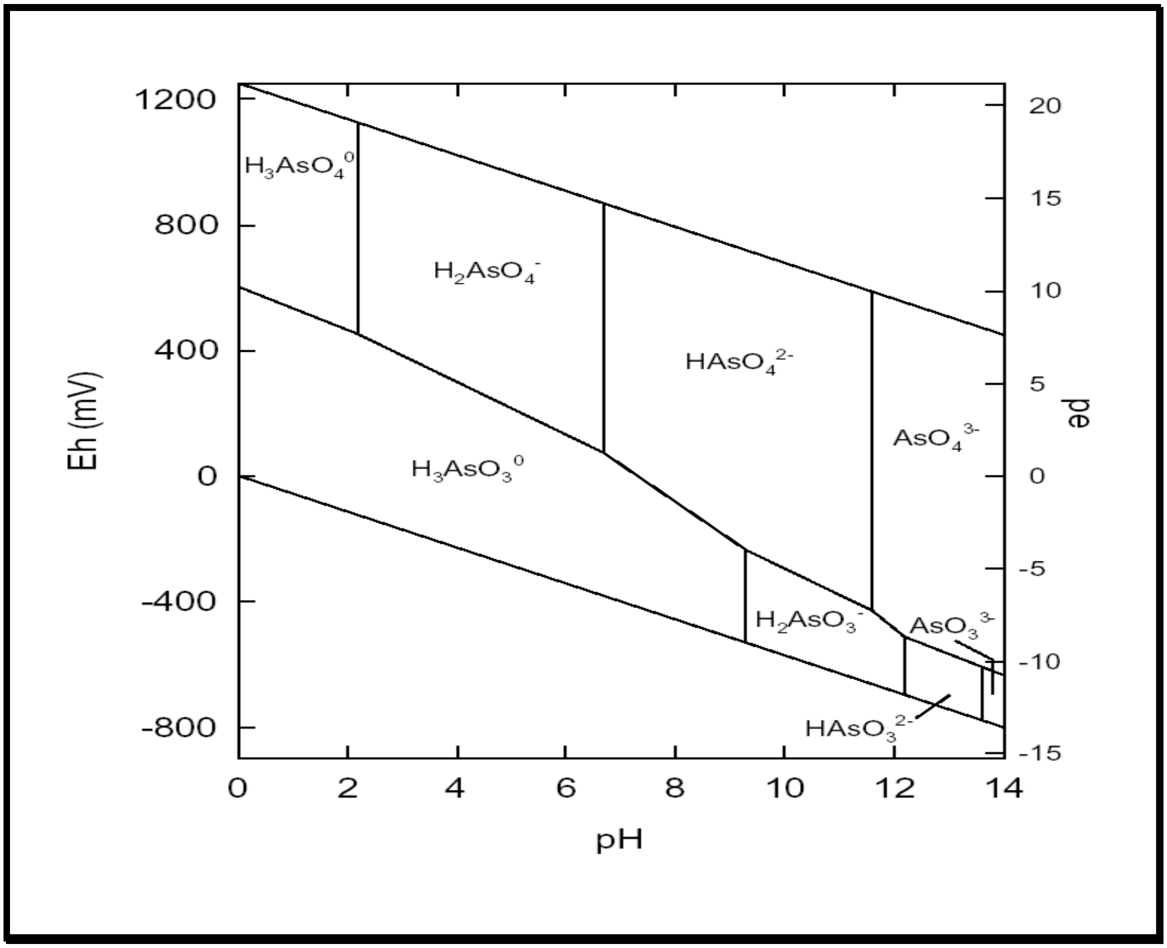


Figure 4. Eh-pH diagram of aqueous arsenic species in the system As-0_2-H_2O at 25^{O}C and 1 bar total pressure

1.2.1 MECHANISMS OF ARSENIC MOBILIZATION

Arsenic mobilization, defined as moving from the solid or adsorbed phase to the aqueous phase, is controlled by parameters that affect changes in 1) the degree of mineral precipitation or dissolution and/or 2) sorption tendency. Table 1 summarizes specific arsenic geochemical mobilizing processes along with associated triggers for those processes (Stuyfzand, 2006). A more detailed discussion of the mobilizing mechanisms follows.

Table 1. Arsenic Mobilizing Processes and Triggering Factors

Mobilizing Processes	**Triggering Factors**
Release due to the oxidation of pyrite (FeS_2) and arsenopyrite (FeAsS)	High redox potential, temperature; microbial activity
Release due to the dissolution of arsenic-sulfide minerals	Changes in pH; increased presence of carbonates
Desorption due to the reduction of iron hydroxides	Decreased redox potential; microbial activity
Desorption due to changes in mineral surface chemistry	Increased pH
Desorption of arsenite/arsenate from minerals due to presence of competing species.	PO_4^{3-}, HCO_3^-, H_4SiO_4, DOC, SO_4^{2-}

1.2.1.1 Oxidation of (Arseno) pyrite

The presence of arsenic in pyrite, arsenian pyrite, is more common than arsenopyrite. Arsenopyrite oxidation can occur via several mechanisms depending on what oxidants are present in a given system. The reaction can be catalyzed by specific microbial enzymes but can occur abiotically as well. Dissolved oxygen (DO), nitrate, and chlorine are all oxidizing agents that may be present in ASR injection water. Because sulfur, iron and arsenic all have several stable oxidation states, there are numerous reaction pathways by which arsenopyrite oxidation can occur, an example of which is provided in Equation 1.

$$2FeAsS_{(s)} + 11/2\ O_2 + 3H_2O \rightarrow 2Fe^{2+} + 2H_3AsO_{3(aq)} + 2SO_4^{2-} \qquad (1)$$

In this case, dissolved oxygen reacts directly with the mineral surface, though it is unknown whether or not this actually occurs in the Southwest Florida geologic setting. Based on Dutch experience, this reaction tends to be slow, though increased temperatures and/or microbial activity can substantially increase observed reaction rates (Stufyzand, 2001).

1.2.1.2 Dissolution of Arsenic Sulfide Minerals

The dissolution of sulfur-based arsenic minerals such as realgar (As_2S_2) and orpiment (As_2S_3) can also lead to increased subsurface concentrations of aqueous arsenic (Kim et al., 2000). Dissolution may be caused by low pH or by decreasing the redox potential in the presence of increased carbonate concentrations. In this case, carbonate-complexed arsenic species [$As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$] can be more stable than mineralized arsenic, thereby driving arsenic toward the complexed, soluble forms (Green et al., 1994). Arsenic sulfide minerals have not been identified as common to the Southwest Florida geological setting.

1.2.1.3 Reductive Dissolution of Iron Hydroxides

Arsenic adsorbs strongly to minerals containing ferric iron (Fe^{3+}) such as ferrihydrite (Fe $(OH)_3$ or goethite (FeOOH). Desorption readily occurs when ferric species are reduced to ferrous (Fe^{2+}) species, which are highly soluble. Therefore, any conditions that catalyze ferric reduction can be considered potentially problematic from an arsenic mobilization perspective. Such conditions include low redox potential and the addition/activation of iron-reducing bacteria (activated by the presence of nutrients and substrate such as organic carbon, hydrogen sulfide, or hydrogen) (Smedley and Kinniburgh, 2002). Given the very low concentrations of ferrous species in the Southwest Florida geological settings, the reductive dissolution of iron hydroxides does not likely account for a substantial portion of the observed subsurface arsenic mobilization.

As previously described, arsenic adsorption is an important mechanism of subsurface aqueous arsenic immobilization. Electrochemical interaction between aqueous arsenic species and mineral surfaces largely drives the occurrence and strength of arsenic adsorption. When the pH of a solution is higher than the isoelectric point of a mineral (pH of neutral surface charge), the net surface charge on the mineral is negative. When the pH of a solution is lower than the isoelectric point of a mineral, the net surface charge on the mineral is positive. Since aqueous arsenic species are negatively charged (if not uncharged), arsenic adsorption tends to strengthen at lower pHs (i.e., increased electrostatic attraction between arsenic and minerals). If the pH of the groundwater matrix increases above the isoelectric point of the local minerals, electrochemical repulsion will drive previously adsorbed arsenic back into solution. Thus, pH is critical in determining the amount of adsorbed arsenic in the subsurface (Smedley and Kinniburgh, 2002). pH changes occur due to both microbial and geochemical activity, particularly in the proximal region close to the ASR well. Typically the pH changes result in a lowering of pH.

1.2.1.4 Competitive Adsorption

The strength of arsenic adsorption is also determined by the presence of other aqueous anionic species in groundwater. Due to their negative charge, species such as phosphate, sulfate, bicarbonate, silicate, fluoride, and some types of dissolved organic matter are competitive with arsenate and/or arsenite for adsorption sites on subsurface minerals. Phosphate is particularly competitive with arsenate, as the two species exhibit similar geochemical behavior (Manning and Goldberg, 1996). Sigg and Stumm (1981) demonstrated that phosphate and silica dominate iron hydroxide sorption sites under certain conditions, such as high pH (> 9.0) and/or high silicate concentrations.

1.2.2 SIGNIFICANCE OF SUBSURFACE MICROBIAL PROCESSES

Though geochemical processes can release arsenic from the geologic matrix, arsenic mobility can be enhanced and accelerated by bacterial activity. Microorganisms can catalyze each of the arsenic mobilization processes described above, as they are often involved in oxidation/reduction reactions that produce changes in dominant chemical species, oxidation states, and even phases (Stolz, 2003). Many of these transformations are important components of arsenic-related biogeochemical processes and cycles (Stolz, 2003). For example, Cummings et al. (1999) showed that microbial reduction of iron minerals by *Shewanella alga* BrY directly releases aqueous phase arsenic species. Other research has shown a decrease in arsenite concentrations during subsurface biological sulfate reduction, with precipitation of arsenic sulfide or coprecipitation of arsenic with other metal sulfides as a control on soluble arsenic concentrations (Kirk et.al., 2004).

Microbially-mediated redox transformations between arsenate (V) and arsenite (III) result from biochemical detoxification mechanisms that permit organisms to expel environmental arsenic from intracellular space (Rosen, 2002). Indeed, several heterotrophic and chemoautotrophic bacteria have been isolated that are capable of utilizing arsenic in metabolic processes in order to provide energy gain and growth (Oremland and Stotz, 2003). Sixteen species of bacteria are known to have the ability to use arsenate as a terminal electron acceptor. These include representatives from the Crenarchaeota and Proteobacteria Phyla. There are over 30 different strains of arsenite-oxidizing bacteria representing nine genera including α–, β–, and γ– Proteobacteria, Deinocci, and Crenarcheota. A γ – Proteobacterium isolated from Mono Lake, California, strain MLHE-1 oxidizes arsenite under anoxic conditions using nitrates as the terminal electron acceptor (Oremland, 2002).

Lab studies have shown equal sorption to hydrous ferric oxides (HFO) under near-nuetral pH, while under acidic conditions As(V) is preferentially sorbed (Welch and Stollenwerk, 2003)

Indeed, microorganisms may ultimately control the subsurface mobility of metalloids like arsenic species (Islam, 2004). Therefore, it is critical to evaluate how the quality of injected ASR water influences subsurface microbial activity. Preliminary data generated in the USGS microbiology laboratory show that injected waters in Southwest Florida have relatively high concentrations of carbon, phosphorous, and ammonium relative to native upper Floridan Aquifer waters. The elevated concentrations of these basic nutrients are the likely cause of the observed increase in associated microbial diversity. The next step is to identify the specific mechanisms by which increased microbial activity and diversity alter arsenic mobilization and attenuation phenomena within the Southwest Florida geologic setting.

1.3 ARSENIC MOBILIZATION DURING ASR OPERATIONS OUTSIDE FLORIDA

1.3.1 Arsenic Mobilization Occurrence at ASR Operations in the Netherlands

For over thirty years, Dutch researchers have focused on water quality changes (including heavy metal mobilization) during artificial recharge and bank filtration (Stuyfzand, 1998). Over 11 independent experiments on deep well recharge have been conducted relying on extensive hydrogeochemical monitoring. These studies examined, among others, the mobilization potential of heavy metals in the following distinct environments: the coastal dunes, the Rhine fluvial plain and the Pleistocene uplands. The aquifers examined in these studies were composed of either Pleistocene or Miocene sands. The native groundwater in these aquifers was generally characterized as fresh (7-70 mg/L chloride), calcite-saturated (pH 6.5 -7.5, 40-100 mg/L $CaCO_3$), anoxic (no detectable oxygen, nitrate and often no sulfate), and with relatively high concentrations of ferro (1-10 mg/L), manganese (0.1-0.6 mg/L), ammonia (0.3-0.5 mg/L), and silicate (18-40 mg/L). In addition, all target aquifers contained small but significant amounts of reactive pyrite. Furthermore, calcium carbonate was typically present at sites where the North Sea and Rhine River had deposited Pleistocene sediments.

In these studies, an oxic influent was used as recharge for an anoxic aquifer containing significant levels of pyrite. The results indicated that the main water quality constituents in each aquifer underwent an evolution of seven distinct phases during the course of the experiments, due to the occurrence of sequential leaching. These phases were, in mean order of increasing duration for the reaction to occur: mixing with native groundwater, cation exchange, SiO_2 desorption, PO_4^{3-} and F^- exchange, pyrite oxidation, acid buffering by calcite dissolution or HCO_3^-, and oxidation of organic matter. Pyrite oxidation, which was observed at all test sites, was considered as the most important water-sediment interaction. Pyrite oxidation was observed to be a relatively slow process taking 10-100 days to completely deplete O_2 and NO_3^- in the influent. In addition, the kinetics of pyrite oxidation were shown to be temperature dependent, as the rate decreased considerably when the temperatures fell below 10^O C (for details on the reaction kinetics see Henning and Stuyfzand, 2004). In all cases, the oxidation of pyrite, quantified by sulfate release, predicted the mobilization of arsenic and nickel, as shown in Figure 5 below.

Concentration (µg/l) of As and Ni and SO_4-increase

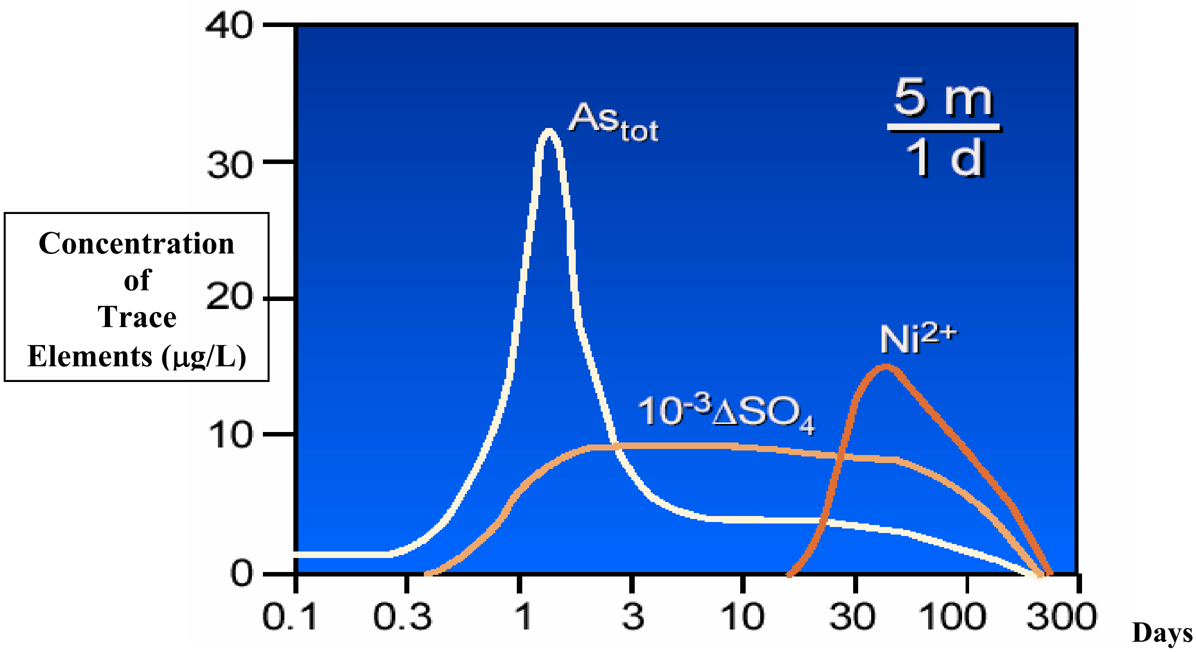


Figure 5. Relationship between observed sulfate release rate and the concentrations of As and Ni in observation wells

The trends shown in Figure 5 are consistent with the geochemical composition of pyrite. The increased concentration of trace elements in the recovered water are directly related to the total release of sulfate. Among the other trace elements within pyrite, zinc did not mobilize, and nickel was much less mobile than arsenic, which was observed farther away from the injection well. It is hypothesized that these metals precipitated with and/or strongly adsorbed to neoformed Fe $(OH)_{3.}$ This phenomenon is most likely due to the strong bonding characteristic of the divalent charges for the Ni and Zn species. Initially, arsenic was more mobile due to its reduced state (occurring in water as H_3As0_3) which prevented it from sorbing to $Fe(OH)_3$. However, after time, oxygen and nitrate present in the recharge water converted the released arsenic into its oxidized state (AsO_4^{3-}), which was less mobile due to preferential sorption to the neoformed $Fe(OH)_3$.

The overall trend of these experiments indicates that approximately 90% of the arsenic mobilized was re-deposited with further aquifer passage, while the remaining 10% migrated and/or appeared in the recovery water. The Dutch studies concluded that pyrite oxidation occurred close to the injection wells within a distance of 20-90 feet and depleted the recharge water of most of its oxygen and nitrate (the other reductant being soil organic material).

The ”dual infiltration” wells in the Netherlands cannot be considered ASR wells as water is injected through one well and recovered from another, at a distance of approximately 100 m; however, the findings are applicable to the behaviour observed at downstream monitor wells and aid understanding of issues of trace element contamination in the Floridan aquifer (Pyne, 2004).

Adsorption of arsenic on ferric hydroxide is also likely to be a significant mechanism in SW Florida, even though ferro iron concentrations in the ambient groundwater are not significant. The primary source of iron is the dissolution of pyrite, as shown in Equation (1), which would combine with any available oxygen to form ferric hydroxide coatings on the pyrite or would form microflocs. The latter may flow with the recharge water away from, and then back towards the ASR well during recovery, unless or until they become physically trapped or precipitate in the storage zone. A potential secondary source of iron is ferric hydroxide present at low concentrations in the recharge water due to water treatment processes. It is hypothesized that a portion of the mobilized arsenic following dissolution would sorb onto the ferric hydroxide, which would then tend to form a “rolling front” of arsenic moving a short distance away from the ASR well during recharge. During recovery either attenuation of arsenic concentrations may occur or a remobilization due to subsurface microbial and/or geochemical mechanisms that are not yet fully understood. Mixing, dispersion, sorption and desorption do not totally account for the observed degree of arsenic attenuation during ASR storage. Microbial activity and pyrite dissolution would probably tend to lower the pH, favoring sorption of arsenic on the ferric hydroxide floc. Furthermore, the ferric hydroxide will tend to coat the pyrite grains, reducing the opportunity for further dissolution.

1.3.2 Observed Arsenic Mobilization during ASR Operations in Australia

In Australia, ASR is a valuable resource management tool, typically used for storing available water (surface or wastewater) for reuse. ASR operations at Bolivar, South Australia, have started to investigate the feasibility of reclaiming and storing treated wastewater for irrigation in the neighboring horticultural region. The ASR field site is located adjacent to the Bolivar Water Reclamation Plant and in close proximity to the Virginia horticultural region where the reclaimed water is used as a seasonal irrigation source (Figure 6). The first ASR cycle at Bolivar recharged 2.5x10^5 m^3 (66 million gallons, MG) with recovery of 1.5x10^5 m^3 (40 MG) following a 16-week storage phase Several scientific investigations have been conducted, including the behavior of trace metal and metalloid species in a carbonate aquifer (Vanderzalm et al., 2004).

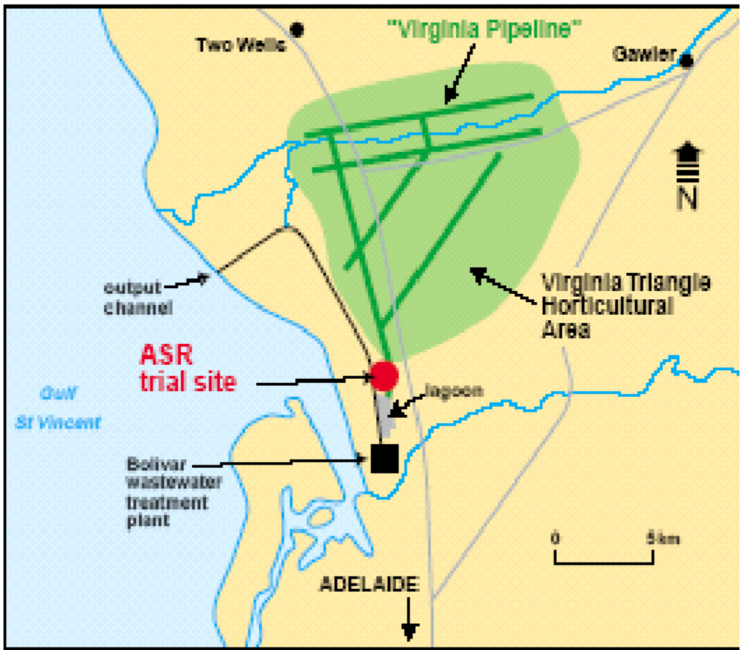


Figure 6. Location of the Bolivar ASR site in South Australia where reclaimed water is used for irrigation (Vanderzalm, 2004)

The mineralogy of the area is dominated by calcite and quartz, with minor contributions from hematite, microcline, and albite. Arsenic was present in the recharge waters at comparable concentrations to the background groundwater concentration, with mean concentrations of 2 and 5 µg/l, respectively. However, arsenic concentrations in the recovered water were, on average, 15 µg/l, indicating mobilization throughout the ASR cycle. Vanderzalm et al. (2004) identified two mechanisms for arsenic mobilization at the Bolivar ASR site:

1. Pyrite oxidation in the near well zone (evident at the 4 m well) accounted for approximately 12 µg/L of arsenic mobilization. However, at 50 m radius from the injection point, there was no indication of arsenic migration (concentrations below 3 µg/L. It was also observed that during the ASR cycle recovery phase, the arsenic concentration recovered was approximately six times that expected from conservative behavior, implying a further dissolution of arsenic from pyrite in the aquifer matrix.

2. The reducing conditions that occurred in the ASR well during the storage phase also appeared to significantly affect arsenic mobilization. Here, reductive Fe(III) dissolution was observed and had the greatest (peak concentration 187 µg/l), but short-lived effect on the magnitude of soluble arsenic concentration.

The results from this study indicated the effect of differing redox conditions induced during an ASR cycle on arsenic mobility. Reduced conditions in close proximity to the ASR well during aquifer storage affected arsenic concentrations in a small volume of recovered water, while pyrite oxidation during injection impacted arsenic concentrations in the bulk of the recovered water.

1.3.3 Arsenic Mobilization Occurrence during ASR Operations in the United States Outside Florida

In 1985 only three states had operational ASR systems (New Jersey, Florida, California); however, ASR has since then expanded to several additional states across the country. Currently, there are over 72 operational ASR sites in 16 states, with 11 additional states either operating pilot systems or conducting other feasibility studies.

Apart from Florida, issues with arsenic mobilization in ASR wells have arisen in Wisconsin and are being reviewed in other states.

Groundwaters in Wisconsin have regional concerns with arsenic and radionuclides. Arsenic mobilization is of particular concern in Wisconsin because high arsenic concentrations already affect a number of production wells in the Fox River Valley where a regional lowering of water levels has exposed sulfide minerals to oxygen. Examining the causes behind arsenic concentrations observed in the production wells of the Fox River Valley can provide a useful point of reference for understanding arsenic water quality changes in Florida ASR wells.

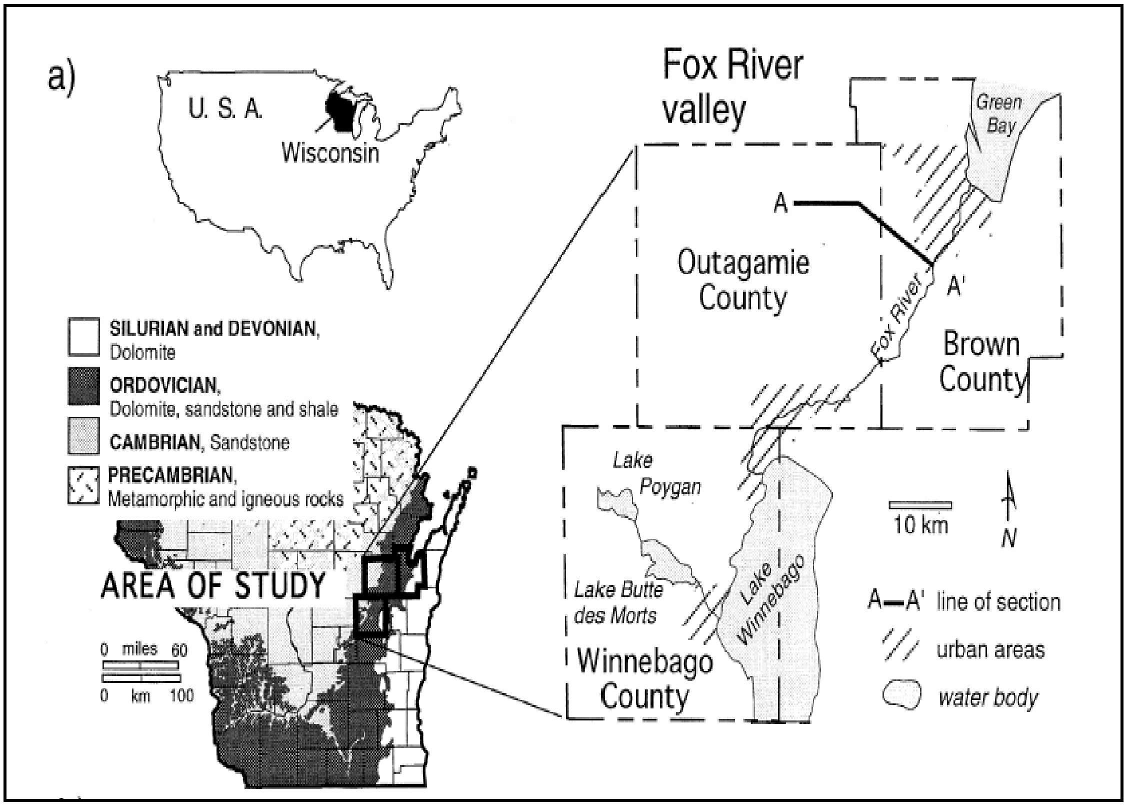


Figure 7: Location and bedrock geology of the Fox River Valley, WI

High arsenic concentrations have been measured in many wells located in the Fox River Valley of Winnebago, Outagamie, and Brown Counties. Studies have shown arsenic concentrations reaching as high as 12,000 µg/L (Schreiber et al., 2000). The apparent arsenic source is the naturally occurring layer of Sulfide Cement Horizon (SCH) which occurs below the base of the Platteville Formation (Simo et al., 1996). The SCH consists primarily of arsenic-bearing pyrite and marcasite crystals (pyrite and marcasite are both iron sulfide minerals). The arsenic content is variable, but can reach 1% to 2% by weight (Simo et al., 1996).

Fox River Valley groundwater typically contains only small amounts of dissolved oxygen, and under normal conditions, pyrite and marcasite are insoluble. However, as stated previously, pyrite and marcasite are subject to oxidative dissolution if oxygen levels rise. It has become clear that in the Fox River Valley, arsenic once contained in the SCH has been mobilized (as arsenate, $AsO_4{}^{3-}$) into the adjacent groundwater in areas where the SCH intersects the regional water table or local water surface. When the pyrite contained in the SCH lies at a water surface, it is exposed to elevated levels of atmospheric oxygen, begins to dissolve, and thus releases arsenic.

In areas where the water table is at or below the SCH, the well bore itself provides a direct conduit for oxygen to come in contact with arsenic-rich pyrite. (Schreiber et al., 2000). Although arsenic is not an anthropogenic contaminant, but rather a naturally occurring element, the mobilization of arsenic is strongly influenced by human-induced changes to the aquifer. Continued pumping operations are lowering water levels in the Fox River Valley. As a result, the SCH will inevitably be further exposed, leading to further arsenic mobilization. Further studies have been recommended to obtain a clear understanding of the aquifer mineralogy, groundwater flow patterns and geochemistry of the region to address the cause of arsenic mobilization in the regional production wells.

Florida ASR wells are in confined artesian aquifers at considerable depth, unlike the unconfined aquifers in this part of western Wisconsin. So it is unlikely that arsenic would be mobilized in SW Florida production wells due to lowering of aquifer water levels. However for Florida ASR wells oxygen is introduced with the recharge water, probably setting in motion some of the same arsenic mobilization processes that occur in Wisconsin. The limited solubility of oxygen in water prevents the oxidation of pyrite during ASR operations, which typically occur under fully saturated conditions (ie: without a vadose zone). Therefore arsenic concentrations in ASR wells may be expected to not reach the levels observed in Wisconsin where atmospheric oxygen has gained access to the exposed iron sulfide minerals.

2.0 POTENTIAL ARSENIC PRETREATMENT PROCESSES

2.1 KEY ARSENIC MOBILIZATION PROCESSES

Section 1.1.4 describes known mechanisms by which arsenic can transfer from a solid or sorbed phase to the aqueous phase under various subsurface hydrogeochemical conditions. To identify pretreatment technologies that are applicable to Southwest Florida ASR operations, the mobilization mechanisms that might be expected within the Suwannee Limestone Unit (SLU) must be determined.

It has been shown that the SLU contains abundant concentrations of arsenian pyrite and arsenopyrite but very low to negligible concentrations of arsenic sulfide and iron hydroxide minerals. Therefore, the oxidation of pyrite/arsenopyrite is likely an important mechanism of subsurface SLU arsenic mobilization, while the dissolution of arsenic sulfide minerals and the reduction of iron oxides are not. Desorption of arsenic species from subsurface minerals due to a rise in groundwater pH would account for some arsenic mobilization in the SLU, however most data to date suggests a decline in pH during ASR storage, which would promote sorption, not desorption. The desorption of arsenic species due to the presence of competing anions such as phosphate and sulfate may be possible as well. In particular, phosphate is a much stronger competing anion than sulfate. Numerous anionic species are already present in the native SLU groundwater. The injection of additional competing anions may or may not be a significant contributor to arsenic mobilization in the SW Florida hydrogeological setting, depending upon the presence of gypsum (high sulfate concentrations) in the aquifer and phosphorus in the recharge water.

In summary, decreasing the redox potential of ASR injectant to avoid the oxidation of arsenopyrite is likely the key to minimizing the mobilization of subsurface arsenic during

ASR operations in Southwest Florida. Depressing injectant pH may also decrease arsenic mobilization. Slowing subsurface microbial activity, which is capable of catalyzing arsenic-mobilizing reactions, may also be important but is not well understood. Consequently, the removal of dissolved oxygen (DO) and nitrate, which are both strong oxidants, forms the basis for our selection of appropriate ASR pretreatment technologies. Processes capable of decreasing injectant pH are also considered.

2.2 BASIS OF DESIGN

To normalize pretreatment alternatives, it was assumed that target DO and nitrate concentrations in ASR injectant were both zero and that initial DO and nitrate-nitrogen concentrations were 8 mg/L and 1 mg/L, respectively. These initial DO and nitrate values are reasonably representative of injectant concentrations from six ASR wellfields in SW Florida, including Bradenton, Peace River, Lake Manatee, Manatee SW, North Port, and St. Petersburg. Higher DO concentrations occur at the City of Tampa ASR wellfield, which recharges drinking water that has been treated with ozone. For pH control, it was assumed that injectant pH was 7.7 (representative of the same six ASR wellfields) while the target pH was 7.4 (average native groundwater pH among wellfields in Peace River, Tampa, Punta Gorda, Lee County, and Manatee SW). A 700 gallons per minute (1 million gallons per day, MGD) pretreatment capacity was also assumed. Typical ASR recharge and recovery rates in SW Florida are within a range of 0.4 to 2.5 MGD. Life-cycle costs were calculated by factoring 1) operation and maintenance costs (power, consumables, NOT labor) and 2) capital costs (equipment, infrastructure, materials, engineering) amortized over 20 years at 5%.

2.3 PRETREATMENT TECHNOLOGIES: DECREASE IN REDOX POTENTIAL

There are two mechanisms by which aqueous DO can be eliminated: 1) it can be reduced to water in an oxidation-reduction reaction, or 2) it can be volatilized. Oxidation-reduction reactions can occur in the presence of a metal or biological catalyst to increase reaction kinetics but can also occur without a catalyst present. Volatilization can occur either by drawing a vacuum that drives gas out of solution or by contacting a solution with a delivered carrier gas such as nitrogen. Table 2.1 lists specific processes by which DO can be removed from water, associated advantages and disadvantages, and ranges for estimated life cycle costs. In this table, "X" refers to any reduced compound; "CSTR" refers to "continuously stirred tank reactor."

Table 2.1 ASR Pretreatment Alternatives - Dissolved Oxygen Removal

General Process Description	**Specific Processes/Modes**	**Advantages**	**Disadvantages**	**Life Cycle Costs ($/1000 gallons)**
Uncatalyzed Chemical Reduction $X_{reduced} + O_2 \Rightarrow X_{oxidized} + H_20$	• $X_{reduced}$: • Thiosulfate ($S_2O_3^{2-}$) • Tetrathionate ($S_4O_6^{2-}$) • Sulfite (SO_3^{2-}) • Hydrazine (N_2H_4) • Diethyl hydroxylamine ($4(C_2H_5)_2$ NOH) • Proprietary chemicals such as AmGuard™ 7800 (sodium sulfite product) or Oxyrase® • Mode: • In-line mixed system • Mixing tank	• Simple process • Proven process	• Can create biological instability in recharge water • Adds dissolved solids to injectant • Reaction with dissolved oxygen may be incomplete if no catalyst is present or temperatures are below 240 °F • Can alter solution pH	0.41->1.00
Metal-Assisted Catalytic Reduction $X_{reduced} + O_2 +$ *metal catalyst* $\Rightarrow X_{oxidized} + H_20$	• $X_{reduced}$: • Hydrogen (H_2) • Hydrazine (N_2H_4) • Catalyst: • Palladium • Cobalt • Mode: • Fixed bed containing doped resin or GAC • CSTR containing catalyst	• Rapid kinetics • Can achieve dissolved oxygen levels of 1 ppb or less	• Hydrogen gas storage may be required (explosion hazard) • By-products are not well-characterized	>1.00
Microbially-Catalyzed-Reduction $X_{reduced} + O_2 +$ *bacteria* $\Rightarrow X_{oxidized} + H_20 +$ *new cells*	• $X_{reduced}$: • Acetic acid (CH_3COOH) • Ethanol (C_2H_5OH • Hydrogen (H_2) • Mode: • Fixed-bed bioreactor • Fluidized-bed	• High removal efficiency • Can be achieved using organisms indigenous to feed water supply • Can remove	• No full-scale track-record in the U.S. • Regulatory/public acceptance required • Can result in sulfide production • Relatively large footprint required • May not be effective if	0.40-0.70

	bioreactor • CSTR (suspended growth)	multiple contaminants including nutrients and substrate to minimize biological instability of injectant. • Proven at full-scale in Europe and at the bench-and pilot-scales in the U.S.	operated in a non-continuous mode	
Volatilization *$O_{2(aq)}$ + carrier gas $\Rightarrow O_{2(g)}$ + carrier gas* *OR* *solution + negative pressure $\Rightarrow O_{2(g)}$ + solution*	• Fine bubble diffusion • Packed tower • Minox Process • Gas Transfer Membranes • VacGDT™ Process • GasTrans Systems	• Can be done with no chemical addition (i.e., under vacuum) • Small footprint requirement • Less prone to biofouling	• Can result in unwanted water quality changes (e.g., pH depression) • Systems can be complex • Except in vacuum applications, resultant solution is supersaturated with respect to the carrier gas, which could volatilize in the subsurface.	0.35-1.50

Nitrate also contributes to the redox potential. There are three mechanisms by which nitrate can be eliminated: 1) it can sorb to synthetic resins during an ion exchange reaction, 2) it can be physically separated by reverse osmosis membranes, or 3) it can be reduced to NH_3, $N_{2(g)}$ or other reduced nitrogen species. Nitrate reduction can occur via an abiotic chemical reaction but can also be catalyzed in the presence of certain bacteria. Table 2.2 lists specific processes by which nitrate can be removed from water, associated advantages and disadvantages, and ranges for estimated life cycle costs.

Table 2.2 ASR Pretreatment Alternatives - Nitrate Removal

General Process Description	**Specific Processes**	**Advantages**	**Disadvantages**	**Life Cycle Costs ($/1000 gallons)**

Ion Exchange
 	
$Resin\text{-}X^- + NO_3^- \Rightarrow Resin\text{-}NO_3^- + X^-$
	• Strong base anion exchange resins (e.g. contains quaternary ammonium functional groups - $N^+(CH_3)_3$)
	• X^-:
	  • OH^-
	  • Cl^-
		• High removal efficiency
		• Proven technology
			• Off-line resin regeneration required
			• Generation of high-strength brine
			• Potential for NDMA leaching from resins
				1.20-3.00

Membrane Separation *Physical separation due to diffusion- or ionic-transport limitations*	• Reverse osmosis • Electrodialysis reversal	• High rejection rates (>95%) • Proven technology • Multiple contaminant removal capability	• Generation of high-strength brine • Operationally complex • Membranes susceptible to fouling	3.00-7.00

Biological Reduction
 	
$X_{reduced} + NO_3^- + bacteria \Rightarrow X_{oxidized} + N_xO_y + new\ cells$
	• $X_{reduced}$:
	  • Acetic acid (CH_3COOH)
	  • Ethanol (C_2H_5OH
	  • Hydrogen (H_2)
	• Mode:
	  • Fixed-bed bioreactor
	  • Fluidized-bed bioreactor
	  • CSTR (suspended growth)
		• High removal efficiency
		• Destroys, instead of concentrating, nitrate
		• Can be achieved using organisms indigenous to feed water supply
		• Can remove multiple contaminants including nutrients and substrate to minimize biological instability of injectant.
		Proven technology in Europe
			• No full-scale track-record in the U.S.
			• Regulatory/public acceptance required
			• Can result in sulfide production
			• May not be effective if operated in a non-continuous mode
				0.40-0.70

Chemical Reduction
 	
$X_{reduced} + NO_3^- \Rightarrow X_{oxidized} + N_xO_y$
	• *$X_{reduced}$ = elemental iron (Fe^0)*
	• *Mode:*
	  • *Packed columns*
	  • *Batch reactor*
		• No advantages yet identified	• Slow kinetics
			• Increase of soluble iron
			• Accumulation of reduction intermediates
			• Difficult to control
			• Not well-understood
				NA (insufficient design information available due to immaturity of the process)

2.4 PRETREATMENT TECHNOLOGIES: pH REDUCTION

There are two mechanisms by which pH can be reduced: 1) A strong acid (i.e., has a low acid dissociation constant) can be added to water to supply H^+ ions, and 2) Carbon dioxide can be sparged into water to form carbonic acid, a weak acid, which can also produce H^+ ions. Table 2.3 lists specific processes by which pH can be depressed, associated advantages and disadvantages, and ranges for estimated life cycle costs.

Table 2.3 ASR Pretreatment Alternatives - pH Reduction

General Process Description	**Specific Processes**	**Advantages**	**Disadvantages**	**Life Cycle Costs ($/1000 gallons)**
Strong acid addition $H\text{-}X \Leftrightarrow X^- + H^+$	• H-X: • Hydrochloric acid (HCl) • Sulfuric acid (H_2SO_4) • Phosphoric acid (H_3PO_4) • Mode: • In-line mixed system • Mixing tank	• Simple process • Fast kinetics • Can reach low pHs if desired • Easily controlled • Operates on demand	• Hazardous • Corrosive	0.04-0.14
Carbon dioxide sparging $CO_{2(g)} + H2O \Leftrightarrow H_2CO_{3*(aq)}$	• In-line aeration • Aeration tank	• Safe • Easily controlled • Non-corrosive • Self-buffering • Operates on demand	• Weak acid (i.e., cannot reach low pHs if desired) • Slower kinetics than strong acid	0.02-0.05

2.5 PRETREATMENT RECOMMENDATION

When considering which pretreatment process(es) require further consideration, it was first assumed that, while pH control may slightly decrease the occurrence of subsurface arsenic mobilization, the critical step in decreasing arsenic mobilization in SW Florida is minimizing the oxidation of (arseno)pyrite. Given that oxygen accepts electrons more readily than nitrate and the fact that average injectant nitrate-nitrogen concentrations are only ~1 mg/L, it was also assumed that removing injectant DO is the critical path for minimizing arsenic mobilization. Consequently, this discussion centers around Table 2.1.

There are four general processes capable of removing DO from water: 1) uncatalyzed chemical reduction, 2) metal-assisted catalytic reduction, 3) microbially-catalyzed reduction, and 4) volatilization. Processes based on metal-assisted catalytic reduction are expensive and relatively complex and therefore are not recommended. Uncatalyzed chemical reduction, microbially-catalyzed reduction, and volatilization require further consideration.

2.5.1 Uncatalyzed Chemical Reduction

The chemical reduction of DO using reductants such as thiosulfate or sulfite are attractive due to their simplicity. These systems would require only a chemical feed system along with an in-line static mixer and possibly a tank for added reaction time. A concern with this approach is the fact that under ambient water treatment plant conditions, uncatalyzed chemical DO reduction can be slow and/or incomplete. To improve reaction kinetics, catalysts such as cobalt or heat can be added to the system or excess reductant could be dosed to the water, both of which would result in substantial increased costs. For example, one DO removal study showed that 160 mg/L of sodium thiosulfate was required to reduce 8 mg/L of DO down to zero in 20-30 minutes, though only 20 mg/L is stoichiometrically required if thiosulfate is oxidized to sulfate (Kirisits et al., 2001). When the dose was decreased below 160 mg/L, complete DO reduction was not achieved even after 5 days. One other concern with chemical DO reduction is that it can result in unwanted changes in pH, depending on which reductant is used.

To identify reaction kinetics, extents of reaction, and resultant water quality changes, it is recommended that a series of simple jar tests are run with thiosulfate, sulfite, and one or two proprietary oxygen scavengers. These tests would require only a few days and would tailor design requirements and cost estimates to SW Florida ASR operations. It is estimated that this testing would cost approximately $3,000 for expenses, plus associated labor.

This approach was used successfully at an ASR site at Swimming River, New Jersey, approximately 15 years ago. The objective was to not only reduce DO but also to oxidize the mineral siderite (ferrous carbonate) around the well. Arsenic mobilization and attenuation was not an issue at this site, however very high concentrations of iron and manganese occurred in the ambient groundwater. Reaction time was allowed to occur in the aquifer around the well instead of only in tanks above ground. Recharge of the sodium sulfite solution began at a very slow rate of a few gallons per minute. With increasing cumulative storage volume the recharge rate was gradually raised, ensuring that contact time in the aquifer was within a target range. This approach would only work in SW Florida if FDEP is amenable to a similar approach, rather than providing full pretreatment prior to recharge and thereby substantially reducing the cost of providing storage above ground. The reaction reduced recharge water pH to between 3 and 4.

2.5.2 Microbially-Catalyzed Chemical Reduction

The use of microbial biomass for the degradation of contaminants, nutrients, and organics has been commonly used in the wastewater field since the early 1900s. However, the biological treatment of drinking water has been much more limited in the United States and only recently has been expanded to include the treatment of a wide variety of organic and inorganic contaminants. In contrast, biological removal of organics, ammonia, and nitrate from drinking water has been practiced for decades in Europe. Biological systems could also be used to remove oxygen, though this is not a common water treatment objective. Oxygen is a highly oxidized compound, which means that microorganisms can gain substantial energy by coupling its reduction with the oxidation of an electron donor such as acetic acid. This reaction can be very fast since aerobic bacteria produce enzymes that facilitate the conversion of oxygen to water.

A fixed-bed bioreactor, which uses a stationary bed of granular media on which biofilms develop, is a simple and relatively inexpensive mode of biological treatment. An electron donor is fed just upstream of the bioreactor. Oxygen-reducing biofilms grow on the surface of the GAC and are partially sheared off during periodic backwash events. The backwash water is typically discharged to the sewer, or the biomass is settled, dried, and land applied. Efficiencies of fixed-bed biological processes are generally >97%. These systems have been used extensively for the removal of other inorganic compounds such as nitrate, perchlorate, and nutrients (Bonnelye, 2006, Brown et al., 2002; 2005). Thus, an additional benefit of a biological process for DO control is that other unwanted compounds (e.g., nitrate, ammonia, phosphorous) can be removed simultaneously with DO. Allowing bacteria to consume substrates and nutrients in a controlled ex situ reactor should minimize subsurface biological activity, thereby minimizing the degree of microbially-assisted arsenic mobilization.

The main concern with the biological DO reduction approach is that if a biological system is not operated relatively continuously, the microbial activity may die off or diminish to below useful levels. It is possible to shut down a biological process for periods up to a few weeks without impacting system kinetics. However if system downtimes are on the order of months, the system may require a two-week startup period prior to the beginning of recharge. The other issue that must be addressed with a fixed-bed bioreactor is the footprint requirement. Because this process requires pressure vessels and a tank for storing backwash water, the required footprint would likely be larger than that needed for a chemical DO reduction process. For example, the fixed-bed bioreactor process footprint for a 700-gpm system would be approximately 30’x30’, about twice as large as that required for a comparable chemical DO removal process.

To identify degradation kinetics, bioreactor backwashing requirements, and required electron donor doses, it is recommended that a short-term, bench-scale column study be performed using GAC as the biogrowth support medium. These tests would require approximately 2 months and would tailor design requirements and cost estimates specifically to SW Florida ASR operations. It is estimated that this testing would cost approximately $7,000 for expenses, plus associated labor.

2.5.3 Volatilization

Henry’s Law states that the aqueous concentration of a gas is proportional to its partial pressure in the adjacent atmosphere. As the partial pressure of a carrier gas (e.g. CO_2) increases, the partial pressure of oxygen decreases, thereby driving aqueous oxygen to partition into the gas phase (i.e., be stripped from solution). Numerous proprietary processes have been developed to increase the efficiency of gas stripping by increasing the gas/water interfacial area. Efficiencies of some stripping systems are high enough that required footprints for a 700-gpm system would be as low as 8'x5'. The main concern with this approach is that the resultant solution is supersaturated with respect to the carrier gas. This could lead to a scenario where gas bubbles form in the ASR well or subsurface, which could severely disrupt system hydraulics. The other concern is that annual CO_2 costs can be as high as $0.90/1000 gallons depending on the target DO concentration.

Air binding of the ASR storage zone due to cascading of water into the well has caused rapid plugging at several ASR sites outside Florida, particularly in unconsolidated aquifers. Restoration of well capacity is possible but requires much time and effort. On the other hand, continuous addition of CO_2 to the recharge water is currently practiced at a few SW Florida ASR wellfields as a means of reducing the pH by about 0.5 units and thereby dissolving limestone. This tends to slowly increase the well specific capacity and yield. It also offsets any plugging that may be occurring.

The other method by which DO could be volatilized during pretreatment is by applying a vacuum to the treatment system. When the vacuum decreases system pressure to below the local vapor pressure, DO will partition from the aqueous phase to the gas phase. Footprint requirements are comparable to those for stripping systems, and no chemicals or gases are applied to the system, which eliminates the concern of carrier gas re-volatilization. However, power requirements tend to be higher for vacuum-driven deoxygenation processes.

To identify required carrier gas dosages, revolatilization kinetics, and/or vacuum power requirements, it is recommended that a short-term, bench-scale study be performed using a proprietary deaeration system. These tests, which could evaluate both stripping and vacuum-based systems, would require approximately 1 month and would tailor design requirements and cost estimates specifically to SW Florida ASR operations. It is estimated that this testing would cost approximately $5,000 for expenses, plus associated labor.

2.5.4 Pretreatment Recommendations

It is recommended that all three processes be pilot tested, following which one process would be selected for further investigation, probably through construction and testing of a demonstration pretreatment system at full scale for a single ASR well at a site to be selected. Pilot testing would require approximately 3 months duration. Estimated total cost for pilot testing facilities, including labor and expenses, would not exceed $50,000.

2.6 ESTIMATED COSTS

Whichever pretreatment option is ultimately selected for full-scale application, the projected life cycle costs, including capital amortization plus operation, are in excess of $0.35 per kgal and may be in excess of $1.00 per kgal. For a typical ASR well storing an estimated 100 MG per year, the associated annual cost would be $35,000 to $100,000 or more.

This may be compared with typical ASR unit life cycle costs averaging about $55,000 per year for a 1 MGD ASR well (~100 MG annual storage volume), plus or minus about $20,000. This is a national average. During the past three years in Florida the cost of ASR has approximately doubled, associated with new regulatory requirements regarding numbers of monitoring wells, analytical costs, coring and core geochemical analysis, extended cycle testing, and other permitting requirements. Historically, Florida ASR unit costs were substantially below the national average, reflecting the high yields of ASR wells in Florida. Florida's ASR costs are now probably at or above the national average. It is evident that pretreatment of ASR recharge water to reduce or eliminate the oxidation-reduction potential would substantially increase the cost of ASR operations in Florida.

Capital, operating and life cycle costs are presented in the following tables:

Table 2.4 ASR Pretreatment Alternative Costs - Dissolved Oxygen Removal

Process	Capital ($/gpd)	O&M ($/1000 gallons)	Life Cycle ($/1000 gallons
Uncatalyzed Chemical Reduction	~0.02	~0.50	0.41 to >1.00
Metal Assisted Catalytic Reduction	~0.02	~1.00	>1.00
Microbially-Catalyzed Reduction	~1.20	~0.15	0.40 to 0.70
Volatilization (stripping)	~0.43	~1.20	1.30 to1.50
Vacuum Deaeration	~0.52	~0.10	0.30 to 0.45

Table 2.5 ASR Pretreatment Alternative Costs - Nitrate Removal

Process	Capital ($/gpd)	O&M ($/1000 gallons)	Life Cycle ($/1000 gallons
Ion Exchange	~1.20	~1.90	1.20 to 3.00
Reverse Osmosis	~ 4.0	~2.50	3.00 to 7.00
Microbially-Catalyzed Reduction	~1.20	~0.15	0.40 to 0.70
Chemical Reduction	NA	NA	NA

Table 2.6 ASR Pretreatment Alternative Costs - pH Reduction

Process	Capital ($/gpd)	O&M ($/1000 gallons)	Life Cycle ($/1000 gallons
Strong Acid Addition	<0.01	~0.07	0.04 to 0.14
Carbon Dioxide Sparging	<0.01	~0.03	0.02 to 0.05

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Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities

Task 3 - Technical Memorandum: Field Data Analysis

Prepared for

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Task 3 – Field Data Analysis: Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities

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Contents:

Executive Summary

Operational data from 52 ASR wells and 41 storage zone observation wells in 12 ASR wellfields of southwest Florida have been analyzed to seek an improved understanding of the subsurface physical, geochemical and microbial processes that mobilize and attenuate arsenic during ASR storage. Following are the conclusions of the analysis, followed by a brief discussion and then by recommendations.

Conclusions

1 Arsenic that is mobilized during recharge of water into an aquifer containing arsenic-bearing minerals such as pyrite has been detected at observation wells generally within a 200 ft radius of the ASR well, even though the radius of the stored water bubble may extend several hundred feet further. Observation wells at greater radial distances have generally not detected elevated arsenic concentrations.

2 Where elevated arsenic concentrations have been detected in the recovered water or in observation wells, they attenuate to acceptable levels within approximately four to six ASR cycles, during each of which the same volume of water recharged is subsequently recovered.

3 During ASR recharge, arsenic mobilization is believed to be caused primarily as a result of dissolved oxygen in the recharge water. However other constituents of the recharge water also contain oxygen and may contribute to arsenic mobilization. For ASR wellfields in southwest Florida, these other constituents may typically include nitrate (NO_3), dissolved organic carbon (DOC), and phosphate (PO_4).

4 At the same time that arsenic is released due to pyrite dissolution, ferrous iron is also released. Even where iron is present at insignificant levels in the recharge water and also in the ambient groundwater, it accumulates to relatively high concentrations in the aquifer close to the ASR well, but within drinking water standards. The iron is in a particulate form, not dissolved, suggesting strongly that it is ferric hydroxide floc, formed rapidly as a result of contact between ferrous iron in solution and oxygen in the recharge water. Arsenic is readily adsorbed onto ferric hydroxide floc, particularly at low pH levels that occur close to the well. The mobility of the ferric hydroxide floc may be a primary determinant of ASR well arsenic concentrations in Southwest Florida's karst limestone aquifers.

5 During ASR recovery, arsenic remains adsorbed on the ferric hydroxide floc close to the ASR well unless a significant water quality change occurs, such as may happen if elevated concentrations of bicarbonate (HCO_3) or sulfate (SO_4), present in the ambient groundwater, are pulled back too close to the well. Increases in pH and temperature can also facilitate displacement of arsenic from

the ferric hydroxide floc by other ions.

6 Sulfate concentrations in the recovered water increased well above background levels in the aquifer or the recharge water at one site (Tampa) in a freshwater storage zone. At another site (Manatee), also in a freshwater storage zone, the increase in sulfate concentration due to ASR operations was minimal, suggesting attenuation of pyrite reactivity after 20 years of operations. At other sites high ambient sulfate concentrations in the groundwater and variable sulfate concentrations in the recharge water masked increases in sulfate concentration associated with pyrite oxidation.

7 A significant correlation exists between arsenic concentration in the recovered water from an ASR well and the cumulative volume of water stored in that well. Where pyrite is present in the storage aquifer and the cumulative volume is negative or small, arsenic concentrations tend to be relatively high. With increasing cumulative volume the arsenic concentration in the recovered water declines. With sufficient cumulative volume stored, arsenic concentrations in the recovered water and also in nearby observation wells at distances greater than about 200 feet generally achieve compliance with the 10 μg/l drinking water standards.

8 If an ASR well has been operating for many years with full recovery of the stored water each year, and no significant cumulative storage volume, the buffer zone will eventually be formed as a result of mixing and dispersion in the aquifer. A portion of the water stored in each cycle will be mixed with residual water remaining from the previous cycle. This is a time-consuming approach to buffer zone formation however for some applications where it is not viable or cost-effective to form the buffer zone in a shorter time period, this alternate approach can also work.

9 The Target Storage Volume (TSV) for an ASR well is defined as the sum of the stored water volume that is required for recovery, plus the volume of water comprising a buffer zone that separates the stored water volume from the surrounding ambient groundwater in the storage zone. The TSV was developed many years ago to address concentrations of conservative constituents such as total dissolved solids (TDS) or chlorides and is utilized widely to quickly achieve acceptable recovery efficiencies in many ASR wells for conservative constituents. Typical TSV values for Florida ASR wells range from 50 to 350 million gallons (MG) per million gallons per day (MGD) of ASR well recovery capacity, or 50 to 350 days.

Based upon data analyzed for this project, the TSV approach, using TDS or chloride concentration as a surrogate constituent, is also effective to simulate operational measures that would control arsenic concentrations. Arsenic is a complex and non conservative constituent. This surrogate solution may suffice until such time as a more complex and accurate model of subsurface geochemical, microbial and physical processes can be developed.

10 Until better data become available, the buffer zone volume is estimated to equal the stored water volume required for recovery at each site. The buffer zone may be formed incrementally during several operating cycles over a period of years or it may be formed at one time, prior to start of ASR operations, or a combination of these approaches. The buffer zone should be formed and maintained, not recovered. If the buffer zone volume is recovered, water quality may deteriorate and require retreatment prior to distribution. Forming a buffer zone around ASR wells is a simple step in the right direction to limit arsenic concentrations by ensuring a reasonably stable water quality close to the ASR well where the arsenic is most likely retained.

11 A few ASR wells in southwest Florida are subject to upconing of brackish groundwater from underlying brackish aquifers during extended recovery periods. These include the Tampa Rome Avenue wellfield and a few wells in Wellfield Two at Peace River. For these wells, formation of a buffer zone will have less benefit for controlling arsenic concentrations or for achieving high recovery efficiencies since water quality during recovery will be partly determined by the volume of water that may be recovered before upconing water reaches the ASR well. Reducing recovery rates will extend the duration of recovery at such wells. ASR wells storing fresh water in brackish aquifers, or in fresh aquifers underlain or overlain by brackish aquifers require adequate confinement, both above and below.

12 The buffer zone comprises the “walls” of the subsurface storage reservoir, maintaining a geochemical environment where arsenic remains immobile. As the need for water storage increases, the volume in the buffer zone will need to be increased. Until such time as additional analyses can be conducted, a suggested buffer zone volume equals the stored water volume required for recovery. In most cases, the cost for buffer zone formation will be small. Offpeak water will be utilized to form the buffer zone, the real cost of which is just the marginal cost for power, chemicals and residuals disposal. This is typically a one-time investment that should be made prior to beginning ASR operational cycle testing.

13 Buffer zone formation is not a complete solution to the current ASR arsenic challenge in southwest Florida. The February 2007 ASR policy issued by the Florida Department of Environmental Protection allows no mobilization of arsenic at any place or at any time in any aquifer containing less than 10,000 mg/l TDS concentration. Pretreatment to remove oxygen from the recharge water is planned at three southwest Florida ASR sites to demonstrate the viability of this approach. It is anticipated that the combination of deoxygenation pretreatment plus buffer zone formation and maintenance will achieve compliance with the new FDEP policy.

14 The physical, geochemical and microbial processes that mobilize and attenuate arsenic during ASR storage are not well understood. Further research is needed to achieve a better understanding of sorption, desorption, ion exchange and microbial metabolism processes occurring during ASR storage, particularly in brackish aquifers. These processes are complex, interrelated and need to be better understood. They may include reduction of arsenic(V) to the more mobile arsenic(III); loss of sorption sites through reductive iron(III) dissolution, or displacement from sorption sites by other anions such as bicarbonate or sulfate. Arsenic speciation reflects pH changes. Temperature changes occurring during seasonal recharge and recovery operations may also affect these processes.

15 Mobilized arsenic may theoretically not be recovered from the ASR well and may move into the surrounding aquifer beyond the buffer zone with the regional groundwater movement, thereby potentially threatening groundwater quality and public health. However, the groundwater in southwest Florida is brackish. This water would require desalination treatment to render it suitable for potable purposes. Such treatment would remove any residual arsenic. It is pertinent that analysis of data from 41 storage zone monitor wells at 12 wellfields has shown that the arsenic does not seem to move very far from the ASR well, typically less than about 200 feet. The storage zones in southwest Florida are typically in karstic aquifers so considerable variability in results may be expected, however the large number of monitor wells and the relatively consistent results suggest that the conclusions are valid.

16 Assuming that pretreatment to remove oxygen is shown to be successful in controlling arsenic concentrations, the combination of pretreatment and formation of a buffer zone for an ASR well will provide greater assurance of ultimate successful compliance with current FDEP policy, which was enacted a year after this project began. Once the buffer zone has been formed it is possible that the need for continued pretreatment of the recharge water may decline or be eliminated. This will depend upon the subsurface reaction mechanisms which are not well understood at this time. To the extent that arsenic mobilization during recovery may be triggered by ion exchange or sorption-desorption processes in which arsenic is displaced from sorption sites and is replaced by ions present in the ambient groundwater, then buffer zone formation and maintenance to keep ambient groundwater away from the ASR well would appear to be a potentially useful operational management strategy for arsenic control. Such a finding would tend to favor pretreatment processes that involve low capital costs and high operating costs since they may only be required for initial buffer zone formation.

Discussion

Reconsideration of the current FDEP ASR policy is suggested in order to achieve a reasonable balance of risk, benefit and cost while still protecting groundwater quality, public health and the environment. Water storage is the key to achieving sustainable and reliable water supplies for all water users and for the environment, not only in Florida but globally, storing water in wet periods for recovery during droughts and emergencies. Water storage underground is more reliable and cost-effective than water storage in surface reservoirs. It can be achieved at approximately 10 to 30% of the capital cost of surface reservoirs, plus saving the added substantial cost for land acquisition since ASR wells require little land. Unlike surface reservoirs, ASR wells have essentially no significant environmental impact. The best solution is a balanced combination of ASR storage and surface reservoir storage, taking full advantage of the best attributes of each technology.

All states have non-degradation laws, rules and policies to protect the quality of groundwater. Several other states and countries provide for a small compliance zone or attenuation zone around an ASR well, within which natural subsurface treatment processes are allowed to occur. Florida provides this also, for several constituents other than arsenic. Compliance with applicable drinking water standards is then measured outside that compliance zone. This is consistent with federal law, as provided in the 1974 Safe Drinking Water Act. With approximately 20 large surface storage reservoirs currently in planning, design or construction, at a combined 2007 cost probably between $4 billion and $5 billion, Floridians will be paying a high price for water storage, both economically and environmentally. Many of these reservoirs will be dry during severe droughts, reflecting high water losses in Florida due to evaporation, transpiration and seepage, and will fill rapidly during hurricanes and other wet periods. Effective implementation of ASR can improve water supply reliability and achieve significant cost savings while meeting water quality standards and environmental goals.

Recommendations

Several recommendations are offered for management policies and procedures that would control arsenic concentrations in the recovered water from ASR wells while also controlling its lateral movement within the ASR storage zone.

1. Accept that formation of a buffer zone around an ASR well expedites arsenic attenuation. Conduct testing at new ASR wells, or existing ASR wells that are experiencing arsenic compliance problems, to confirm that formation and maintenance of a buffer zone around an ASR well is as effective or more effective at expediting arsenic attenuation compared to conducting multiple successive cycles at the same volume stored and recovered, or compared to no buffer zone development. This will be the quickest, easiest and least expensive approach to solving the current arsenic problems at some Florida ASR wellfields in southwest Florida. During such testing, ensure that sufficient geochemical monitoring is undertaken to assess arsenic speciation and mobility under spatially varying redox conditions.

2. Reconsider the current FDEP policy in light of this analysis of ASR operating results. A strong basis of operating data exists and has been carefully analyzed, showing that no significant adverse impacts upon public health or the environment have occurred, or are likely to occur, and that impacts upon

groundwater quality are localized and transitional. While additional scientific investigations are recommended in order to achieve improved understanding of subsurface arsenic mobilization and attenuation processes, a strong scientific basis exists to support a suggested change in FDEP policy. Consider whether allowing formation and maintenance of a buffer zone around ASR wells would significantly threaten public health, groundwater quality or the environment. If the threat is recognized to be insignificant, allow existing water utilities to implement plans to form buffer zones to help solve their arsenic problems. Initially at least, pretreatment processes to remove oxygen from the recharge water may be added in order to provide added protection of groundwater quality and to thereby comply with current FDEP policy. The need for continued operation of these expensive pretreatment facilities may then be reevaluated once buffer zones have been formed and the arsenic challenge at each site has subsided.

3. If the current FDEP constraint upon ASR operations is deemed to be more of a legal issue than a technical or scientific issue, as we understand may be the case, then it is recommended that FDEP or SWFWMD prepare a legal brief regarding measurement of compliance with drinking water standards. Based upon a similar legal brief (Sam Poole, 1993), historic ASR practices in southwest Florida are believed to be consistent with federal law (Safe Drinking Water Act, 1974) but are inconsistent with the EPA Underground Injection Control (UIC) regulations that were promulgated in 1981 pursuant to that law. EPA is fully aware of this discontinuity between the federal law and their UIC regulations and, for other states, has found a way to accommodate state-specific needs and opportunities. Other states (Arizona, California, Wisconsin) measure ASR compliance at monitor wells located at distances up to about 700 to 1200 feet, beyond the typical radius of a Target Storage Volume for an ASR well.

   The suggested essence, and the primary goal, of the argument for this legal brief would be to demonstrate that ASR operations do not cause the owner of an adjacent well to have to change his/her treatment process, as provided in federal law. Compliance measurement at a monitor well is not the suggested object of the legal brief, per se. Scientific and technical demonstration that the arsenic mobilization and attenuation is very localized and transitional is the foundation upon which this primary legal goal can be achieved.

   Measurement of compliance at one or more suitably-located monitor wells, rather than at the ASR well, is a likely regulatory outcome if the legal brief is deemed to be convincing. Reflecting the karstic nature of the Floridan aquifer, and the likely distribution of arsenic-bearing pyrite along the fractures and flow channels in the limestone, monitor wells are poorly suited for measuring compliance since they may or may not intercept the fractures or flow channels. If they are utilized anyway, they should be located outside the buffer zone.

4. Regulate ASR wellfields in such a manner as to allow blending of the recovered water from multiple ASR wells, and from other sources, in order to achieve

arsenic standards in the public drinking water supply. This would be an interim treatment approach until arsenic concentrations from all wells attenuate to acceptable levels.

5. In areas subject to the occurrence of arsenic, operate ASR wellfields in such a manner as to avoid recovery of the buffer zone once it has been formed. If additional storage volume is required for recovery, first expand the buffer zone. This will entail development of design criteria for ASR facilities, addressing storage volume required for recovery and also storage volume required for establishment of the buffer zone. The sum of these two volumes is the Target Storage Volume (TSV).

6. Conduct research to better understand arsenic mobilization and attenuation processes and to define the buffer zone required for arsenic attenuation, adapting the Target Storage Volume concept already utilized to achieve high recovery efficiency for ASR wells in brackish aquifers. This may require construction of several monitor wells and/or core holes at one ASR well site at radial distances within 200 feet and in several directions in order to better characterize hydraulic and water quality changes occurring close to the ASR well, and the mechanisms for those changes in water quality. Investigate arsenic speciation in the storage zone during ASR recharge, storage and recovery. In the absence of such research it will be necessary to rely upon analysis of field data from selected wellfields, such as provided in this technical memorandum.

   Consider obtaining additional data from other ASR wellfields besides Bradenton, with frequent samples and field data collection during the first few hours of ASR recovery. This relatively easy and inexpensive testing at Bradenton provided useful insight into substantial water quality changes in the proximal zone around an ASR well and could easily be replicated at other operating ASR wellfields.

7. If the municipality has a water treatment system located reasonably close to the ASR well, add the recovered water to the existing source and re-treat the water to remove the arsenic. This would be an interim measure until such time as arsenic concentrations decline to acceptable levels. Alternatively post-treatment could be provided for a limited time at the ASR well before pumping the recovered water to the distribution system. Pretreatment to prevent arsenic mobilization may be required continuously during recharge periods for the life of the well and would therefore have a greater life cycle cost. Alternatively, operating experience may show that pretreatment can be reduced or eliminated once the buffer zone is formed. Pretreatment options and associated costs have been addressed in a separate Technical Memorandum for Task 2.

8. Update the FDEP ASR database format to facilitate graphical analysis, including estimated values for cumulative storage volume associated with each sample and also deleting the "<" sign for sample concentrations that are below the method detection limit, replacing the latter with a color code or a separate column.

Distilling conclusions from the current database is time-consuming, at least partly due to the current format. Also, provide for inclusion of supplemental data in the database, if such data is collected and may be useful.

9. Consider using TDS or chloride concentration as a surrogate for arsenic concentration when using brackish aquifers for ASR storage. These are inexpensive and rapid analyses compared to that for arsenic. The strongest relationship found from the data analysis was between arsenic and TDS. The assumed linear relationships are not strong and it is clear that these particular constituents are not the causative factors for arsenic mobilization. However their presence in the recovered water is associated with the presence of other constituents at concentrations that probably do cause arsenic mobilization. Additional work is required to try to enhance the value of these and possibly other surrogate analyses.

10. Storing water in one or two ASR wells in the Avon Park formation beneath the new wellfield at Peace River would probably help to manage recovered water quality so that upconing would occur with fresh water, not brackish water. Yield of individual Avon Park wells is estimated at 3 to 5 MGD and they could be constructed as part of the next ASR wellfield expansion. This is pertinent to solution of current arsenic issues since it is hypothesized that variable salinity may inhibit subsurface microbial activity close to the ASR wells, affecting natural processes that alter the pH of the aquifer matrix in the proximal zone, very close to the well, and thereby potentially affecting the speciation and mobilization of arsenic. Increasing salinity is also believed to contribute to displacement of arsenic sorbed onto ferric hydroxide floc close to the ASR well during extended recovery periods.

11. Issue TSV Water Use Permits for initial formation of the Target Storage Volume for ASR wells. This would be a one-time permitting activity, independent of the existing long duration Water Use Permits, utilizing water that would be diverted, treated and stored during low demand periods when surface water flows are high. Water would be utilized upon completion of well construction and prior to operational cycle testing.

1.0 Introduction

A draft analysis of operational data from 57 ASR wells at 13 wellfields storing drinking water in the Floridan aquifer was completed in November 2004 (Pyne et al, 2004). The technical memorandum included several preliminary conclusions, among which was the observation that arsenic concentration in the recovered water from an ASR well is related to the development of a buffer zone. Where a buffer zone is absent or is too small, arsenic is evident in the recovered water. Where an adequate buffer zone has been formed, arsenic is likely to occur at acceptable concentrations in the recovered water. The data indicated that the Target Storage Volume (TSV), which includes the stored water volume to be recovered plus the buffer zone volume, needs to exceed 70 days (ie: 70 million gallons per MGD of recovery capacity) in order to achieve arsenic attenuation. The data set included 17 storage zone monitor wells at 7 wellfields, located sufficiently close as to experience freshening due to ASR recharge. At all but one of these monitor wells arsenic was not detected at concentrations exceeding 7 µg/l, suggesting that arsenic mobilization does not extend very far from the well. At one monitor well arsenic was detected at initial concentrations of 21 to 27 µg/l, attenuating to 6 µg/l after three cycles with approximately equal volumes.

Partly stimulated by the findings of the November 2004 Technical Memorandum, extensive additional data have been obtained since that time. Thirteen additional storage zone monitor wells have been constructed at the Peace River ASR wellfield and five additional monitor wells at the Tampa Rome Avenue ASR wellfield. Considerable additional operational data have been collected at other existing and new ASR wellfields. The present analysis is an update of that conducted in November 2004, considering data from the twelve Southwest Florida ASR wellfields listed in **Table 1**. A total of 52 ASR wells are included in the analysis, plus 41 storage zone monitor wells.

For each ASR well, the analysis was conducted to relate arsenic concentration to cumulative stored water volume. The resulting data set was then evaluated to consider site specific variables that could impact comparison of the results from different sites such as well yield, thickness of the storage interval, etc. The analysis was initiated with the City of Bradenton data set, which is one of the best-documented sites within the SWFWMD jurisdictional area, demonstrating the value of a buffer zone to attenuate arsenic. The data from this site are analyzed in considerable detail. The analysis was then extended in a second analysis phase to include the Tampa and Peace River data sets, which provide a broad range of experience including the absence of a buffer zone and also partial development of a buffer zone. During the third phase the lessons learned from the Bradenton, Tampa and Peace River sites were tested against the operational data from all of the other operational ASR wellfields in southwest Florida for which adequate data are available.

Table 1
ASR Wellfields in SW Florida Evaluated in this Analysis

	Wellfield	**No. ASR Wells**	**No. Storage Zone Monitor Wells**
1	City of Bradenton	1	1
2	City of Tampa	8	5
	Peace River/Manasota Regional Water Supply Authority		20
3	Old Wellfield	9	
4	New Wellfield	12	
5	Manatee County	6	2
6	Englewood Water District	1	1
7	City of Punta Gorda	4	3
8	City of Northport	1	1
	Lee County		
9	Olga	1	2
10	North Reservoir	1	1
	Collier County		
11	Marco Lakes	3	2
12	Corkscrew	5	3
	Total	52	41

Pursuant to Florida Department of Environmental Protection (FDEP) directions, none of the arsenic samples were filtered. This is different than normal procedures for sampling metals. As a result, high values may indicate the presence of particulates in the water rather than the occurrence of arsenic in solution.

During the course of this investigation a prolonged dry period occurred during Spring and early Summer 2006, approximately three months in duration. Several of the ASR wellfields included in this survey recovered all or most of the buffer zone surrounding many of their ASR wells, in order to meet water demand. This provided an opportunity to observe recovered water quality response under such circumstances.

Just prior to completion of this investigation, the Florida Department of Environmental Protection (FDEP) indicated a proposed change in policy for regulating ASR wells in Florida. Under the new policy no elevation in arsenic concentration is allowed anywhere, or at any time, within the aquifer due to ASR operations, whether within or outside the stored water bubble. Almost all of the Florida operational ASR wellfields are storing fresh water in brackish aquifers with total dissolved solids (TDS) concentrations up to about 20,000 mg/l. This change in FDEP policy would appear to preempt the use of a buffer zone as the only approach for control of arsenic concentrations, necessitating pretreatment of recharge water as an additional process in locations where arsenic may be present in the storage zone. The cost of such pretreatment is substantial and its efficacy for achieving the desired results is unproven. Whether this policy change achieves a reasonable balance of risks, benefits and costs has yet to be determined. The following analysis of operational data from operating Florida ASR wellfields confirms the technical viability of buffer zone formation as a low cost option for controlling arsenic concentrations and sheds light on the subsurface mechanisms responsible for arsenic mobilization and attenuation within the close proximity of ASR wells in southwest Florida.

1.1 ASR Conceptual Model

It is helpful to try to understand what typically happens around an ASR well during recharge, storage and recovery cycles. A schematic diagram is shown in **Figure 1**.

Some of the arsenic mobilization and attenuation geochemical reaction processes that are believed to occur underground include sorption and desorption, anion exchange, redox changes, oxidation of ferric sulfide minerals, reduction of ferric hydroxides and dissolution of arsenic minerals such as As_2S_3. In addition microbial processes occur, impacting the geochemical processes by reducing oxygen concentrations and also reducing the pH of the recharge water. Close to the ASR well it is possible that physical processes also occur since high velocities may scour particulates from the sides of flow channels through the karstic limestone and may transport ferric hydroxide flocs that contain arsenic.

Most ASR wells store water in deep, anoxic, confined or semi-confined aquifers. Carbon and nutrients in the recharge water stimulate microbial activity in a “proximal zone” adjacent to the well screen or open borehole, typically within a few tens of feet. Microbial metabolism affects the geochemical activity that also occurs close to the well.

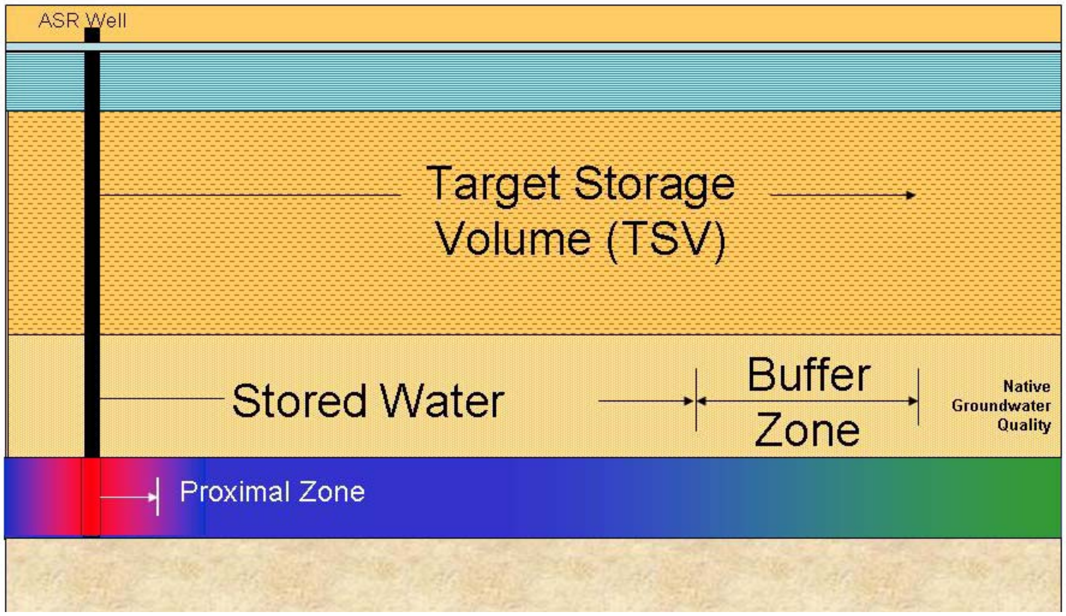


Figure 1 ASR Conceptual Model

As water flows through the pore spaces of the aquifer, the number of pore volume flushes diminishes exponentially with increasing distance from the well. Geochemical and microbial gradients also decline exponentially with distance. Consequently the "reactivity" of the storage zone is greatest near the well, diminishing with increasing distance. Some reactions occur in as few as 3 or 4 pore volume flushes while others may require several hundred.

The stored water volume typically extends several hundred feet from the ASR well. At the outer edge of the stored water volume is a buffer zone separating the stored water from the surrounding ambient groundwater. The buffer zone comprises a mixture of stored water and surrounding ambient groundwater. Based upon Florida experience a preliminary estimate is that the buffer zone volume approximately equals the stored water volume. The buffer zone in a fresh water aquifer with low potential for geochemical activity may be minimal however in a brackish or saline aquifer, or in an aquifer that is known to be geochemically sensitive, it is important not to recover the buffer zone since it serves a function similar to the walls of a ground storage reservoir. Rapid water quality deterioration may be expected if the buffer zone is recovered.

Microbial activity close to the well tends to reduce the pH, thereby affecting sorption-desorption processes, and also reduces the dissolved oxygen (DO) concentration and oxidation-reduction potential (ORP). Carbonate dissolution should tend to buffer the acidity produced through microbial or geochemical processes. At one site where frequent field measurements of pH were obtained at the beginning of a recovery cycle, a low pH zone around the well was noted. For the recharge water, ORP is usually quite high, indicating the presence of dissolved oxygen and other oxidants that cause ORP values to often reach positive several hundred millivolts. At such high values of ORP arsenic is mobilized, typically in Florida through oxidation of pyrite. The mobilized arsenic reprecipitates (becomes adsorbed) on the ferric hydroxide floc. Pyrite oxidation releases ferrous iron and also the arsenic. The ferrous iron reacts rapidly with oxygen in the recharge water, producing ferric hydroxide, which forms a floc. Subsurface physical, geochemical and microbial processes, such as oxidation of arsenic or organic matter, typically cause a decline in ORP. Depending upon storage zone reactivity and the consumption of injected oxidants, ORP values may decline but remain positive, or may become slightly negative, or may decline to as much as about minus 400 mv, indicating methanogenic conditions. As the redox condition shifts to iron(III) reducing conditions, arsenic sorbed to oxide surfaces will be released into solution. However under sulfate-reducing conditions arsenic may be removed from solution if precipitation of sulfides occurs.

Eh and pH changes occurring during ASR cycles, caused by geochemical and microbial activity, impact arsenic speciation, as shown in **Figure 2**. Under typical groundwater conditions As(V) species have a charge and tend to sorb or precipitate onto the aquifer matrix or to ferric hydroxide floc, while As(III) species do not have a charge and will be more mobile. However, all arsenic species are known to adsorb to ferric hydroxide that is formed around the wellbore during ASR recharge due to oxidation-reduction processes. Little is known about arsenic speciation in Florida's limestone aquifers.

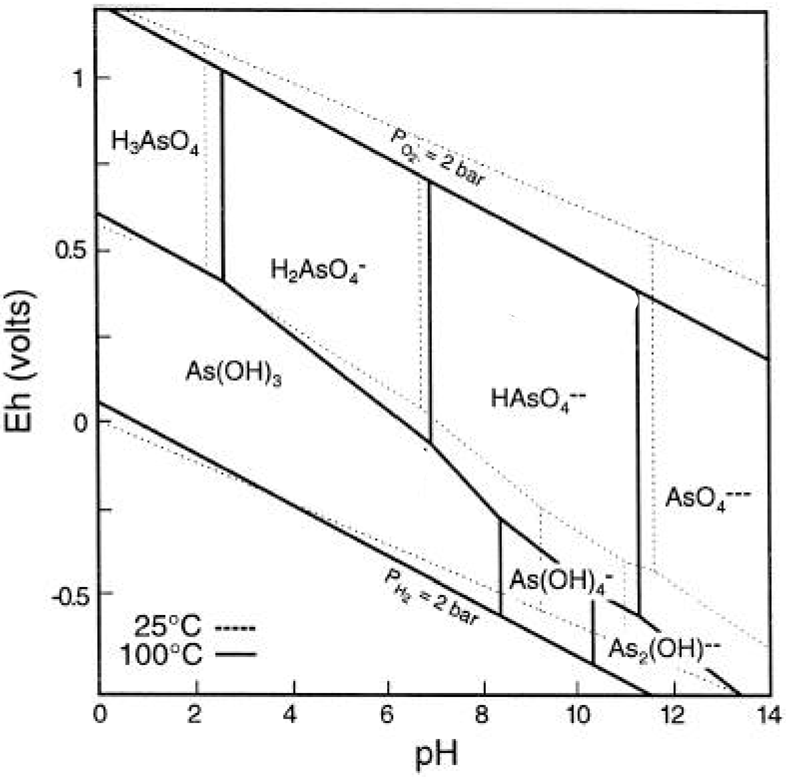


Figure 2 Eh – pH Diagram for Arsenic Species

These are typical subsurface processes. However if the aquifer is not anoxic, or if the recharge water and ambient groundwater contain no significant amount of dissolved organic carbon, nitrogen and phosphorus, or if a chlorine residual from the recharge water persists in the aquifer, then typical microbial processes will not occur. More likely, a longer period of time will be required for a microbial biomass to develop near the ASR well, slowing down microbial attenuation mechanisms. In some cases where subsurface storage time is very short, it may be necessary to dechlorinate the recharge water so that subsurface THM attenuation may occur more rapidly. This appears to be the situation for some ASR sites in southern California where a few ASR aquifers are unconfined, oxic, low in dissolved organic carbon, and consequently experience very slow rates of chlorine consumption. In such situations THM may not attenuate rapidly during ASR storage except after a prolonged period during which biomass slowly may accumulate in the aquifer around the ASR well.

The science has yet to be developed regarding the complex interplay of microbial and geochemical processes occurring during ASR storage.

These processes can be inferred from other investigations regarding bank filtration, wastewater treatment, hazardous waste and soil aquifer treatment (SAT) processes however there are several unique aspects relating to ASR wells:

- Contact time between the stored water and the aquifer matrix is typically weeks to months for ASR wells compared to hours to days in SAT systems, some bank filtration wells and wastewater treatment plants.
- Most, but not all ASR wells are in deep, confined or semi-confined, anoxic aquifers under reducing to highly reducing conditions. Some ASR wells are in oxic aquifers. These latter sites tend to occur in the southwestern United States.
- Flow in ASR storage zones is, by definition, in two directions, away from the well during recharge and back towards the well during recovery. The lateral reach of the stored water "bubble" typically does not extend more than a few hundred feet from the ASR well.
- About one-third of all ASR wells store water in brackish or saline aquifers, and almost all of the remainder store water in fresh aquifers that have at least one water quality constituent present in the ambient groundwater at concentrations that would require treatment to achieve drinking water standards.

1.2 Target Storage Volume

The stored water volume described above, including the proximal zone, is the volume required for recovery to meet water distribution system needs. Surrounding the stored water volume is the buffer zone, which separates the stored water volume from the surrounding ambient groundwater. The sum of the stored water volume and the buffer zone volume is the Target Storage Volume (TSV), as shown in **Figure 1**. A preliminary rule of thumb, based upon southwest Florida experience, is that the buffer zone volume approximately equals the stored water volume. However the buffer zone volume is a one-time addition of water to the well, usually occurring at or soon after the beginning of ASR well operations. In some situations it may be necessary to periodically supplement the buffer zone to offset losses due to regional lateral movement of the stored water, however this is uncommon. Groundwater velocities in Florida are typically very slow, on the order of a few feet per year. Where velocities are more rapid and where storage periods may extend for several years, replenishment of the buffer zone may be an operational consideration.

It will also be necessary to replenish the buffer zone for situations where the ambient total dissolved solids (TDS) concentration in the storage zone exceeds about 5,000 mg/l. Under these conditions density stratification of the stored fresh water in a highly brackish aquifer causes a decline in recovery efficiency with increasing TDS values. One ASR project, at Marathon, Florida, demonstrated the viability and cost-effectiveness of storing drinking water in a seawater aquifer (TDS = 37,000 mg/l), however long-term recovery efficiency was about 50%. Most ASR storage zones in Florida have less than 5,000 mg/l TDS so close to 100% recovery efficiency should be expected.

TSV values are measured in terms of million gallons per MGD of recovery capacity, or "days." A TSV of about 150 days is reasonably representative of a well in the upper Floridan aquifer, within a range of 50 to 350 days. Lower values are typical of thin aquifers with relatively low hydraulic conductivity and low TDS concentrations, and of water systems with small variability in water supply, water demand and/or water quality. Higher values are typical of thick aquifers with relatively high hydraulic conductivity, high TDS concentrations, and of water systems with large variability in water supply, water demand and/or water quality.

TSV values that have been established are as follows:

- Peace River, FL - 350 days
- Miami-Dade, FL - 200 days
- Delray Beach, FL - 114 days
- Kiawah, SC - 60 days
- Tampa, FL - 165 days
- Bradenton, FL - 75 days

The Peace River TSV is high since the primary source of supply is highly variable, potentially providing no water for up to about six consecutive months. The Miami-Dade West Wellfield ASR system has a moderate TSV, primarily reflecting the thick storage zone (about 400 feet thick) and the relatively high ambient TDS concentration (about 5,000 mg/l). Delray Beach has a relatively thin aquifer (184 ft) but a high TDS concentration (4,200 mg/l). All of these three ASR systems are in karstic limestone aquifers. At Kiawah Island, SC, the storage zone is a confined, shelly limestone conglomerate aquifer and is only 20 feet thick but has a TDS concentration of 8,730 mg/l.

TSV values have been established based upon mixing criteria in brackish storage zones. TDS has been the primary constituent of interest. However the same concept may be applied to evaluate non-conservative constituents such as arsenic. Depending upon the complex interplay of subsurface geochemical and microbial mechanisms which are currently not well-understood, arsenic may be present in the recovered water from an ASR well at concentrations greater or less than those that might be expected based upon TDS considerations. The November 2004 paper described above indicated that wells with TSV values greater than 70 days experienced no arsenic in the recovered water. Those wells with TSV values less than 70 days were increasingly likely to experience arsenic during recovery as the TSV values decreased. The present analysis seeks to investigate this relationship in greater detail, based upon additional data.

1.3 Arsenic Response in ASR Wells

For the 52 ASR wells included in this survey, the pattern of arsenic concentrations in the recovered water was considered. As shown in **Figure 3**, several patterns were evident. Most wells showed low initial ASR concentrations during recovery, increasing steadily during recovery, reaching a peak concentration and then declining until the end of recovery (case B).

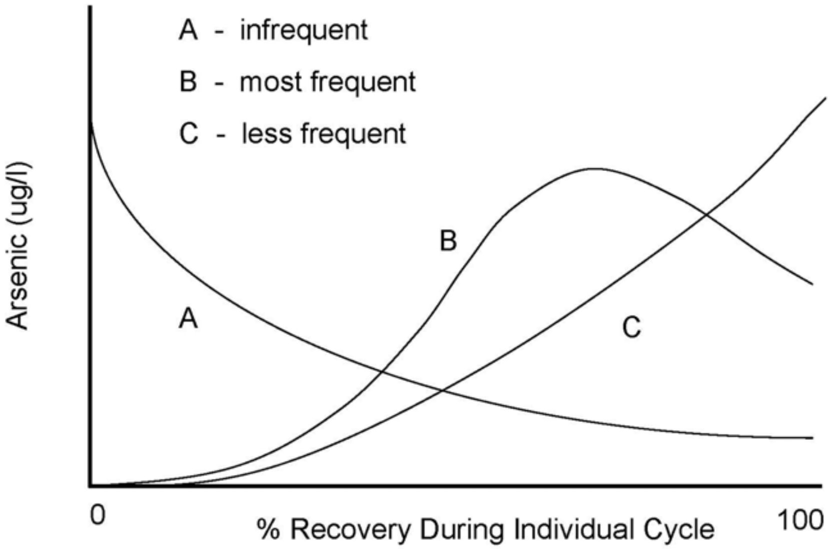


Figure 3 - Arsenic Concentration vs. Recovery Time for Individual Cycles, Typical Curve Shape Response

For a few ASR wells the peak occurred at the beginning of recovery and then declined (case A). For other wells the concentration continued to climb until the end of recovery (case C). To the extent possible with available data, the proposed conceptual model for ASR should help to explain these different responses at different ASR wells.

1.4 Arsenic Response in Monitor Wells

For the 41 storage zone monitor wells considered in this survey, the monitor well response was reasonably consistent. Distances from the ASR wells to the monitor wells ranged from 90 to 450 ft and most were at about 150 ft. In almost every case the arsenic concentration reported at the monitor well during recharge and storage was below 10 µg/l, usually showing no change even though it was clear from other water quality data that the stored water extended past the monitor well. Where elevated arsenic concentrations occurred at the monitor well they tended to occur during recovery, particularly toward the end of extended recovery when the more brackish water in the buffer zone was pulled in past the monitor well. Had an adequate buffer zone been formed and left in place, it is our opinion that no elevation of arsenic would have occurred at the monitor wells.

Monitor wells at distances greater than 200 ft from the ASR well showed no elevation of arsenic concentrations. Where elevated arsenic concentrations occurred in the monitor wells, they attenuated rapidly with successive operating cycles, typically reaching acceptable levels in approximately three cycles with approximately equal volumes stored in each cycle.

For monitor wells at Tampa, Bradenton and Corkscrew the opportunity occurred to observe water quality changes during extended storage periods when no recharge or recovery was occurring. No significant relationship is evident between arsenic concentration and either pH or ORP. In contrast, the strongest relationship appears to occur between arsenic concentration at the ASR well and conservative constituents such as TDS and chloride. As shown in Bradenton, the increase in arsenic during extended recovery following Cycle 6 did not correspond to any significant change in ORP unless a travel time of several weeks' duration is required for mobilized arsenic to move from the storage zone monitor well to the ASR well.

1.5 Water Quality Data Availability

Table 2 shows the Florida Department of Environmental Protection (FDEP) regulatory requirements for collection of hydraulic and water quality data during ASR cycle testing for the City of Bradenton. Very similar requirements were imposed by FDEP for each of the other ASR wellfield sites considered in this analysis.

Comments are provided in this technical memorandum regarding data for selected constituents deemed most significant for achieving the objectives of this project. For those persons interested in evaluating the data for other constituents, the data are readily available from FDEP or from ASR Systems.

Table 2 - Cycle Testing Schedule

	Recharge [a]	Storage	Recovery [b]	Storage
Cycle	Volume (MG)	Duration (days)	Volume (MG)	Volume (MG)
1	5-10	7	5	0
2	5-10	7	5	0
3	5-10	7	5	0
4	5-10	28	5	0
5[+]	50	0	5	45
6[+]	105	0	5	145
6a[+]			55	90

a Cycle 1-4 recharge volumes will each be the the same volume.
b Recover to storm drainage system.
+ Only w/FDEP written authorization.
Note: Schedule may be adjusted with written concurrence from the FDEP; injection rate ≤ 1.0 mgd.

Table 2 (continued) Monitoring Parameters & Sampling Frequency

Parameter	Units	Recording Frequency	Frequency of Analysis		
			ASR-1	***SZMW***	***AFMW***
Flow Rate, max.	Gpm	continuous	D/M		
Flow Rate, min.	Gpm	continuous	D/M		
Flow Rate, avg.	Gpm	continuous	D/M		
Total Volume Recharged	Mg	Daily	D/M		
Total Volume Recovered	Mg	Daily	D/M		
Injection Pressure, max.	Psi	continuous	D/M		
Injection Pressure, min.	Psi	continuous	D/M		
Injection Pressure, avg.	Psi	continuous	D/M		
Water Level	feet (NGVD)	Daily		D/M	D/M
Gross Alpha	pCi/L		M	M	
Total Uranium	µg/L		M	M	
Arsenic	µg/L		W[a]	W[a]	M
Ammonia (as N)	mg/L		W	W*	M
Bicarbonate (HCO^{3})	mg/L		W	W*	M
Carbonate (CO^{3})	mg/L		W	W*	M
Calcium	mg/L		W	W*	M
Chloride	mg/L		W	W	M
Dissolved Oxygen	mg/L		W	W	M
Iron, total	mg/L		W	W	M
Magnesium	mg/L		W	W*	M
Oxidation-Reduction Potential	mV		W	W	M
pH	std. units		W	W	M
Sodium	mg/L		W	W*	M
Specific Conductivity	µmhos/cm		W	W	M
Sulfate	mg/L		W	W*	M
Temperature	°C		W	W	M
Total Alkalinity	mg/L		W	W*	M
Total Dissolved Solids	mg/L		W	W*	M
Total Trihalomethanes	mg/L		W	W*	M
Turbidity	NTU		W	W*	M
Iron, dissolved	mg/L		O+		
HAA5	mg/L		O+		
Sulfide, total	mg/L		O+		
226Ra / 228Ra	pCi/L		O+		
Primary and Secondary stds.			A++		

a - Twice weekly during recovery
\+ - Beginning and end of recovery cycle only
++ - Treated drinking water (source water) prior to injection, within one year of the beginning of cycle testing.
W - weekly; B - twice-monthly; D/M - daily and monthly; O – Other; M - monthly; A - annually
***** - During extended storage periods (after 30 days) these parameters may be sampled and analyzed monthly.

1.6 Arsenic Speciation Diagrams

Common to each of the analyses of operating data from ASR wellfields is the need for a basic awareness of arsenic speciation diagrams. These are shown in **Figure 2** and also in a different format in **Figure 4**, indicating the speciation of As(III) and As(V) as a function of pH. The relative proportion of the various arsenic compounds at different pH levels is indicated. The pH range most pertinent to this analysis is between about 6.5 and 8.5.

It is notable that, for both species, as the pH increases the proportion of the various arsenic compounds that have an increasingly negative charge (monovalent, divalent, trivalent) increases whereas with declining pH the proportion with a less negative or neutral charge becomes dominant. This suggests that arsenic compounds with neutral charge (reduced Arsenious acid, H_3AsO_3, and oxidized Arsenic acid, H_3AsO_4) would become more prevalent and mobile as the pH declines within the range of interest. More strongly charged compounds would tend to sorb more easily to the aquifer matrix and to any available ferric hydroxide. Conversely less strongly charged or neutral compounds would more easily move with the water during recharge and be dissociated from the aquifer matrix or from ferric hydroxide floc during recovery. For As (III) in the pH range of interest, the dominant As species is neutrally charged and therefore more likely to be mobile. For As (V) in the pH range of interest most species are negatively charged and therefore less likely to be mobile.

As shown in the data for the various ASR wellfields, a small, localized decline in pH may generally occur close to the ASR well during recharge and also occurs at the ASR well as recovery proceeds from beginning to end. This may be due to blending, geochemical activity or possibly microbial activity, or more likely a combination of these mechanisms. At the storage zone monitor wells significant pH changes were not observed.

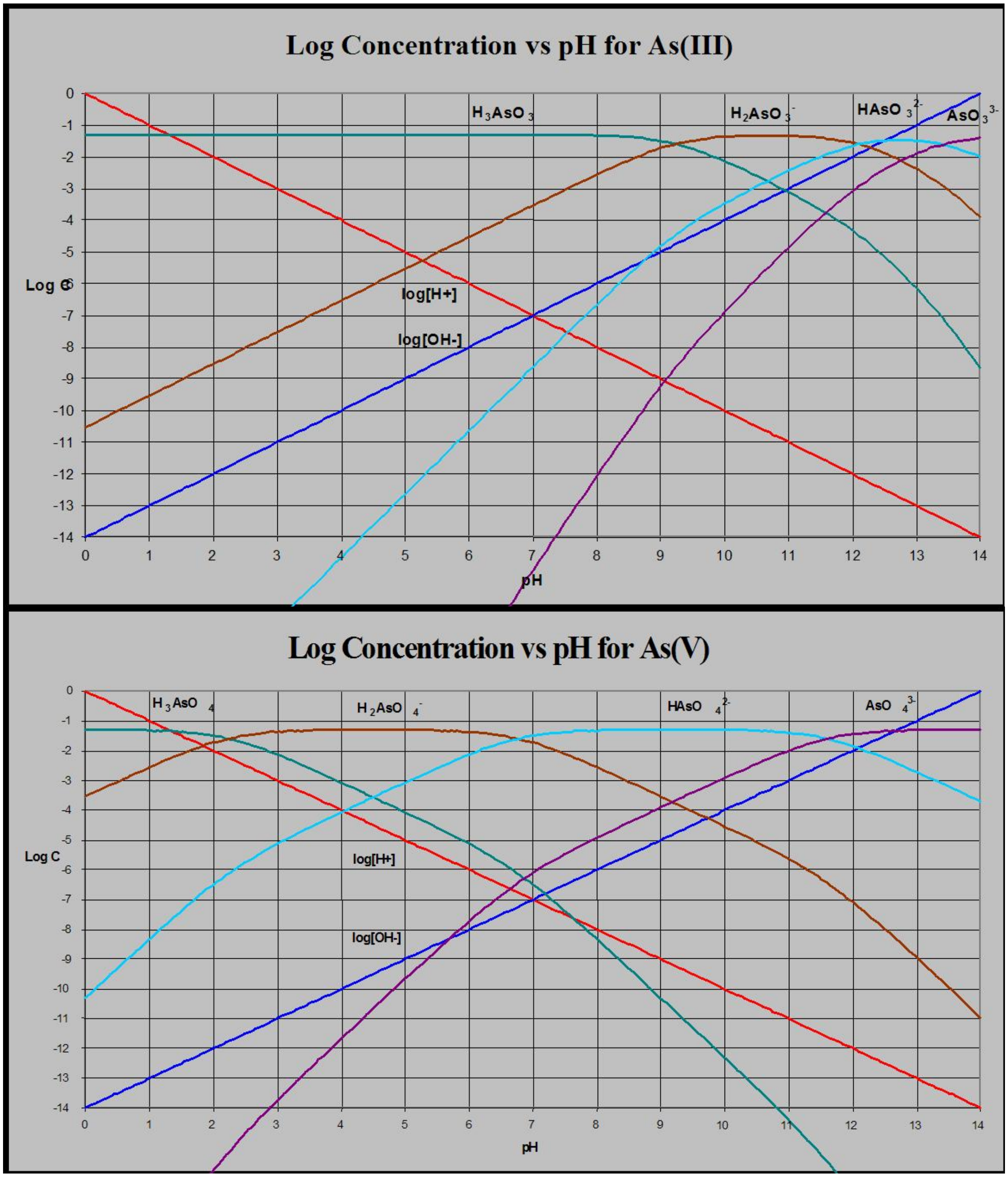


Figure 4 Speciation Graphs for Arsenic (III) and Arsenic (V) vs pH

2.0 City of Bradenton

The Bradenton ASR well is constructed in the upper Suwannee formation, a semi-confined limestone artesian aquifer. The objective of this ASR well is to store drinking water to help meet increasing peak demands and to improve system reliability during emergencies. A well profile and hydrogeologic cross-section for the site are shown in **Figure 5**.

The well is cased to 415 feet and is open hole to 505 feet. The site includes one storage zone monitor well at a radial distance of 224 feet, one monitor well in the next overlying minor producing interval, and one water table monitor well. The ASR well is designed to produce at variable rates ranging between 900 and 1800 gpm and to recharge, either by gravity or under pressure, at rates varying between 85 and 800 gpm. Aquifer hydraulic characteristics are as follows:

Transmissivity	-	15,700 gpd/ft
Storativity	-	1.1×10^{-4}
Leakance	-	5.1×10^{-3} /day

Transmissivity is defined as the rate of flow through the vertical section of an aquifer one foot wide and extending the full saturated height of an aquifer under a hydraulic gradient of 1 and at the ambient temperature of the aquifer. It is calculated by multiplying the estimated average hydraulic conductivity times the aquifer thickness. Storativity is the volume of water taken into or released from storage per unit change in head per unit area. For a confined aquifer this is due to compression of the aquifer and expansion of the water when pumped. Leakance is defined as the rate of vertical flow into an aquifer from one square foot of overlying and underlying confining layers resulting from a reduction in head of 1 ft.

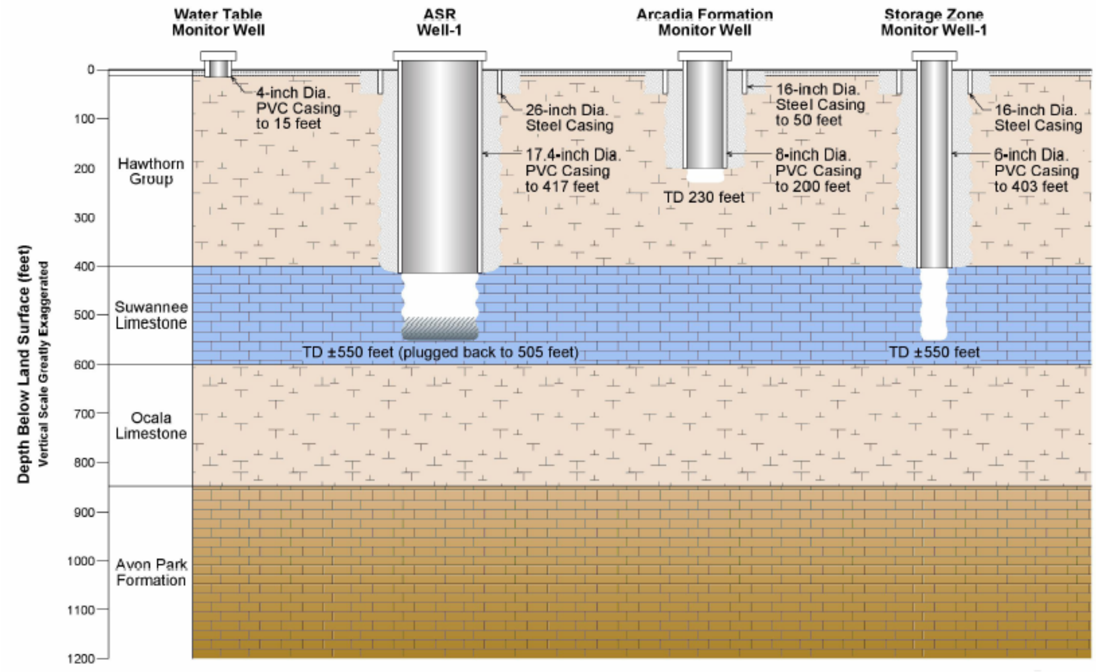


Figure 5 Bradenton ASR Well Profile and Hydrogeologic Cross-Section

Ambient groundwater quality for selected constituents is as follows:

Arsenic, µg/l - 4
Iron, mg/l - 0.003
TDS, mg/l - 1,156
Chloride, mg/l - 100
Sulfate, mg/l - 650
Odor, TON - 33
Temperature, ^{o}F - 26.3
pH - 7.3
Diss. Oxygen, mg/l - 0.02

In addition, hydrogen sulfide occurs in the ambient groundwater, as evidenced by the rotten egg odor emanating from the well prior to ASR recharge.

Recharge water is treated drinking water from a surface reservoir source. Seasonal variability occurs for several constituents. Temperature ranges from 18 to 30^{o}F. Total organic carbon (TOC) ranges from 0.3 to 7.1 mg/l, averaging 4.4 mg/l during June through March when ASR recharge might reasonably be expected to occur. TOC of the ambient groundwater is 1.4 mg/l. The City adds ammonia and orthophosphate to the drinking water for disinfection and corrosion control, respectively. These constituents of the drinking water would tend to encourage subsurface microbial activity and would contribute to the oxidation of pyrite.

Six ASR cycles were conducted, beginning during November 2004 and continuing to January 2006. During each of the first four cycles (November 2004 through March 2005) 10 million gallons (10 MG) were recharged and recovered, providing no opportunity for buffer zone formation. The first three cycles included approximately one week of recharge, one week of storage and one week of recovery. The fourth cycle was identical except that the storage period was one month.

Extensive water quality data are available for analysis of this site, as indicated in the sampling program stipulated in the permit from the Florida Department of Environmental Protection (FDEP) that is shown in **Table 1**. Substantial additional data at more frequent time intervals were obtained by the City of Bradenton during the first four cycles, providing more detailed understanding of water quality changes.

Arsenic

For the first four cycles, arsenic concentrations during recovery were generally at background levels for the first half of recovery and then climbed steadily toward the end of recovery in each cycle, reaching peak concentrations of 15 to 23 µg/l. Each of these cycles included 10 MG recharged and 10 MG recovered. A four month waiting period then ensued before cycle testing could continue. During Cycle 5 the storage volume was increased to 50 MG, after which 10 MG was recovered in September 2005. Peak arsenic concentration during Cycle 5 recovery was 3 µg/l. During Cycle 6 the planned TSV of 150 MG was achieved. Cycle 6 recovery of 10 MG also showed arsenic concentrations below 3 µg/l. **Figure 6** shows arsenic concentrations at the ASR well for the first four cycles. Cycles are designated as C1, C2, C3 and C4.

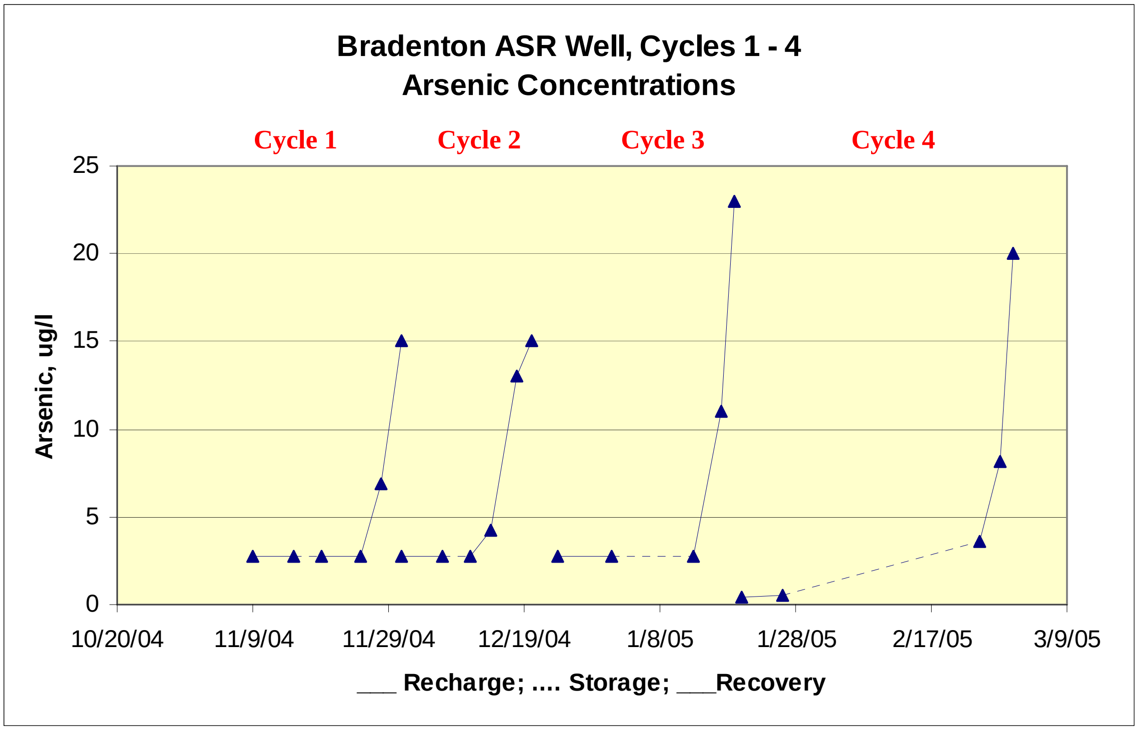


Figure 6 Bradenton ASR Well, Cycles 1 to 4, Arsenic Concentrations

Figure 7 shows the same information for the first six cycles. Cumulative storage volume was based upon daily records during the first four cycles and weekly records for the remaining portion of the testing period.

For these and all succeeding figures it was necessary to adjust the FDEP data set so that arsenic values recorded as less than any given value were shown as that value. The "<" sign was deleted to facilitate graphical presentation using Excel. FDEP notes that were inserted relating to some of the data points were also deleted to facilitate plotting. For some data sets cumulative volumes were interpolated from FDEP monthly records assuming steady flow rates during the month.

It is apparent that providing a buffer zone of 40 MG during Cycle 5 was more than sufficient to sustain recovery of 10 MG without elevated arsenic concentrations in the recovered water. Similarly, providing no buffer zone (Cycles 1 to 4) was associated with acceptable arsenic concentrations only during the first half of recovery and elevated arsenic concentrations during the last half of recovery. Based upon this response, a reasonable working hypothesis is that, for this site, the volume of water required in the buffer zone is approximately equal to the stored water volume that is required for recovery. Forming an adequate buffer zone is easily achieved and provides operational flexibility in the event that a greater volume of water needs to be recovered, such as during a severe drought.

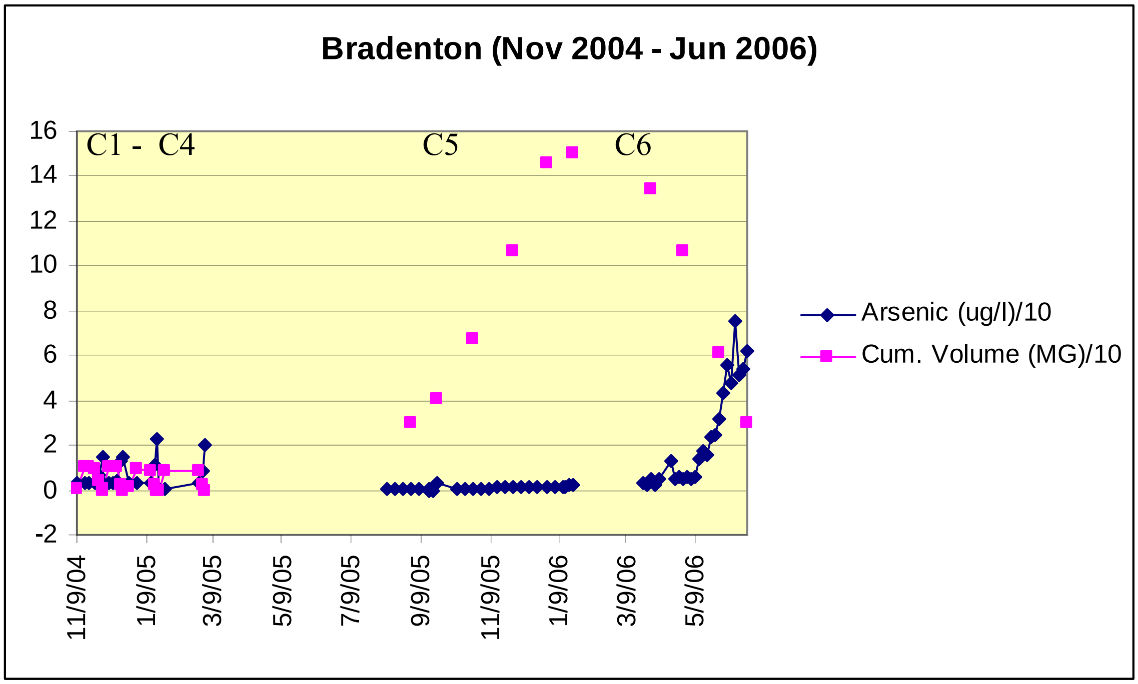


Figure 7 Bradenton ASR Well, Cycles 1 to 6
Arsenic Concentration vs Cumulative Storage Volume

A 10 MG recovery volume is not sufficient to meet the City's plans for use of this ASR well to help meet peak demands. A Target Storage Volume (TSV) of 150 MG was then formed, providing an estimated 75 MG of stored water. The 75 MG remainder of the water constitutes the buffer zone. If more than about 75 MG is required for recovery, it would be necessary to expand the TSV above 150 MG.

Of considerable interest is that, following completion of Cycle 6 and a subsequent two month waiting period the City continued recovery of the stored water, recovering 120 of the 150 MG stored. This occurred between March and June 2006, following completion of Cycle 6. As shown in **Figure 7**, for approximately the first 60 MG of recovery, arsenic and TDS concentrations were acceptable. Once recovery passed this point and the buffer zone was increasingly depleted, arsenic concentrations in the recovered water climbed steadily to 75 µg/l and then declined at the end to about 54 µg/l. The drinking water standard for arsenic is 10 µg/l. The important point is that, following formation of the TSV, had the buffer zone not been recovered arsenic concentrations at this site would have been acceptable.

Oxidation Reduction Potential, ORP

During Cycles 1 – 4, ORP in the recharge water was in the range of +374 to +490 mv but this rapidly declined to within a range of minus 79 to +96 mv at the end of storage and to minus 242 to minus 324 mv by the end of recovery. A slight increase in ORP occurred during the first three hours of recovery for Cycle 4, from minus 44 mv to +60 mv and then dropping to +6 mv. One day later it was at minus 109 mv. This is shown on **Figure 8**.

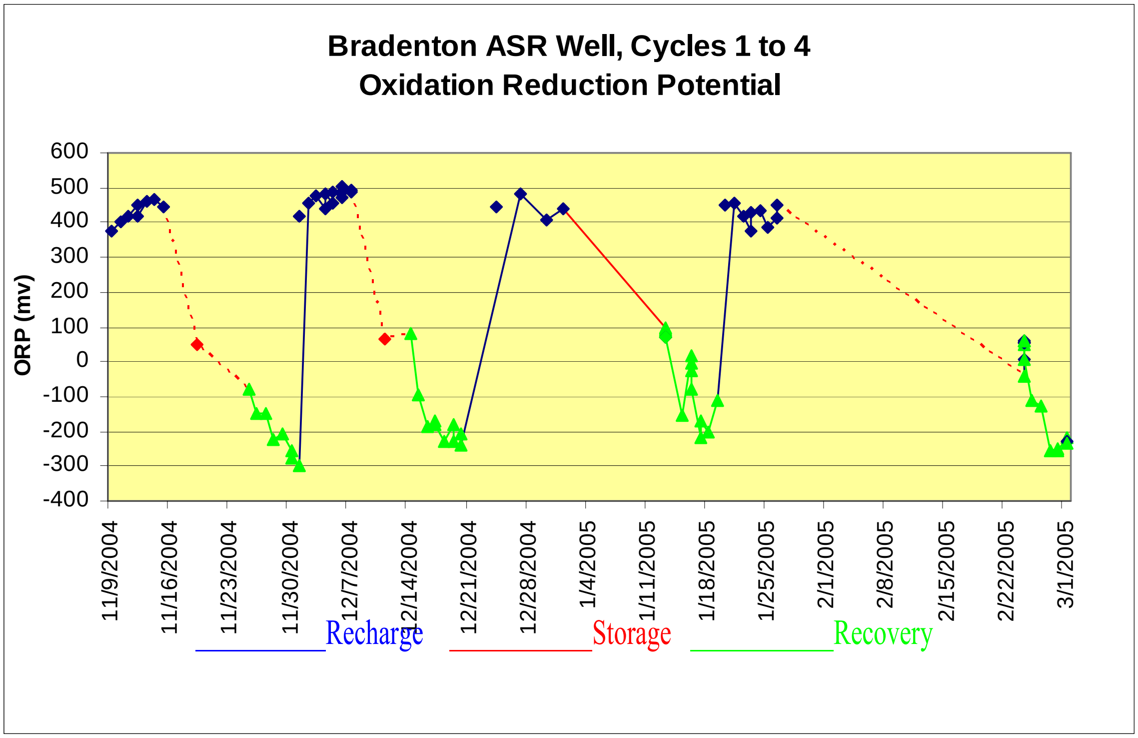


Figure 8 Bradenton ASR Well, Cycles 1 to 4, Oxidation Reduction Potential

During Cycle 6 recovery of 10 MG, ORP concentrations declined from +309 to +99 mv. During the subsequent 60 days with no recharge or recovery activity, ORP declined further to +34 mv. During the next 46 days of extended recovery ORP values ranged between minus 16 to minus 238 mv, showing considerable variability and a slight declining trend. At that point arsenic values increased above 10 µg/l, associated with recovery of the buffer zone, and reached a peak of 75 µg/l. ORP values were relatively steady, ranging between minus 42 and minus 166 mv. This is shown in **Figure 9**.

Arsenic concentrations at the storage zone monitor well remained acceptable for the first 75 MG of recovery following Cycle 6, associated with ORP values varying widely but generally declining from +33 to minus 345 mv. ORP values then stayed relatively steady, between minus 98 and minus 364 mv to the end of recovery, during which time arsenic values in the storage zone monitor well climbed to as high as 20µg/l before declining to 15 µg/l at the end of recovery. Baseline ORP in the SZMW was minus 264 mv, remaining in a range of minus 256 to minus 360 mv during Cycles 1 to 4 recharge and recovery. This is shown on **Figure 10**, along with cumulative storage volume.

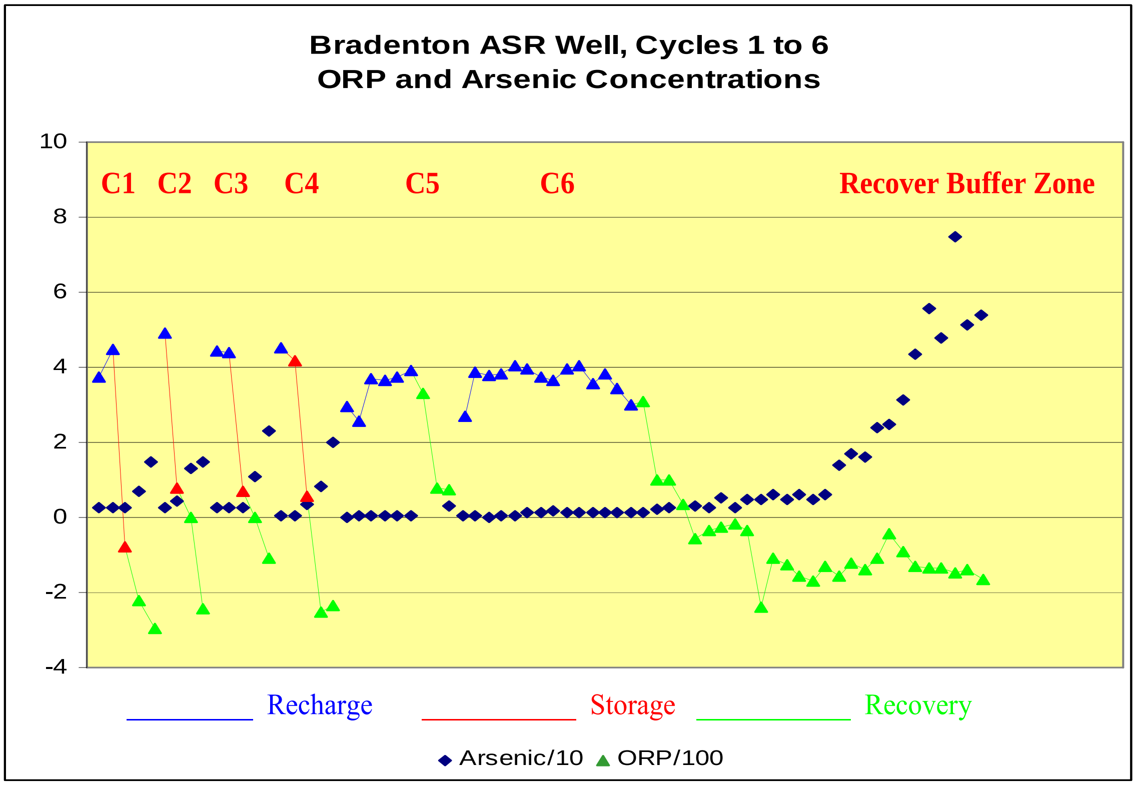


Figure 9 Bradenton ASR Well, Cycles 1 to 6, ORP and Arsenic Concentrations

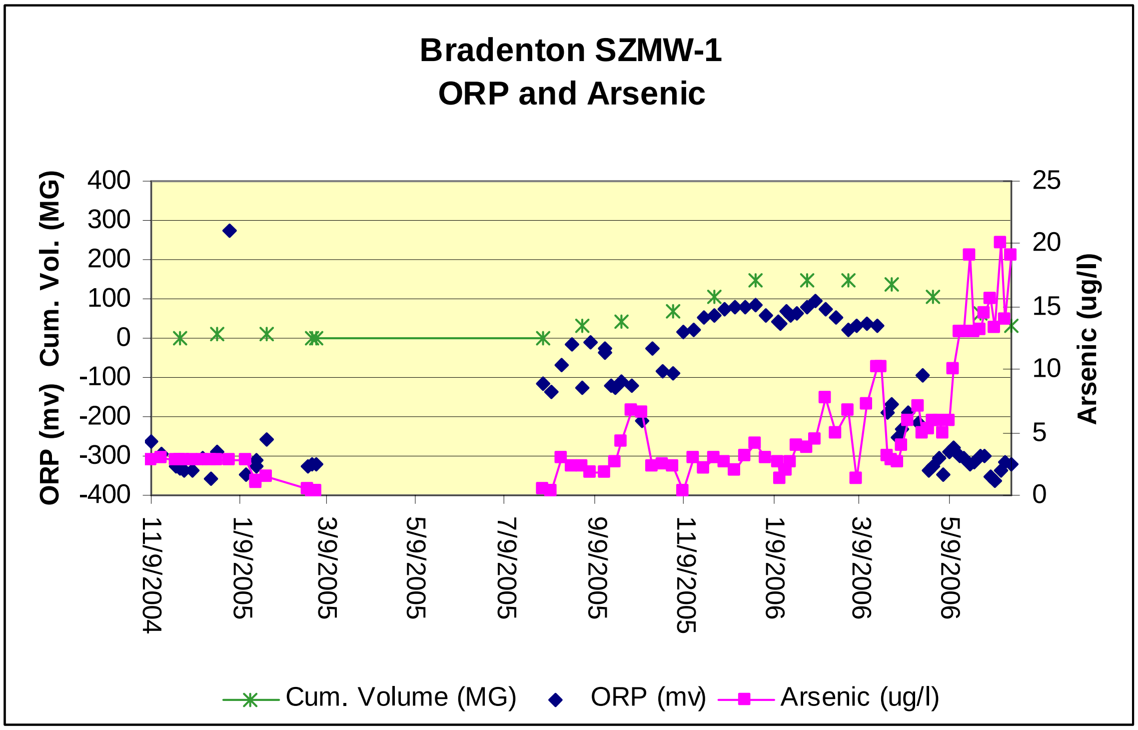


Figure 10 Bradenton Arsenic Response at SZMW-1 Relative to Cumulative Volume Stored and to ORP

ORP at the ASR well during recharge ranged from 269 to 502 mv during the six cycles. Further field investigations will be required in order to determine whether reduction of the ORP of the recharge water will control arsenic mobilization underground.

For the storage zone monitor well, ORP varied from minus 350 to plus 94 mv, as shown on **Figure 10**. Highest values were during Cycle 6 recharge when the TSV of 150 MG was being formed, pushing drinking water past the monitor well. Lowest values were during Cycles 1 through 4 and also during Cycle 6 recovery. Intermediate values of ORP were recorded during the extended recovery period following completion of Cycle 6, when peak arsenic concentrations occurred in the SZMW. No clear pattern is evident relating arsenic concentration to ORP at the SZMW. Arsenic concentrations were highest during the extended recovery period following Cycle 6, reaching 20 ug/l, however at similar ORP values of -300 to -400 mv during Cycles 1 to 4 no elevated arsenic concentrations were noted.

Figure 11 shows the absence of any apparent significant linear relationship between arsenic concentration and ORP at the storage zone monitor well, using data pairs during recharge, storage, recovery and the extended pumping period following Cycle 6 recovery. A hypothesized linear relationship between the two variables for all recharge, storage and recovery data yields an R^2 of 0.093. If the data set is reduced so that it only includes data pairs during recovery, the R^2 value increases to 0.200, as shown on Figure 11 These values are both insignificant. This suggests that increases in arsenic concentration that occur toward the end of an extended recovery period are perhaps unrelated to changes in ORP.

A positive finding from Figure 11 is that, for ORP values exceeding about minus 50 mv at the storage zone monitor well, no arsenic concentrations exceeding 10 µg/l were observed. This is important since, with successive ASR cycles and achievement of the TSV, it is reasonable to expect a steady change in water quality inside the buffer zone, changing from ambient groundwater to stored drinking water. An increase in ORP would therefore be expected and would correspond to a decline in arsenic concentrations.

It is possible that arsenic is desorbed during recovery due to displacement by other anions such as bicarbonate and sulfate. Bicarbonate concentration of the recharge water typically ranges from 48 to 73 mg/l while for the ambient groundwater it is probably about 110 mg/l. This mechanism has been proposed (Appelo et al., 2002) however it is unclear whether there exists sufficient contrast in bicarbonate values. Most likely it is a combination of subsurface processes that impact arsenic concentrations, such as potential desorption by competing ions; loss of surface sorption sites due to reductive dissolution of Fe(III) to Fe(II), and reduced potential for sorption due to reduction to As(III).

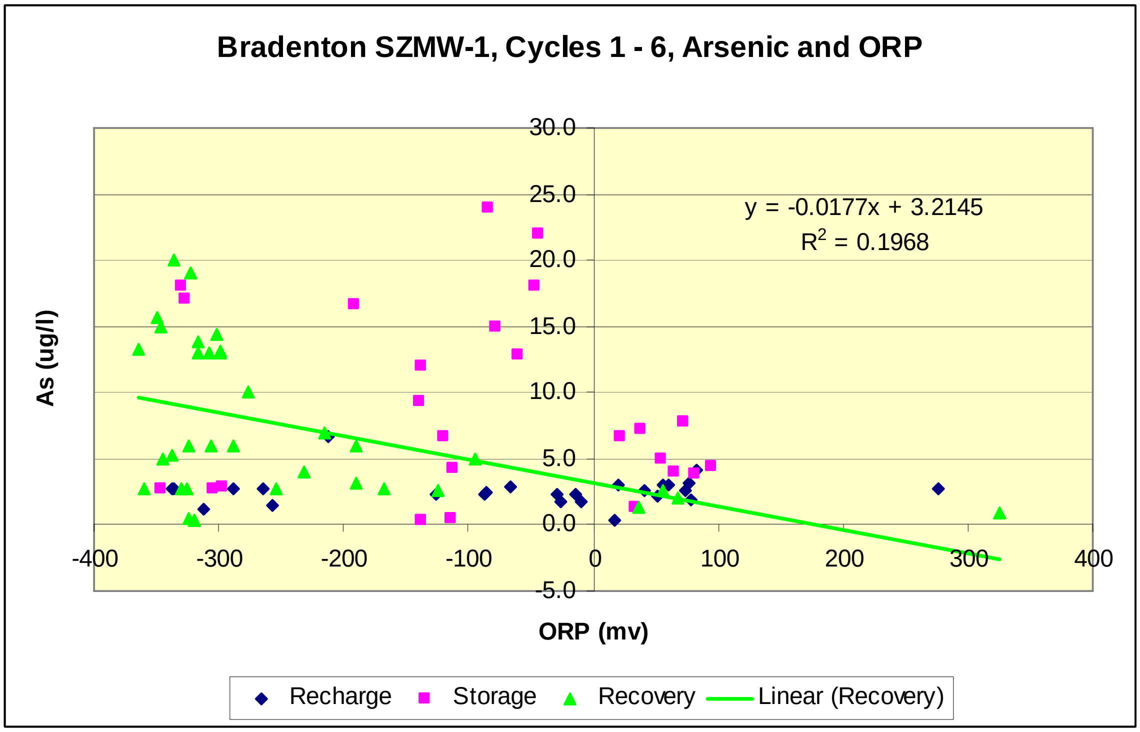


Figure 11 Bradenton Cycles 1 – 6, Relationship between Arsenic and ORP

pH

During Cycles 1 – 4, pH in the recharge water ranged from 7.1 to 8.1. During recovery, pH at the ASR well generally declined steadily within a range of 7.7 to 7.2. Of particular interest is that during the first three hours of Cycle 4 recovery pH started at 6.4 and climbed to a peak of 7.7. One day later the pH was 7.6. The data suggest that the proximal zone around the well has a low pH, at least at this site. Arsenic is more readily absorbed to ferric hydroxide floc at low pH.

Figure 12 shows changes in pH during recharge and recovery at the ASR well and also at SZMW-1 during Cycles 1 through 4. The values for the SZMW-1 have been reduced by 3.00 to facilitate graphic comparison with the data from the ASR well. The pronounced decline at the ASR well during the first three hours of recovery of Cycle 4 (February 24, 2005) after one month of storage is of interest, indicating substantial pH reduction close to the wellbore. Also of interest is the consistent slight decline of pH with increased recovery during each cycle. A lack of pH response at the storage zone monitor well during this period is evident, even though significant changes occurred in conductivity, chloride and TDS at the monitor well.

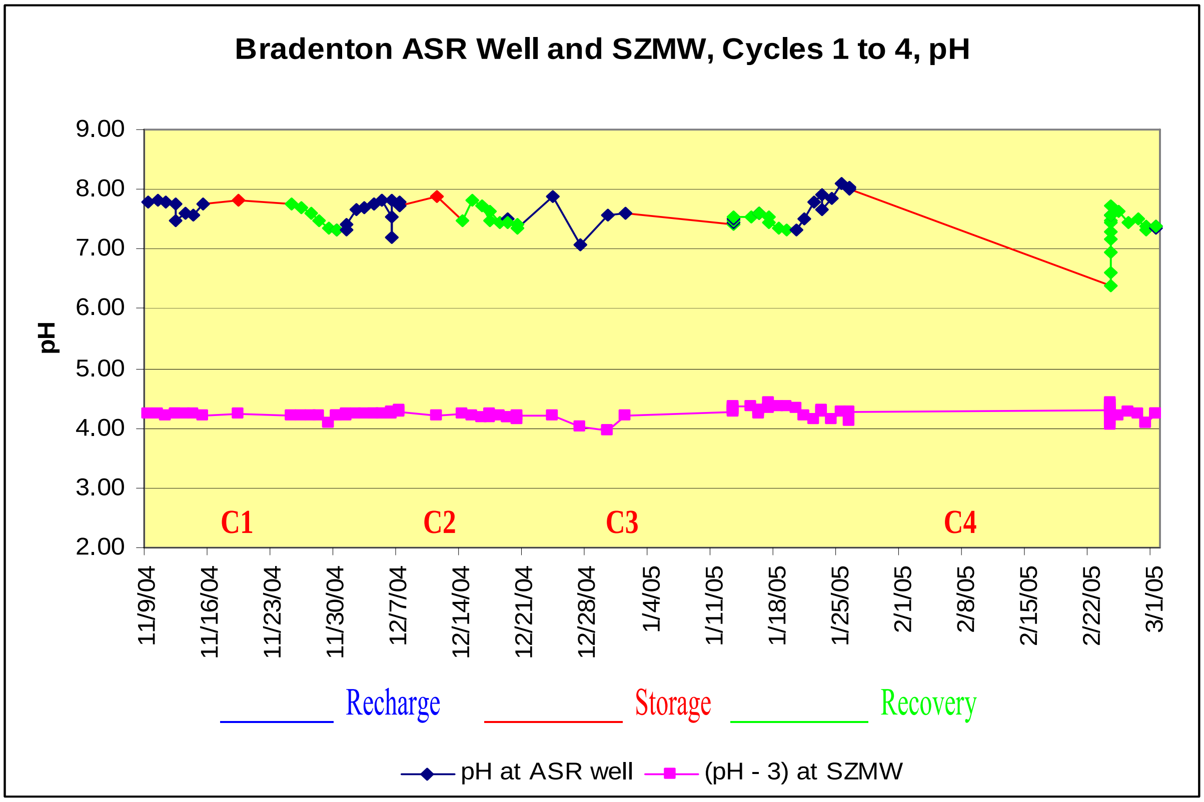


Figure 12 Bradenton ASR Well and SZMW, Cycles 1 to 4, pH

Figure 13 shows pH response for the remainder of cycle testing at Bradenton, after Cycle 4. This was a period during which a cumulative storage volume of 150 MG was formed, and then 120 MG was recovered. During Cycle 6 recovery followed by the extended pumping period during which the buffer zone was recovered, pH showed a slight declining trend. During initial portions of the recovery period higher pH values were in the range of 7.5 to 8.0, similar to recharge water pH, while during later portions of the recovery period they were generally in a range of 7.0 to 7.5, similar to ambient pH in the aquifer. It was during these later portions of the recovery period that elevated arsenic concentrations occurred in the recovered water. The arsenic response to changing pH does not appear to be immediate, but lags by several days.

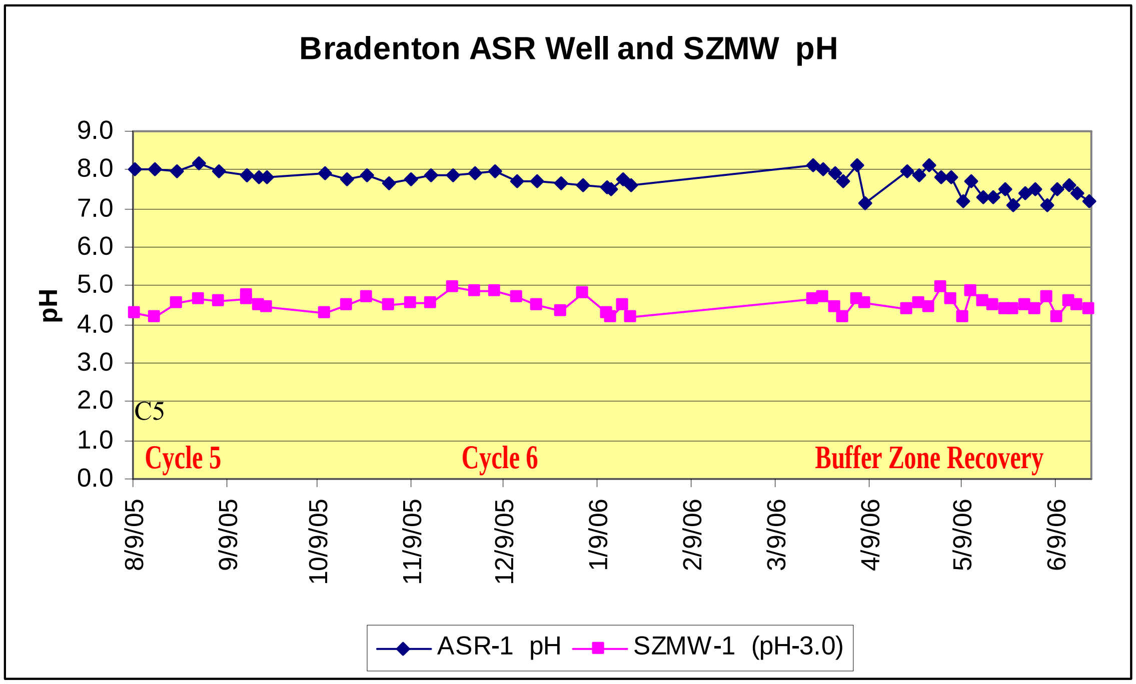


Figure 13 Bradenton pH After Cycle 4 at ASR-1 and SZMW-1

Other Water Quality Constituents

Figures 14, 15 and 16 show variation in Chloride, Dissolved Oxygen and Ammonia during Cycles 1 to 4. Chloride serves as an effective natural tracer for mixing between recharge water and ambient brackish groundwater. A background sample obtained from the ASR well immediately prior to Cycle 1 recharge showed a chloride concentration of 100 mg/l.

Dissolved oxygen shows rapid depletion during storage, due to geochemical and microbial activity. Dissolved oxygen concentration in the recharge water ranged between 8.3 and 10.2 mg/l during the first four cycles. At the end of the four storage periods DO levels had declined to between zero and 2.9 mg/l. Comparison with ORP data suggests that elimination of DO would correspond to an ORP value below about +50 mv. Any residual DO at the beginning of recovery was eliminated by the end of recovery during these four cycles. Of some interest is that DO at the beginning of Cycle 4 recovery was 0.3 mg/l, increasing to 1.4 mg/l after one hour of pumping and then declining again. Also of interest is that D.O. at the beginning of recovery for the first three cycles steadily increased, probably indicating increased oxidation of the zone immediately surrounding the ASR well after successive seven day storage periods. However when the storage period was increased to 28 days during Cycle 4, the D.O. concentration fell again to essentially zero.

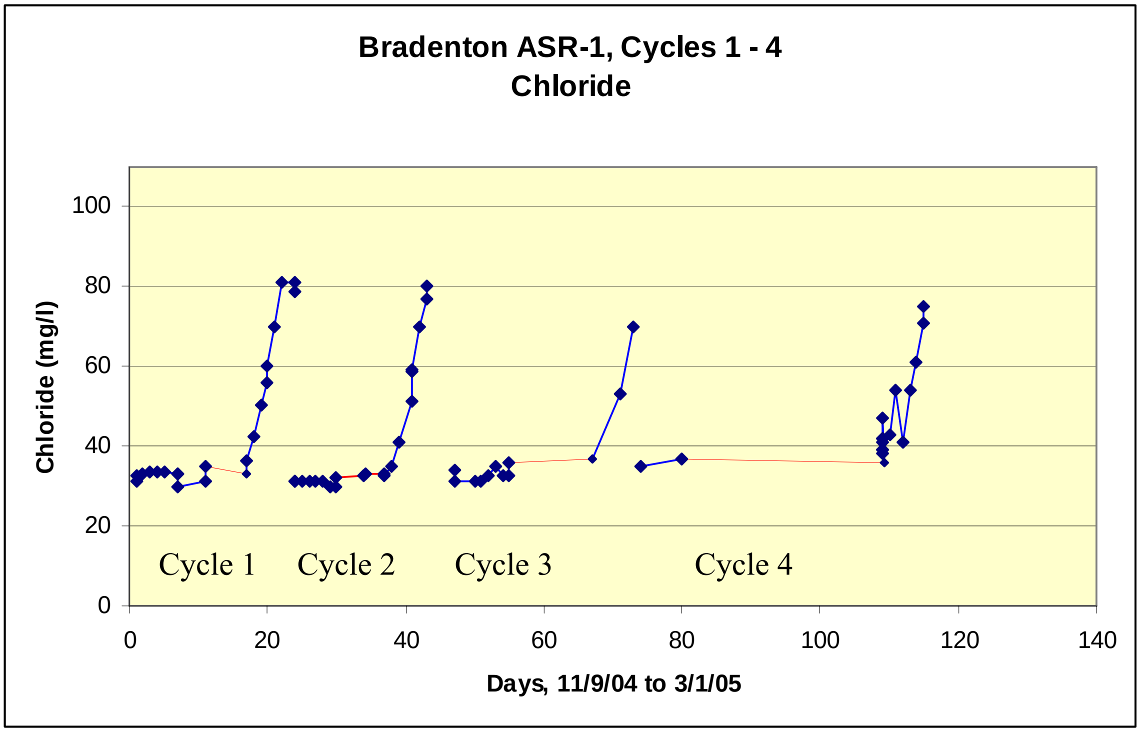


Figure 14 Bradenton Cycles 1 – 4, Chloride Concentrations

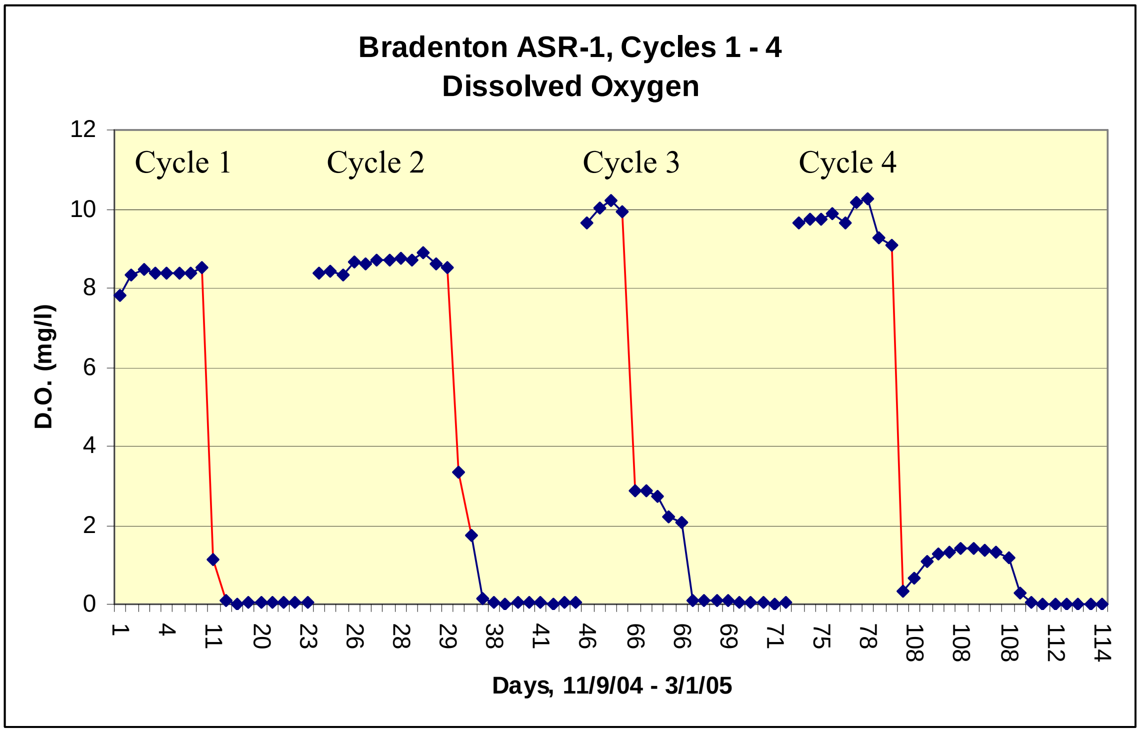


Figure 15 Bradenton Cycles 1 – 4, Dissolved Oxygen Concentrations

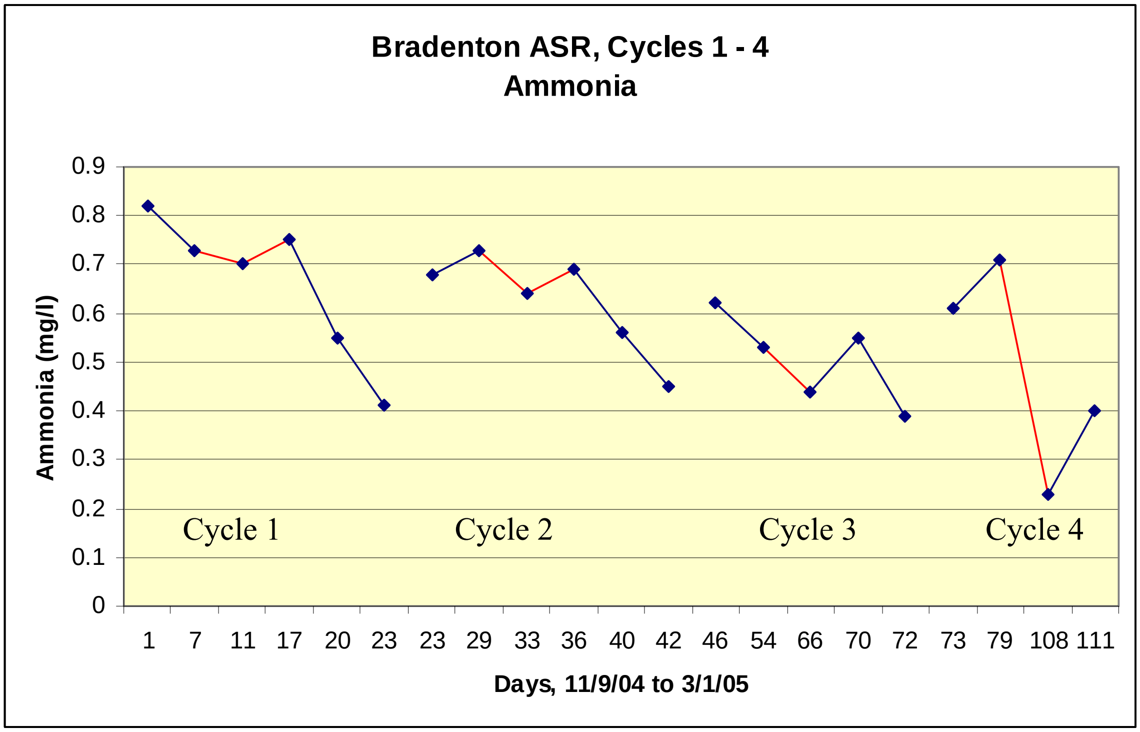


Figure 16 Bradenton Cycles 1 – 4, Ammonia Concentrations

Ammonia depletion suggests microbial activity, with a reduction of about 50% during one month of storage. This is similar to ASR test program results from Port Malabar (now Palm Bay) approximately 15 years ago. A reasonable hypothesis is that microbial activity is utilizing ammonia in the source water as a nutrient source.

Figure 17 shows the absence of any significant relationship between arsenic concentration and dissolved oxygen at the ASR well during recovery. The four highest D.O. readings and associated low arsenic concentrations all occurred at the beginning of recovery periods, either as a result of residual D.O. from the previous recharge period or due to atmospheric oxygen entering the well through the open borehole during the storage period. At the storage zone monitor well D.O. readings ranged from non-detect to 0.54 mg/l, however arsenic concentration varied widely from non-detect to 24 µg/l.

Figure 18 shows the relatively strong relationship between TDS and arsenic concentration at the ASR well for Cycles 1 through 6, suggesting that TDS may perhaps be utilized as a surrogate, or rapid indicator of arsenic concentration during ASR storage in brackish aquifers containing arsenic-bearing minerals. A variance (R^2) of 0.68 was calculated for this (assumed to be linear) relationship.

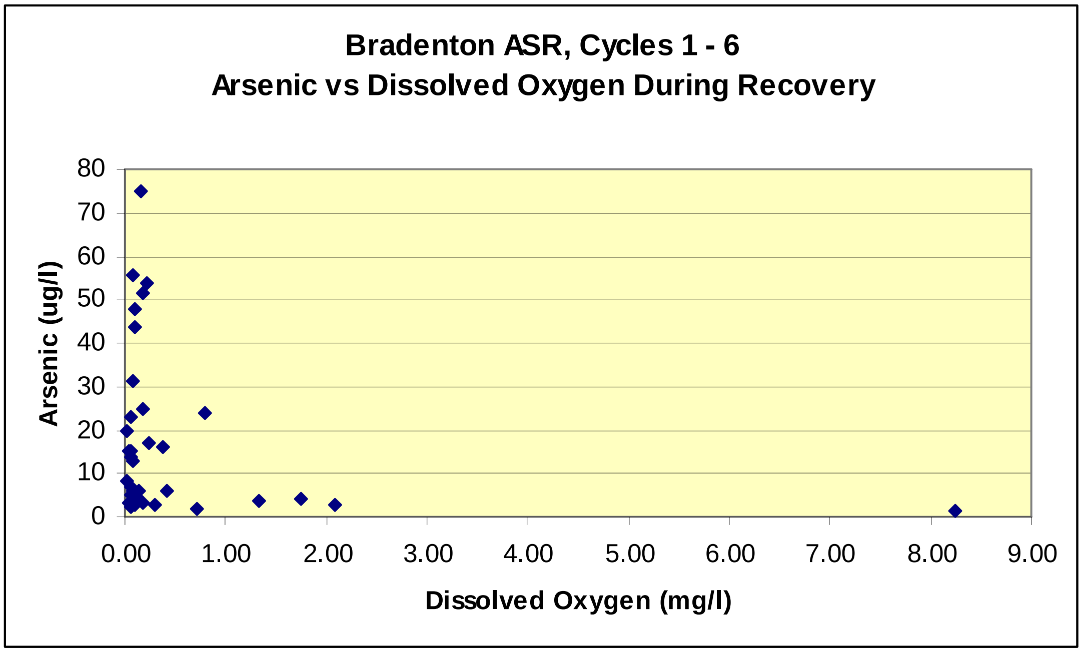


Figure 17 Arsenic vs Dissolved Oxygen During Recovery

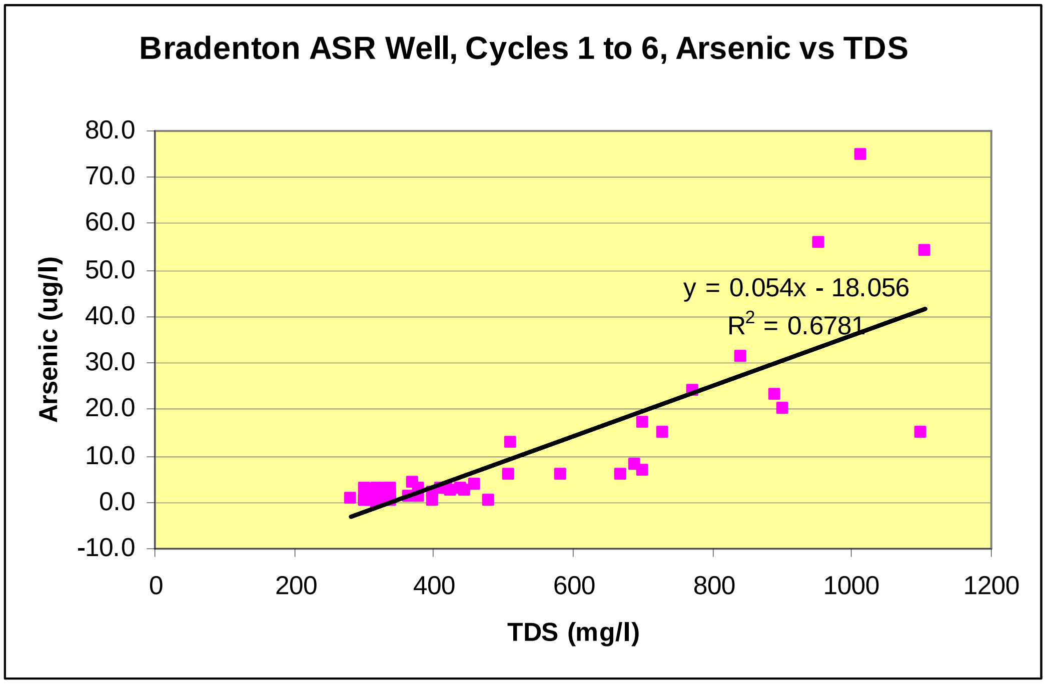


Figure 18 Bradenton ASR Well, Cycles 1 to 6, Arsenic vs TDS

If this relationship is confirmed through subsequent investigations, the viability of the TSV concept would be indicated as a plausible method for control of arsenic concentrations in the recovered water. As indicated previously in this technical memorandum, the TSV concept was developed for control of TDS concentrations during recovery of fresh water stored in brackish aquifers. It may also be applicable for control of water stored in aquifers containing arsenic-bearing minerals.

Figure 19 shows a similar relationship between arsenic and chloride concentration for Cycles 1 to 6. Fewer data pairs are available, however the variance (R^2) is 0.75, which is more significant than the corresponding relationship for arsenic vs TDS. Ambient chloride concentration in the aquifer is estimated at 38 mg/l while recharge water chloride concentration varies between 26 and 36 mg/l.

To gain further understanding of subsurface arsenic processes, additional analysis was conducted regarding changes in arsenic concentration relative to changes in iron, bicarbonate, sulfate and sulfide concentrations and also temperature changes during ASR recharge and recovery.

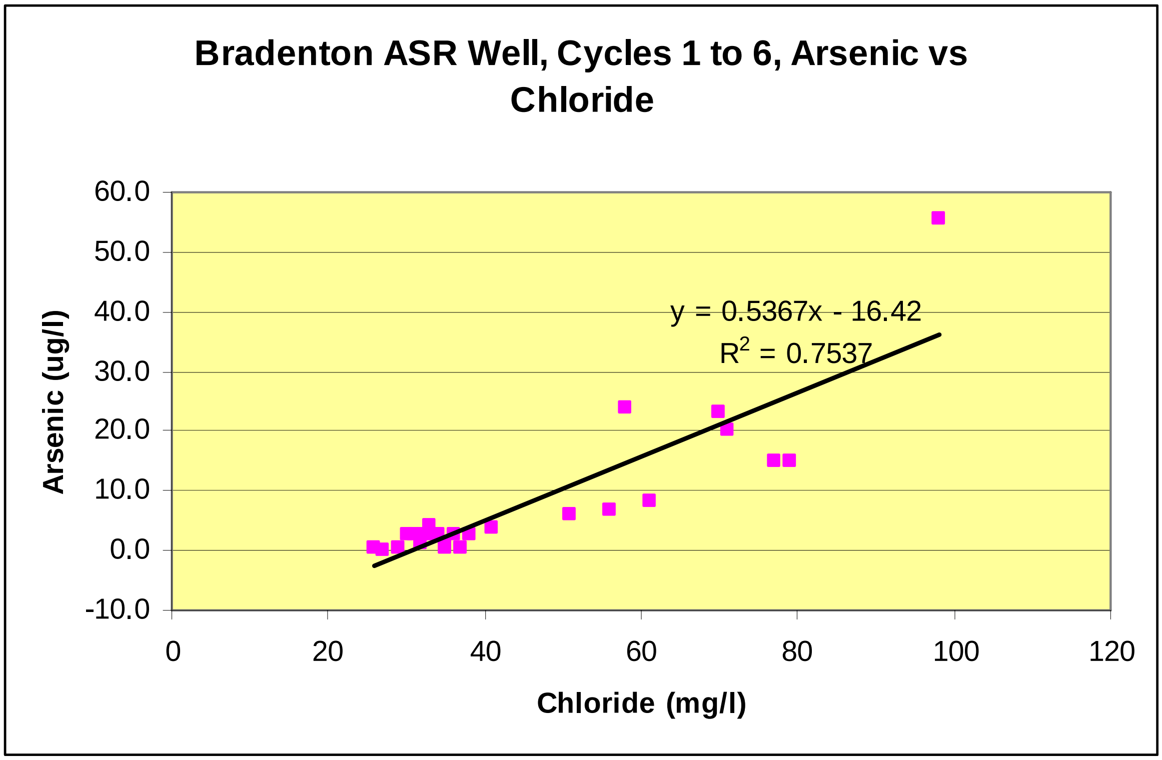


Figure 19 Bradenton ASR Well, Cycles 1 to 6, Arsenic vs Chloride

Iron

Extensive additional data is available for iron during Cycles 1 through 4, obtained by the City of Bradenton but not included in the FDEP database.

Background concentration in the aquifer for total iron was 3 µg/l while dissolved iron was 2 µg/l. Based upon daily samples analyzed by the City of Bradenton, total iron concentrations during the recharge portion of Cycles 1 to 4 ranged from zero to 14 µg/l, averaging 3 µg/l. Corresponding dissolved iron concentrations ranged from zero to 4 µg/l, averaging 0.4 ug/l. These are all very low iron concentrations. As indicated previously, the first three cycles were identical with 10 MG recharge, 7 days storage and 10 MG recovery. The fourth cycle was similar except for a 28-day storage period. During ASR recovery for the first four cycles, total iron concentrations suggest an evolving pattern of increasing iron concentrations close to the ASR well. During the first cycle recovery it steadily increased from 3 to 66 µg/l. During the second cycle it increased from 2 to 14 µg/l. During the third cycle total iron concentration increased from zero at the beginning to 5 µg/l at the end, however concentrations as high as 17 µg/l occurred soon after the beginning of recovery. During the fourth cycle, relatively high total iron concentrations ranging from 54 to 206 µg/l occurred during the first three days of recovery however subsequent samples dropped rapidly to zero during the last third of recovery. Dissolved iron concentration during recovery for all four cycles was stable, ranging from zero to 5 µg/l with an average of 0.5 µg/l.

This suggests the development of significantly higher total iron concentrations close to the ASR well, probably associated with pyrite dissolution and perhaps also due to microbial activity. As shown in **Figure 12**, a significant decline in pH also occurred close to the ASR well at the beginning of recovery for Cycle 4. Since arsenic is known to sorb to ferric hydroxide and to desorb from ferric hydroxide under changing ambient water quality conditions, the development of high iron concentrations close to the ASR well, even when recharge and ambient groundwater concentrations are quite low, is potentially a significant factor for understanding the mobilization and attenuation of arsenic during ASR recharge and recovery.

From the FDEP data set for Cycles 1 to 4, significantly less data is available however it is from a certified commercial laboratory. The recharge total iron concentrations ranged from 11 to 35 µg/l while during recovery concentrations increased from 11 to 160 µg/l in Cycle 1; 23 to 48 µg/l in Cycle 2; 21 declining to 11 µg/l in Cycle 3 and 44 declining to 11 µg/l in Cycle 4, following the same pattern as for the City of Bradenton data set. During Cycles 5 and 6, plus the extended recovery period, total iron concentration during recovery was less than 29 µg/l for the first three samples and 38 µg/l at the end of recovery. No data was obtained for dissolved iron.

The total iron concentrations at the storage zone monitor well were virtually all below the method detection limit, either <11 µg/l or <29 µg/l, for Cycles 1 through 6 and the subsequent extended recovery period. No change in iron concentration was evident when arsenic concentrations at the monitor well increased above 10 ug/l toward the end of the extended recovery period following Cycle 6. Peak arsenic concentration was about 24 µg/l about 6 weeks before the end of recovery. Almost all of the previously stored water, including the buffer zone, was recovered during this extended period. This supports the previous observation that elevated iron concentrations probably occur close to the ASR well but do not extend as far as the monitor well.

Bicarbonate

Bicarbonate concentrations in the recharge water ranged from 62 to 77 mg/l during the first four cycles. In the recovered water the pattern was consistent, increasing from either 75 or 82 mg/l at the beginning of recovery to 110 mg/l at the end of recovery. During Cycle 6 recovery and the following extended recovery period bicarbonate concentrations increased from 74 to 103 mg/l. No background concentration is available for bicarbonate in the ambient groundwater, however it is assumed to be about 110 mg/l. The potential role of bicarbonate for displacing arsenic sorbed to ferric hydroxide floc during ASR recovery has been suggested by Appelo, 2002. Whether the relatively small difference between recharge and ambient groundwater concentrations of bicarbonate are sufficient to cause this effect at the Bradenton site is unclear.

Sulfate and Sulfide

Recharge sulfate concentrations increased steadily during Cycles 1 to 4, from 130 to 210 mg/l, reflecting normal seasonal variability of the City's water supply source. During Cycles 5 and 6 they varied between 140 and 171 mg/l. Ambient groundwater sulfate concentration is 650 mg/l. During the recovery periods for Cycles 1 to 6 the sulfate concentrations increased during each cycle, as shown below. For Cycle 6 the three samples were obtained during the last half of recovery. Source water quality variability and the high ambient concentrations would tend to mask any sulfate variation due to arsenic mobilization and attenuation, however no significant difference between sulfate and chloride patterns is evident.

Cycle	Sulfate Concentration During Recovery (mg/l)	
	Beginning	End
1	190	510
2	160	490
3	200	440
4	240	470
5	-	-
6	(265)	518

Hydrogen sulfide concentrations at the beginning and end of recovery were all 0.32 mg/l except for a single measurement of 1.5 mg/l at the end of Cycle 1.

While the general trend of increasing sulfate concentrations during ASR recovery is not unexpected considering the corresponding changes in TDS and chloride concentration shown on **Figures 18 and 19,** the sulfate concentration may be more significant for the purpose of understanding arsenic mobilization and attenuation since, like bicarbonate, sulfate may also displace arsenic from ferric hydroxide floc during ASR recovery. Recovery of the stored water would not cause such water quality changes, however recovery of the surrounding buffer zone may bring with it not only an increasing blend of ambient groundwater but also the reaction products resulting from the release of arsenic displaced from ferric hydroxide floc trapped in the aquifer matrix close to the ASR well. As suggested by Stuyfzand (2007) the arsenic may be displaced by changes in sulfate concentration and possibly by other changes in constituent concentrations in the recovered water such as bicarbonate and temperature.

Seasonal temperature changes generally between 17°C and 31°C were observed at this site during recharge periods. During Cycles 5 and 6 a cumulative total of 150 MG were recharged at temperatures that steadily declined from 30.6 to 19.9°C. Most of this water was then recovered with temperatures steadily increasing from 22.5 to 26.1°C. Background temperature in the aquifer is 26.3°C.

Storage Zone Monitor Well

Arsenic concentration at the storage zone monitor well did not change during Cycles 1 through 6 of the cycle testing program, remaining below 2.6 µg/l. The monitor well is 224 ft from the ASR well. Elevated arsenic concentration at the SZMW only occurred following Cycle 6 recovery, as a result of continued pumping that recovered most of the buffer zone. Peak concentration reached 24 µg/l. TDS concentrations at this radial distance of 224 feet declined from 1,100 mg/l to as low as 348 mg/l during Cycles 1 through 6, confirming that the stored water bubble extended past the monitor well.

It is apparent from this data set that most of the arsenic mobilized near the ASR well during recharge probably does not get transported into the surrounding aquifer as rapidly as the movement of the stored water. Instead it appears to be adsorbed, re-precipitated and/or metabolized relatively close to the well, perhaps within the proximal zone where the greatest changes in ORP and pH occur. This is consistent with the “rolling front’ of arsenic that has been noted in research from the Netherlands (Stuyfzand, 2005), where an arsenic peak occurs in the aquifer a few tens of meters from the recharge well.

A small portion of the mobilized arsenic may be transported radially away from the ASR well with the recharge water due to its neutral charge and, with ASR, would move back towards the well during recovery. Variation of arsenic and ORP at the SZMW is shown in **Figures 10 and 11** while the lack of variation in pH is shown in **Figure 12**. During extended recovery from the ASR well when the buffer zone is recovered, arsenic concentrations increase. The reason for this is uncertain however a plausible hypothesis is that it is more closely related to the relatively rapid increase in TDS or chloride concentration than it is related to the small decline in pH or to the slightly more significant change in ORP. This may reflect a sorption or ion exchange process, caused by the recovery of relatively brackish water into the proximal zone around the well where the arsenic is assumed to accumulate. Alternatively, a supplemental microbial mechanism is suggested, whereby metabolism may be adversely impacted by cyclical variability in salinity occurring in ASR wells.

As indicated previously, the strongest relationship appears to occur between arsenic concentration and conservative constituents such as TDS and chloride. A relatively weak relationship is evident between arsenic concentration and either pH or ORP. It is pertinent that ASR wellfields in SW Florida that are experiencing elevated arsenic concentrations also are experiencing variable TDS concentrations in their recovered water, as will be discussed subsequently in this technical memorandum. With very few exceptions, total iron concentrations at the monitor well remained below the method detection limit of 0.011 or 0.029 mg/l.

Additional Discussion

A general relationship between arsenic concentration and ORP is probable since recharge water, which has high ORP, dissolves arsenic from the pyrite occurring in the aquifer. However it is clear that other factors are probably impacting observed arsenic concentrations. The declining pH that occurs during recovery would tend to affect sorption of the arsenic to the ferric hydroxide floc and to the aquifer matrix by changing the charge differential across boundary layers at sorption surfaces. Decreasing the pH to within the range of about 7.1 to 7.5 should theoretically enhance the adsorption of arsenic to iron oxyhydroxide, not mobilize arsenic. This suggests the occurrence of arsenic (III) which is neutral as opposed to arsenic (V) which has a positive charge. Other processes may also be at work.

The City of Bradenton obtained additional water quality and hydraulic data during Cycles 1 to 4 in order to better understand subsurface reactions pertaining to arsenic mobilization and attenuation. The data are available but are not in the FDEP database. They included more frequent samples to better characterize changes in recovered water quality, and also sampling approximately every 10 minutes during the first three hours of recovery of Cycle 4 in order to characterize changes in water quality close to the well. This relatively simple and inexpensive analysis provided useful data regarding water quality variability in the proximal zone close to the ASR well. It could easily be replicated at other ASR sites.

Total dissolved solids (TDS) in the recharge water ranged between 112 and 560 mg/l, increasing as cycle testing proceeded. This reflected normal seasonal variability in the source water quality from the Evers Reservoir, which is a reservoir which supplies the City's water. During recovery for the first four cycles TDS values reached 980 to 1,052 mg/l, approaching background levels toward the end of recovery and reflecting the absence of any buffer zone formation. With formation of the buffer zone during Cycles 5 and 6, recovered water TDS values dropped to about 400 mg/l.

Understanding the reasons for subtle changes in ORP and pH around an ASR well will be critical for achieving an improved understanding of arsenic speciation, mobilization and attenuation, and the physical, geochemical and microbial processes that are contributing to these changes. Currently there exists little understanding of these issues during ASR storage, particularly under Florida hydrogeologic conditions.

3.0 City of Tampa

Preliminary results from analysis of the comprehensive Bradenton ASR monitoring data set were then compared with the data from the Tampa ASR wellfield. The primary difference between the two nearby sites is their mode of operation since the Tampa ASR wellfield is operated with essentially no formation of a buffer zone. In addition the storage zone is fresh, however under extended pumping conditions some upconing of brackish water occurs from beneath the storage zone, as discussed subsequently.

The storage zone at the Tampa Rome Avenue Park ASR wellfield is the lower Suwannee formation, a confined limestone artesian aquifer containing ambient fresh water. Based upon aquifer performance tests, single well pumping tests and hydrogeologic computer modeling studies, aquifer hydraulic characteristics for the storage zone are as follows:

Transmissivity - 152,000 gpd/ft
Storativity - 9.8×10^{-5}
Leakance - 3.9×10^{-3} gpd/ft^3

Eight ASR wells were constructed, tested and placed into operation between 1996 and 2002, plus five storage zone monitor wells and several other monitor wells in overlying or underlying aquifers. One ASR well was constructed and tested first, along with several monitor wells. The remaining ASR and monitor wells were then added in a second phase. The ASR wells have open hole completions between depths of about 300 to 400 feet, overlain by a semi-confining layer in the middle of the Suwannee Limestone formation and underlain by less permeable limestones and clays of the Ocala Limestone formation. **Figure 20** shows a site location map, indicating the ASR wells and the storage zone monitor wells.

Background ambient groundwater quality samples were obtained for each of the eight ASR wells and were analyzed for all Primary and Secondary Drinking Water Standards. Typical results are as follows:

Arsenic - <2 to 3.6 µg/L
Chloride - 14 to 56 mg/L
Iron - <0.05 to 0.085 mg/L
Sulfate - 3 to 36 mg/L
pH - 7.1 to 7.8
TDS - 210 to 500 mg/L

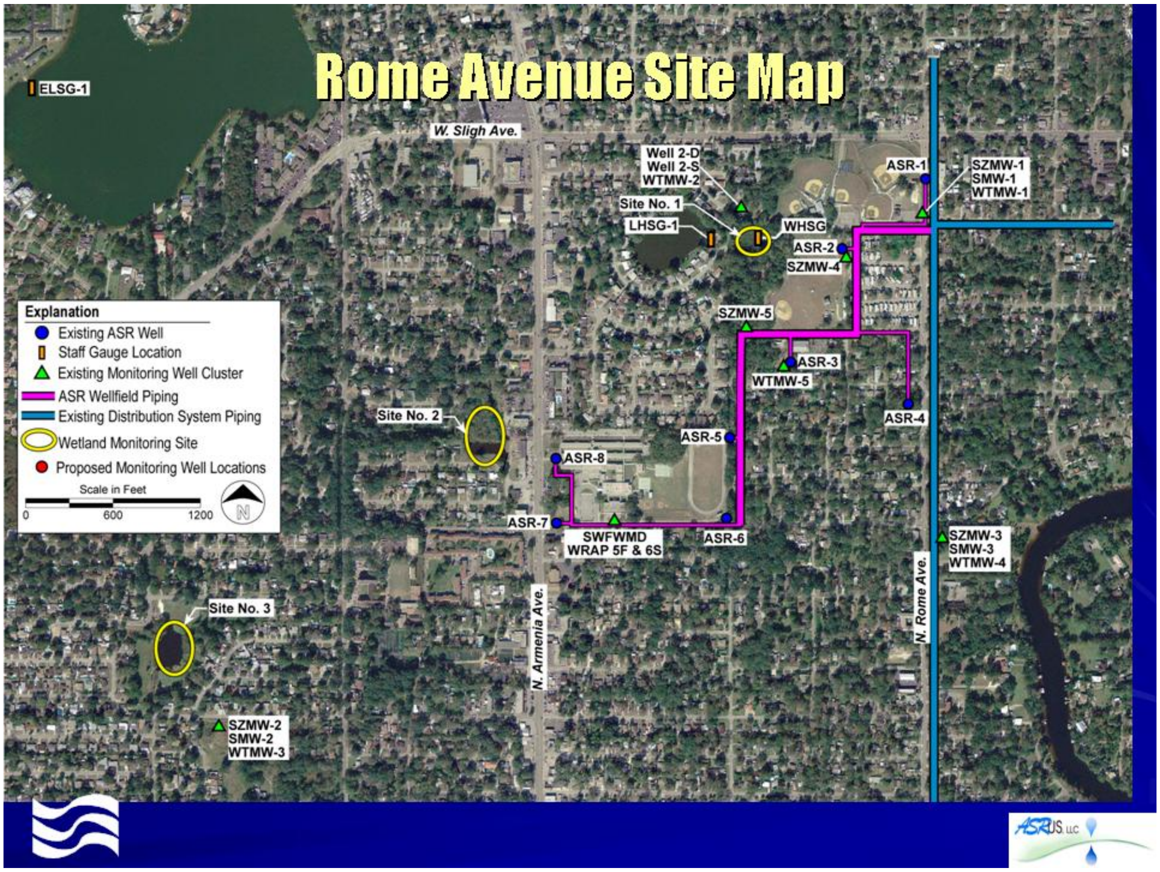


Figure 20 Tampa Rome Avenue Park ASR Site Map
(courtesy Mark McNeal/ASRus)

Recharge is with treated drinking water obtained from the Hillsborough River. Beginning January 4, 2002, the treatment process for the recharge water was modified to provide ozonation for disinfection. As a result subsequent recharge water samples exhibited much higher concentrations for dissolved oxygen and therefore higher oxidation reduction potential (ORP) compared to prior ASR cycle testing operations. An increase in subsequent arsenic concentrations is evident. This increase suggests that a reduction in DO of the recharge water may reduce arsenic concentrations.

Full scale cycle testing of the 8 wells began in 2001 and has continued to this time. Each cycle requires a full year and stores approximately one billion gallons of water, distributed between the eight ASR wells. Data from four operational cycles were analyzed, generally occurring during extended dry periods of Spring and early Summer 2002, 2003, 2004 and 2005.

A complicating factor at the Tampa ASR site is that during extended recovery periods upconing of brackish water occurs from the underlying aquifer, causing a significant increase in TDS of the recovered water. During Spring 2005 the average recovered water TDS climbed from native concentrations of 479 to 1,509 mg/l. To the extent that arsenic mobilization and attenuation reactions may be microbially-dependent, it is hypothesized that the cyclically-varying salinity of the water in the storage zone around the well may inhibit such activity. We are unaware of research that would support or refute this hypothesis for subsurface conditions simulating ASR cyclic operations.

All water recovered from this ASR wellfield site is directed to the water treatment plant where it is retreated to remove arsenic and is then blended with water from other sources, meeting all drinking water standards and providing a uniform water quality for all customers. Over-recovery of the stored water has been consistently practiced, providing a supplemental water supply for the City to help meet peak demands. As shown in the following analysis, recovering more water than has been recharged has probably contributed to the continuing elevated arsenic concentrations observed at this wellfield by preventing formation of an effective buffer zone. Some of the wells developed a small buffer zone while others did not.

Available records include beginning and ending cumulative storage volumes for each well and for each cycle. Records of cumulative storage volume at each well at the time of approximately weekly water quality sampling are not available to support direct comparison with sample results for arsenic and other constituents. Consequently it is only possible to consider any potential relationship between concentration of a water quality constituent and interpolated cumulative storage volume based upon assumed steady pumping rate from the beginning to end of recovery.

Tampa Well ASR-1

For all four cycles, the cumulative stored water volume was consistently negative, indicating that no buffer zone had been formed through prior operations and that none was formed during the analysis period. The results are shown on **Figure 21**. This was the first ASR well, operations at which began in 1997.

Some recharge occurred between each cycle, however never enough to form and maintain a buffer zone. A brief period with acceptable arsenic concentrations (less than 10 µg/l) occurred at the end of recovery in Cycle 2 and the beginning of recovery during the last three cycles, and the peak arsenic concentrations declined during these cycles. The significant difference between Cycle 2 and the remaining cycles is that recharge with ozonated water began during Cycle 2. As shown in **Figure 21**, prior to ozonation the decline in peak arsenic concentration was quite rapid.

Of some interest is that the peak arsenic concentration for Cycle 2 occurred at the beginning of recovery while for the last three cycles it occurred during approximately the middle and toward the end of recovery, not at the end of recovery. This suggests the possibility of a sorption-desorption process occurring in the aquifer close to the well and also may reflect mixing occurring in the formation toward the end of recovery, blending high arsenic water near the well with an increasing proportion of low arsenic water from the surrounding aquifer.

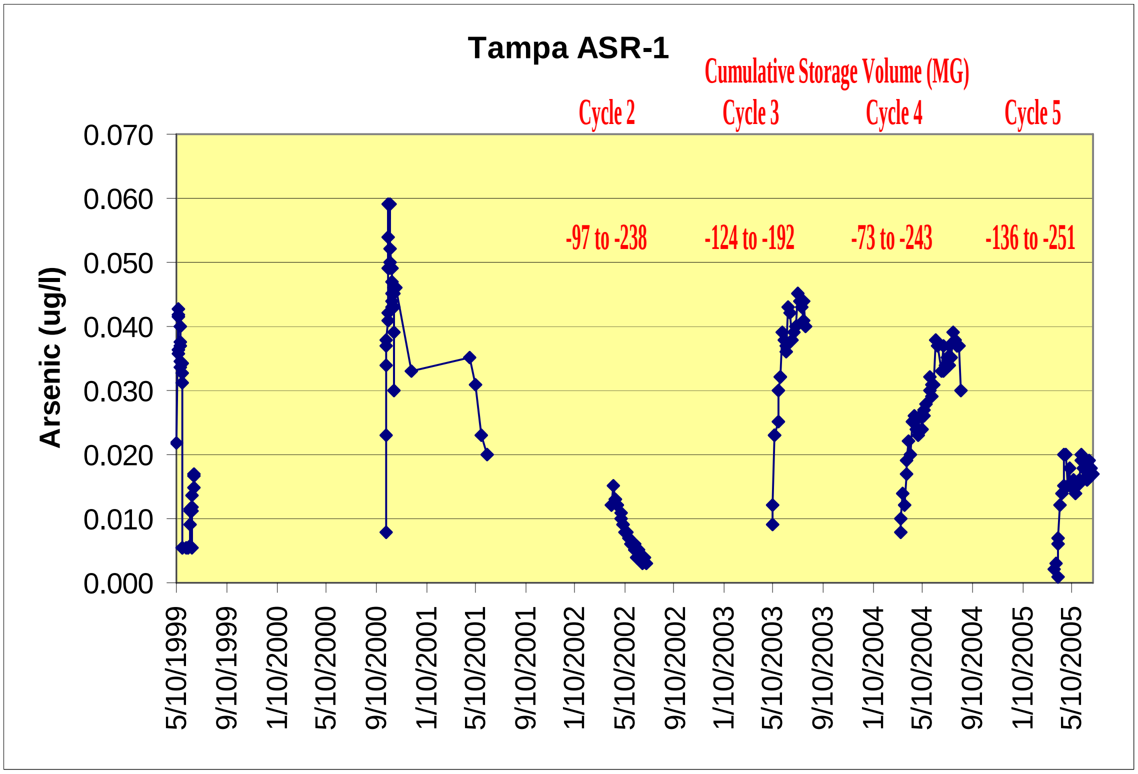


Figure 21 Tampa ASR-1 Cycles 2 – 5 Arsenic

Tampa Well ASR-2

Well ASR-2 operations were generally conducted with a positive cumulative storage volume, forming a very small buffer zone. The results are shown on **Figure 22**. Positive cumulative storage volumes are shown on the upper line in black type while negative cumulative storage volumes are shown in red type on the lower line.

Not shown on this figure are two samples collected during the brief storage period immediately following Cycle 4 and before starting recharge for Cycle 5. These samples were 88 µg/l for arsenic on July 8, 2004, and 76 µg/l on July 15, 2004. Since the well had been idle for two and ten days, respectively, it is likely that particulates were in the water, associated with startup of pumping the well to obtain the samples. As indicated previously, FDEP protocols for arsenic sampling do not allow filtering the sample as is normally done with other metals. It is pertinent that the highest arsenic concentrations recorded during Cycle 4 were near the beginning of recovery.

The reduction of arsenic concentrations with successive cycles is evident. Data for Cycle 5 suggests that a buffer zone of 76 MG is almost adequate to achieve arsenic attenuation to an acceptable level at or below 10 µg/l. The buffer zone volume for this well (at least 76 MG) comprised at least 155% of the recovered water volume (49 MG) in Cycle 5.

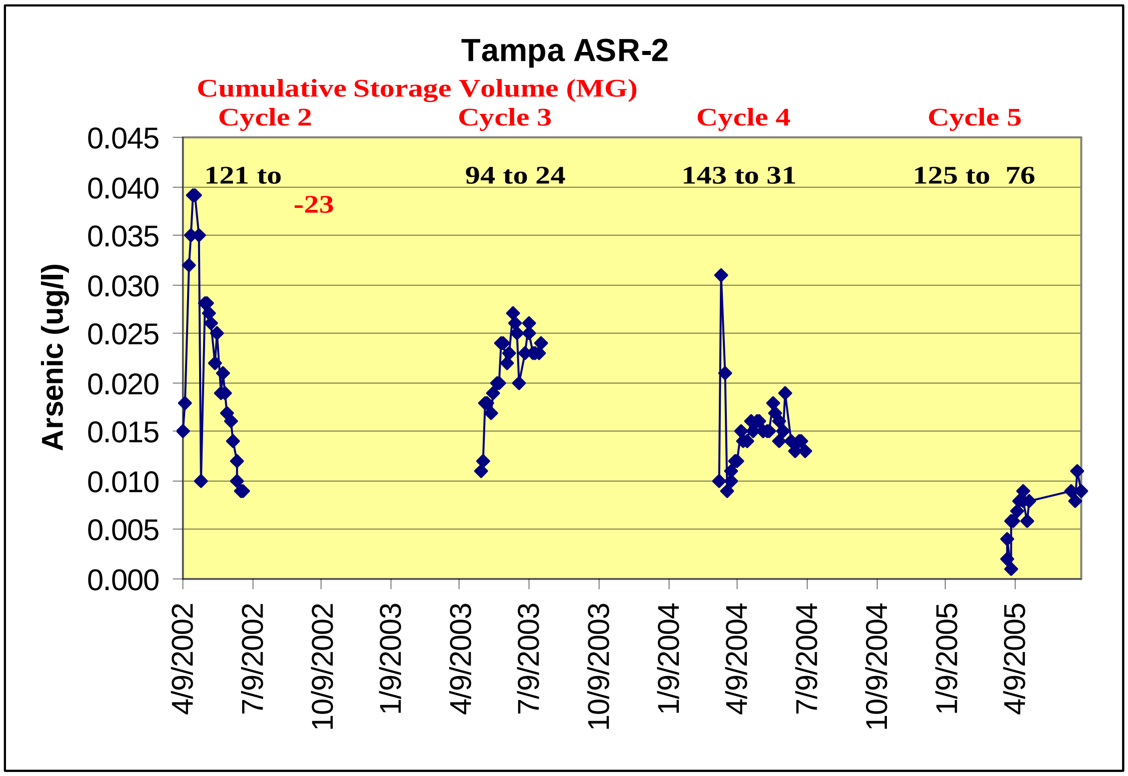


Figure 22 Tampa ASR-2 Cycles 2 – 5 Arsenic

Tampa ASR Well 3

No significant buffer zone was formed in this well. Instead a slightly declining trend of cumulative stored water volume occurred. **Figure 23** shows the results.

A steady decline is evident in peak arsenic concentrations with successive cycles. However, acceptable arsenic concentrations at the ASR well (10 µg/l) were achieved only near the beginning of Cycle 5.

Within each recovery period for Cycles 3 through 5, the uniform trend of increasing arsenic concentrations from the beginning to the end of recovery suggests that, had recovery continued, higher concentrations may have been observed. The high peak concentration during the middle of Cycle 2 recovery indicates a different pattern, occurring immediately after the initiation of ozonation of the recharge water. This also was observed for other wells during Cycle 2.

Tampa Well ASR-4

Three cycles were conducted during the analysis period, during each of which previously stored water was over-recovered. Consequently no buffer zone was formed. Results are shown in **Figure 24.**

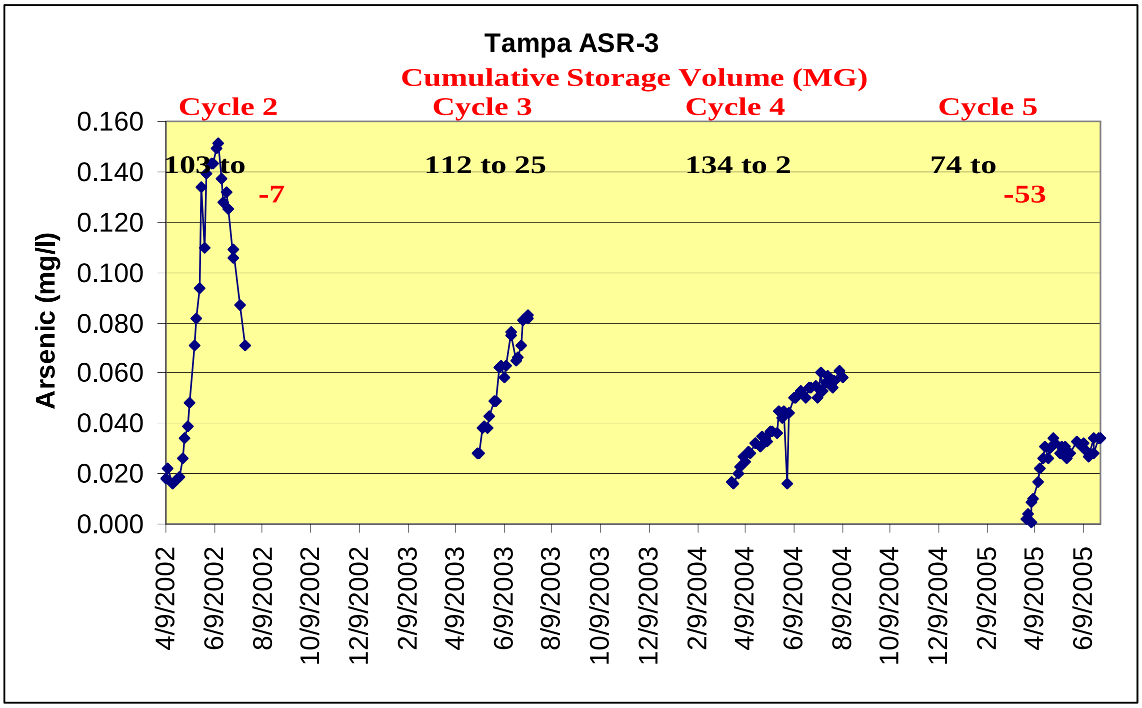


Figure 23 Tampa ASR-3 Cycles 2 - 5 Arsenic

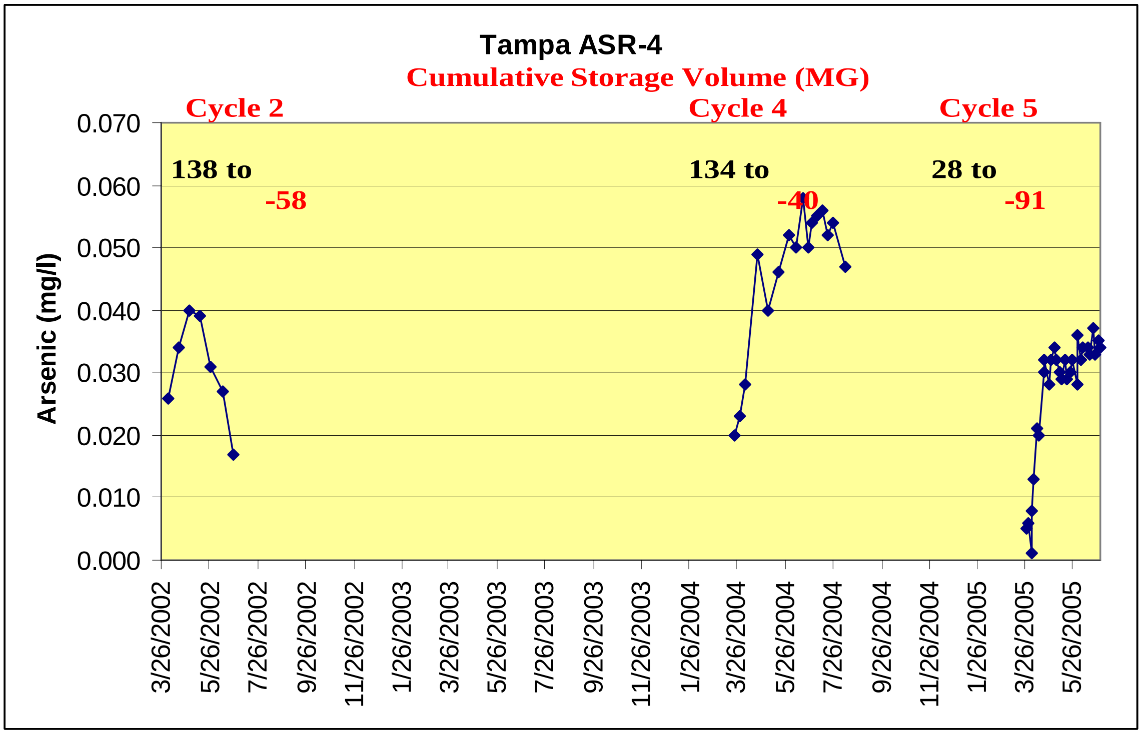


Figure 24 Tampa ASR-4 Cycles 2 – 5 Arsenic

No significant reduction in peak arsenic concentrations was observed, although initial concentrations at the beginning of recovery declined in successive cycles and were acceptable for two weeks at the beginning of recovery of the fifth cycle. The change in arsenic concentration pattern of response for Cycles 2 and 4 compared with Cycle 5 reinforces the prior observation that sorption/desorption and mixing processes in the aquifer are occurring, and that mixing processes are most apparent in Cycle 5, for which the least amount of recharge and the greatest amount of over-recovery occurred.

Tampa Well ASR-5

This well has experienced the greatest amount of over-recovery in the Tampa ASR wellfield. Recharge volumes have been relatively small and recovery volumes have been relatively large. No buffer zone formation has occurred. Arsenic concentrations have been the highest of all the ASR wells in the wellfield. Peak concentrations steadily climbed during the first three cycles, declining only during Cycle 5. That arsenic results declined at all during Cycle 5 is significant, considering the substantial over-recovery. Results are shown in **Figure 25**.

Tampa Well ASR-6

This is an interesting well for analytical purposes since Cycle 2 maintained a positive cumulative storage volume while the remaining cycles each over-recovered the water previously stored. Results are shown in **Figure 26**.

It is pertinent that very little water was recharged prior to Cycle 3, so this cycle was really a continuation of recovery from Cycle 2. Significant recharge occurred prior to Cycle 4 however all of that water and more was then recovered. Cycle 5 recharge was also substantial, but all of that water and more was then recovered. Arsenic peak concentrations steadily declined, but not to acceptable standards except during the first three weeks of recovery of Cycle 5.

Tampa Well ASR-7

Three operating cycles were conducted, during each of which a significantly greater volume of water was recovered than had been previously stored. Results are shown in **Figure 27.**

Peak arsenic concentrations were very high but declined with successive cycles.

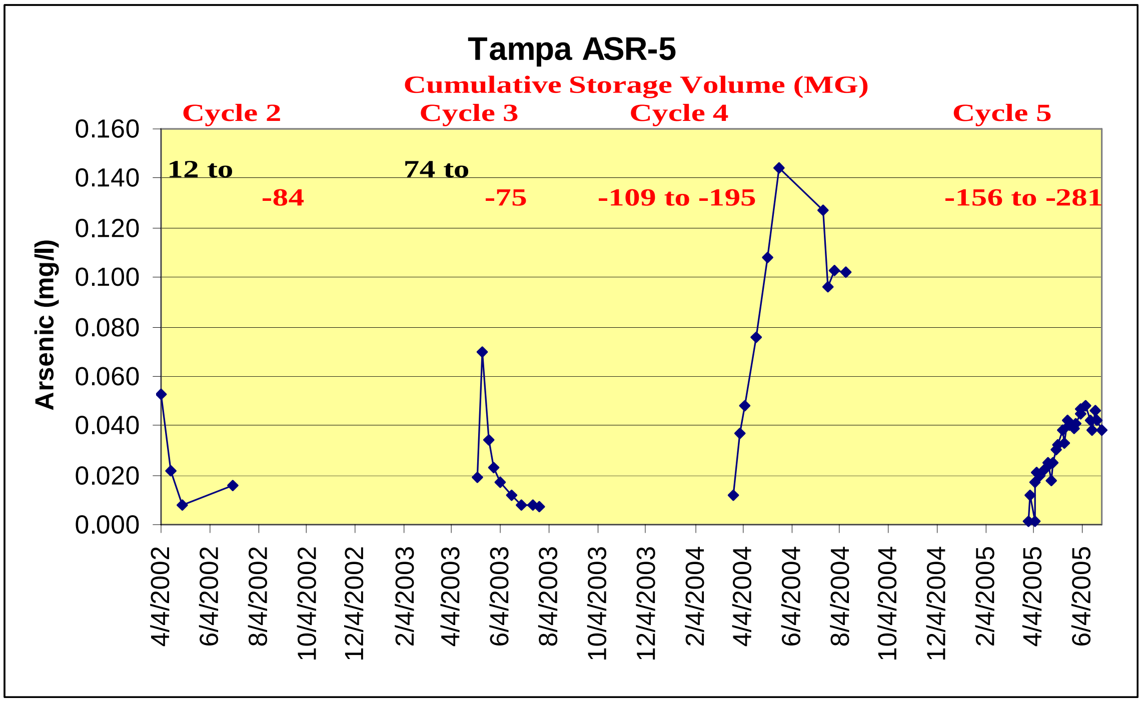


Figure 25 Tampa ASR-5 Cycles 2 – 5 Arsenic

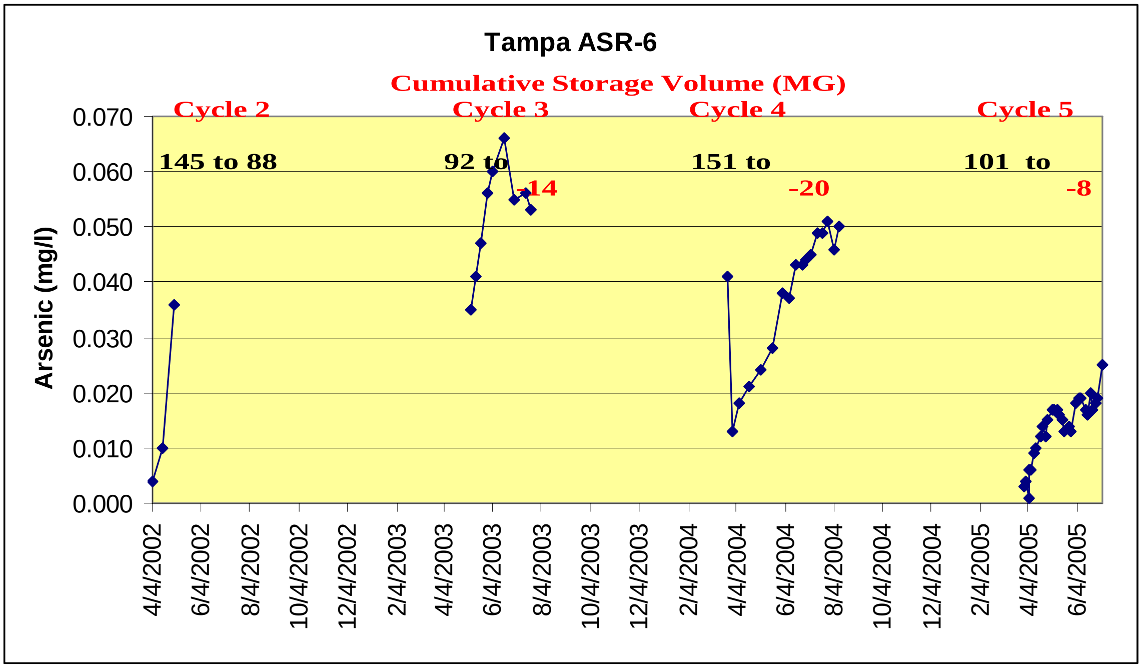


Figure 26 Tampa ASR-6 Cycles 2 – 5 Arsenic

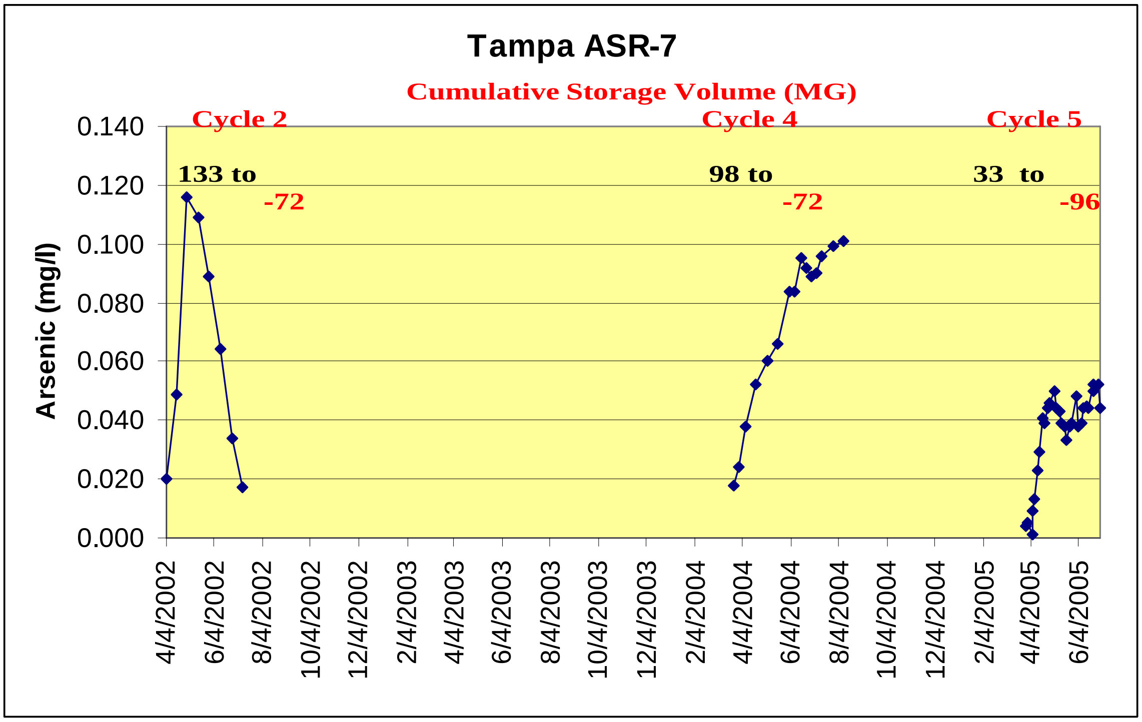


Figure 27 Tampa ASR-7 Cycles 2 – 5 Arsenic

Tampa Well ASR-8

A small but positive cumulative storage volume was maintained in this well throughout the four cycles. During the first cycle only 23 MG was recovered out of a stored water volume of 160 MG (14%). Arsenic concentrations ranged between 20 and 28 µg/l during recovery. Peak concentration climbed to 49 µg/l in the following cycle when 73% of the stored water was recovered. Peak concentrations declined with subsequent successive cycles at approximately the same storage and recovery volumes, probably reflecting slow formation of a small buffer zone around the well. Results are shown in **Figure 28.**

The general improvement of recovered water quality with successive cycles at approximately the same volumes of water stored and recovered is an indication that mixing in the storage zone is creating a small buffer zone around the ASR well. Improvement in recovered water quality may be aided by coalescence of stored water in this well with water stored in adjacent wells, complicating data analysis but further improving water quality. With further cycles at the same storage and recovery volumes, or with early formation of a larger buffer zone, recovered water quality at this well should become acceptable without the need for pretreatment or retreatment. Ultimately a large buffer zone would surround the entire wellfield, reducing the effect of well interference during recovery. Potential for upconing would still remain.

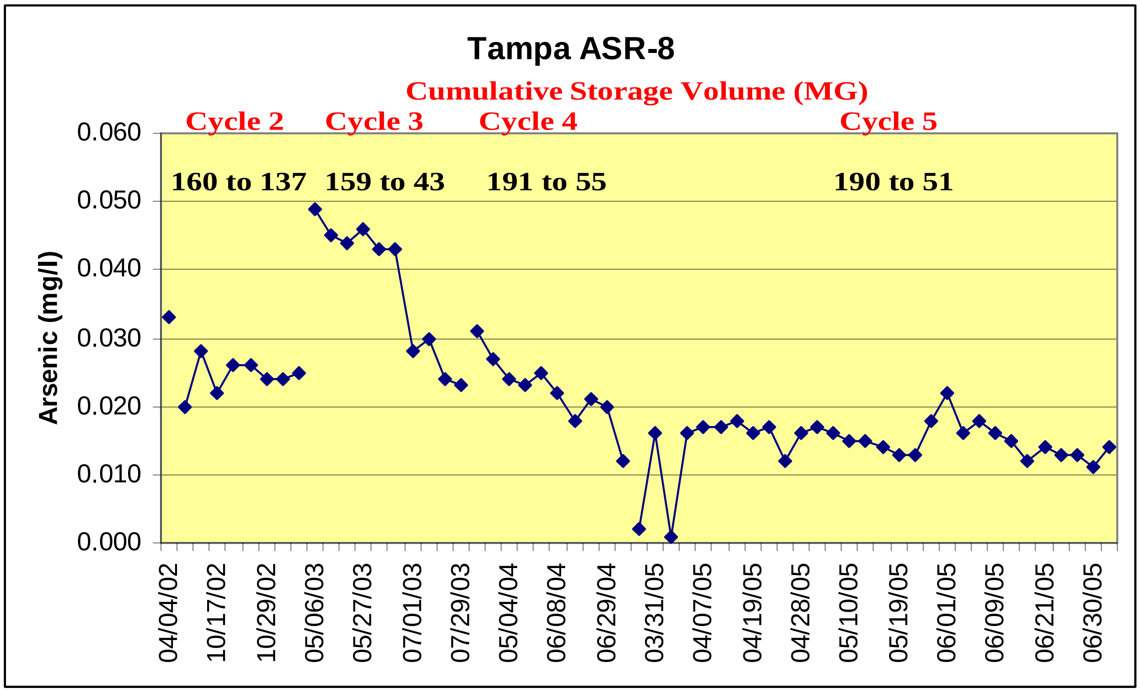


Figure 28 Tampa ASR-8 Cycles 2 – 5 Arsenic

Tampa Storage Zone Monitor Wells

SZMW-1 is located 190 ft from Well ASR-1, the first ASR well in the wellfield that was constructed and started testing in 1997. **Figure 29** shows the variation of ORP during Cycles 2 through 5 at this well while **Figure 30** shows similar data for pH. No pH or ORP trends are clearly evident.

Figures 31 and 32 show the arsenic and TDS data during the same period of time for monitor well SZMW-1. Arsenic generally declined during the recovery period of each cycle, and with successive cycles. Peak arsenic concentration during the analysis period was 37 µg/l. During Cycle 5 recovery in 2005 all but four arsenic concentrations were below 10 µg/l and the highest was 14 µg/l. It is apparent that arsenic has mobilized at this storage zone monitor well location, which is about 190 ft from adjacent ASR-1, and also that recharge peak concentrations generally declined during the last two cycles. Comparison with the data from ASR-1 presented above indicates a similar decline but at somewhat lower concentrations during recovery. No TDS data were obtained at SZMW-1 during recovery periods, only during recharge and storage. Higher values suggest upconing. Ambient TDS in the storage zone varies among the eight wells between 210 and 500 mg/l.

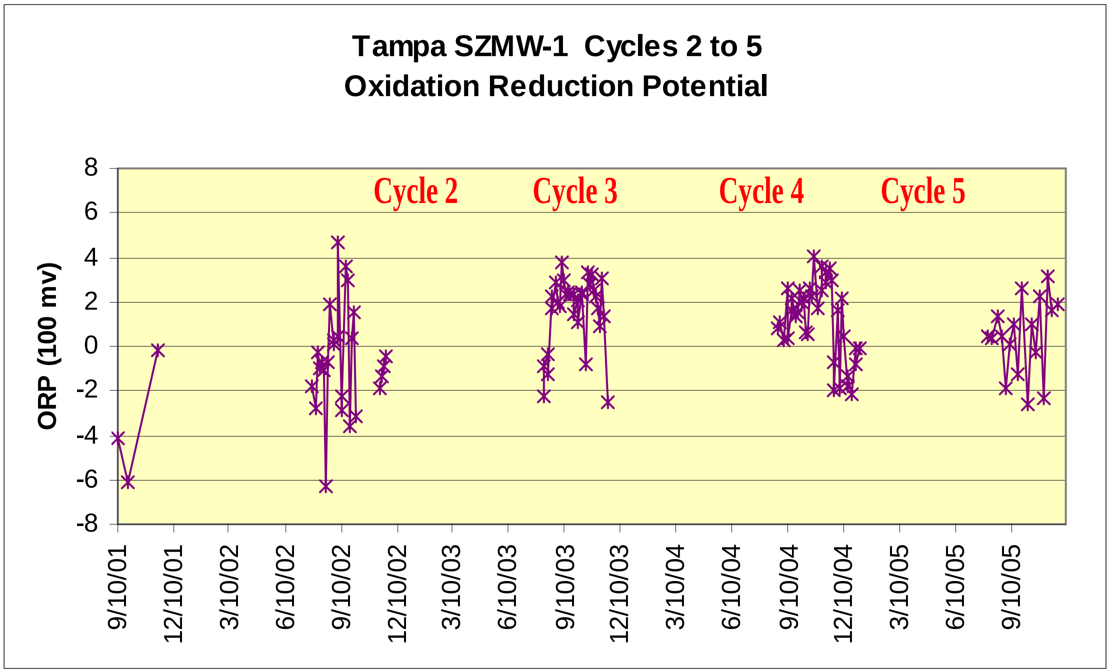


Figure 29 Tampa SZMW-1 Cycles 2 through 5 ORP

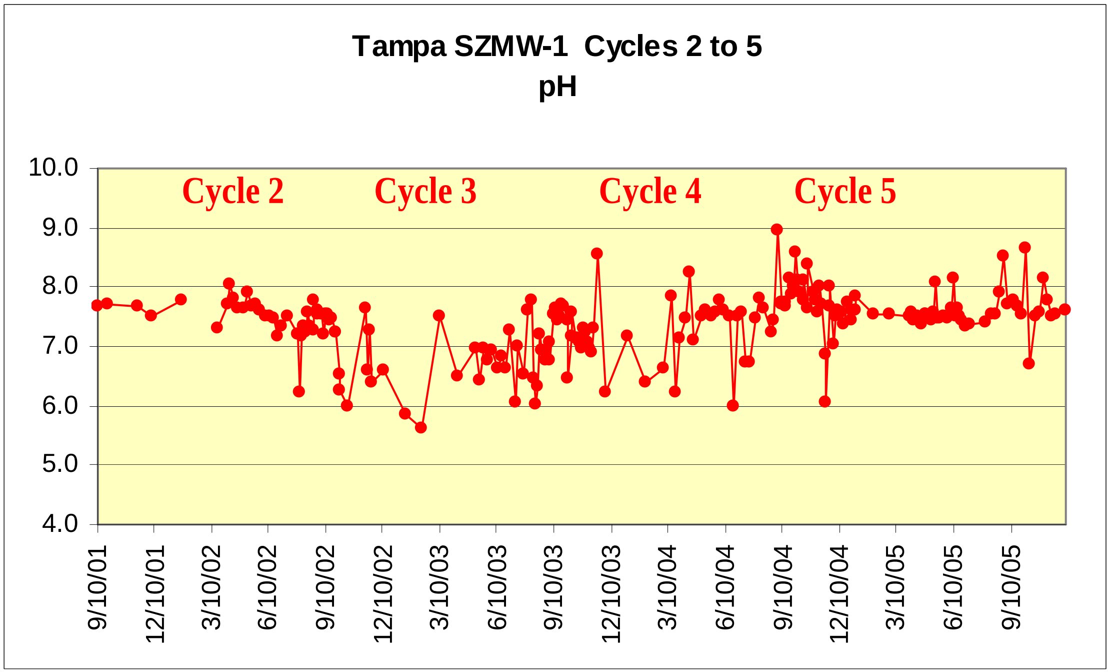


Figure 30 Tampa SZMW-1 Cycles 2 through 5 pH

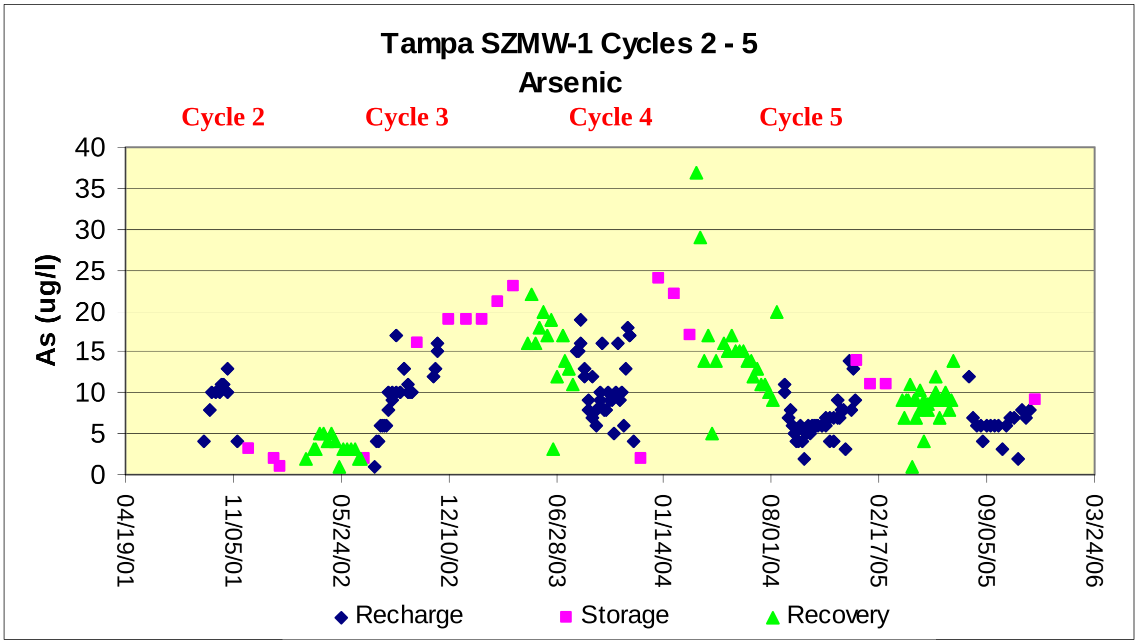


Figure 31 Tampa SZMW-1 Cycles 2 to 5 Arsenic

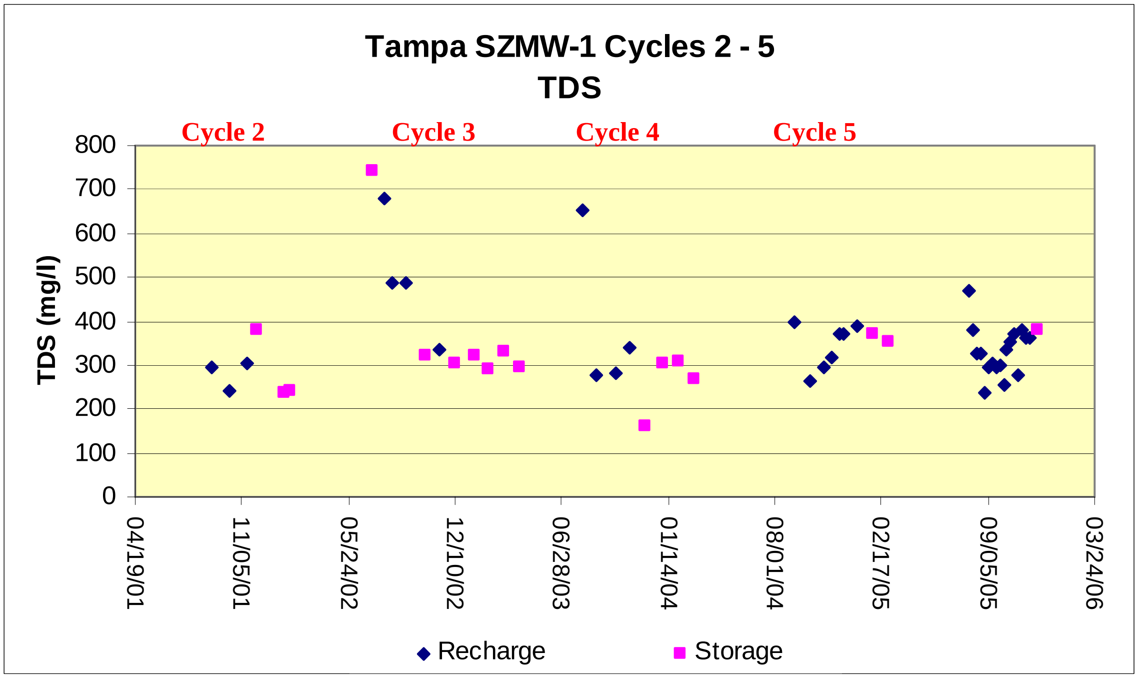


Figure 32 Tampa SZMW-1 Cycles 2 to 5 TDS

Figure 33 shows the absence of any significant relationship between arsenic concentration and pH at the storage zone monitor well. An assumed linear relationship has an R^2 value of only 0.199. The only data pairs available were during recharge at adjacent well ASR-1. No data pairs are available for storage and recovery periods.

Figure 34 shows the absence of any significant relationship between arsenic concentration and ORP at the storage zone monitor well. An assumed linear relationship during recharge has an R^2 value of only 0.003. During storage it is only 0.013 and during recovery it is only 0.005.

No relationship is evident between arsenic concentration and TDS at this wellfield. This is probably due to the upconing occurring at the ASR wells during recovery and also the ambient fresh water in the storage aquifer.

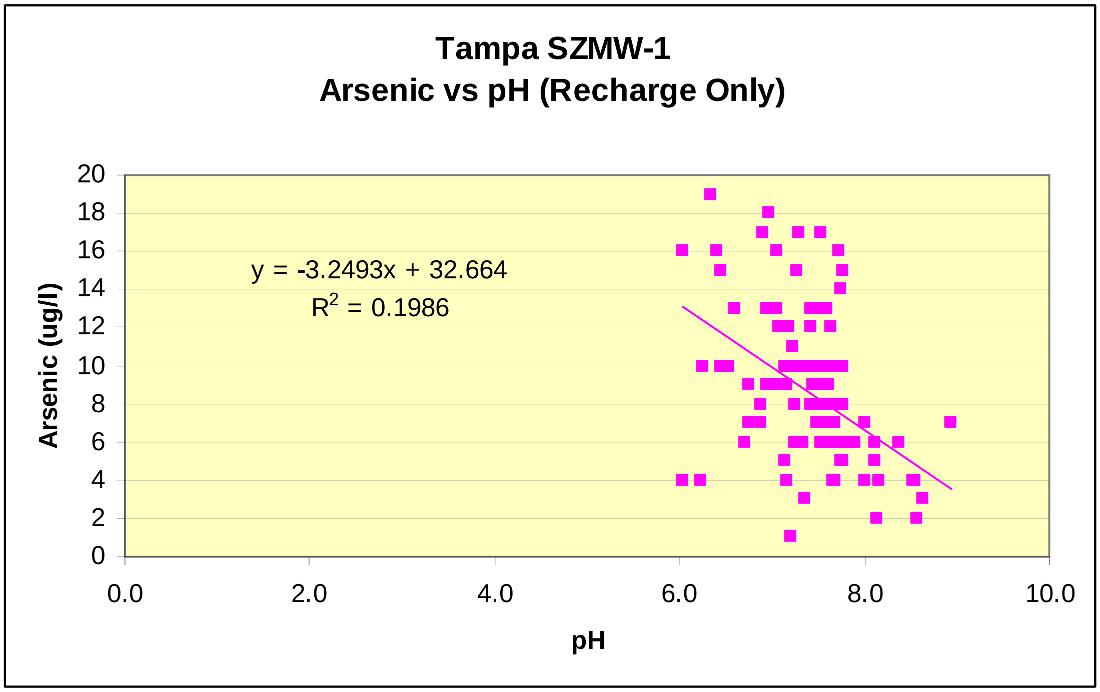


Figure 33 Tampa SZMW-1 Arsenic vs pH

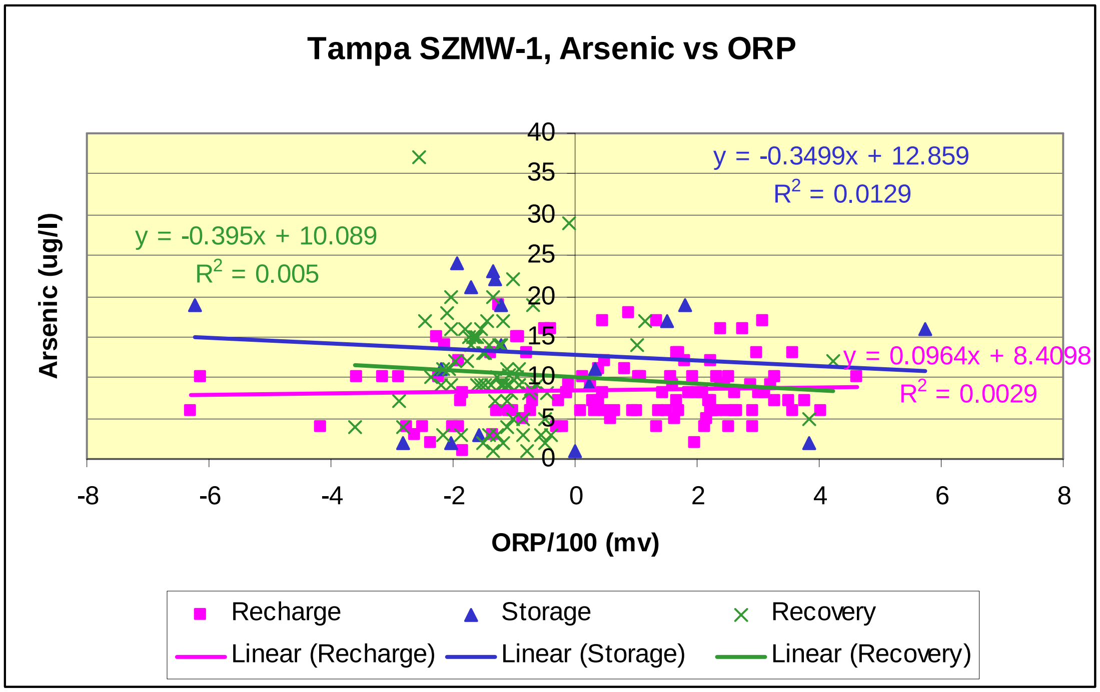


Figure 34 Tampa SZMW-1 Arsenic vs ORP

Wells SZMW-2 and SZMW-3 are located at greater distances from the Rome Avenue wellfield, showing no arsenic impacts. Wells SZMW-4 and SZMW-5 were constructed within the wellfield, close to ASR-4 and ASR-5. At SZMW-4 peak concentrations during recharge declined from 24 to 18 to 7 to 6 µg/l in successive cycles, as shown in **Figure 35**. Arsenic concentrations were acceptable during all four recovery periods. At SZMW-5 the same pattern was observed, with peak recharge concentrations declining from 21 to 12 to 1 to 3 µg/l during the four cycles, and with acceptable concentrations during recovery periods as shown in **Figure 36**.

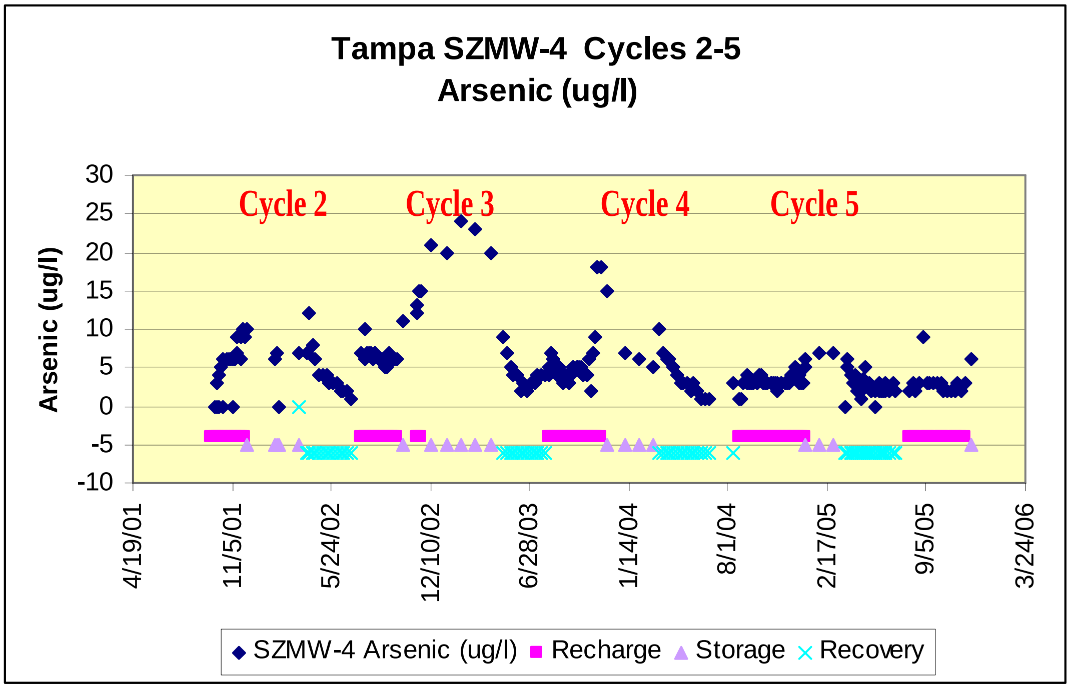


Figure 35 Tampa SZMW-4 Cycles 2 – 5 Arsenic

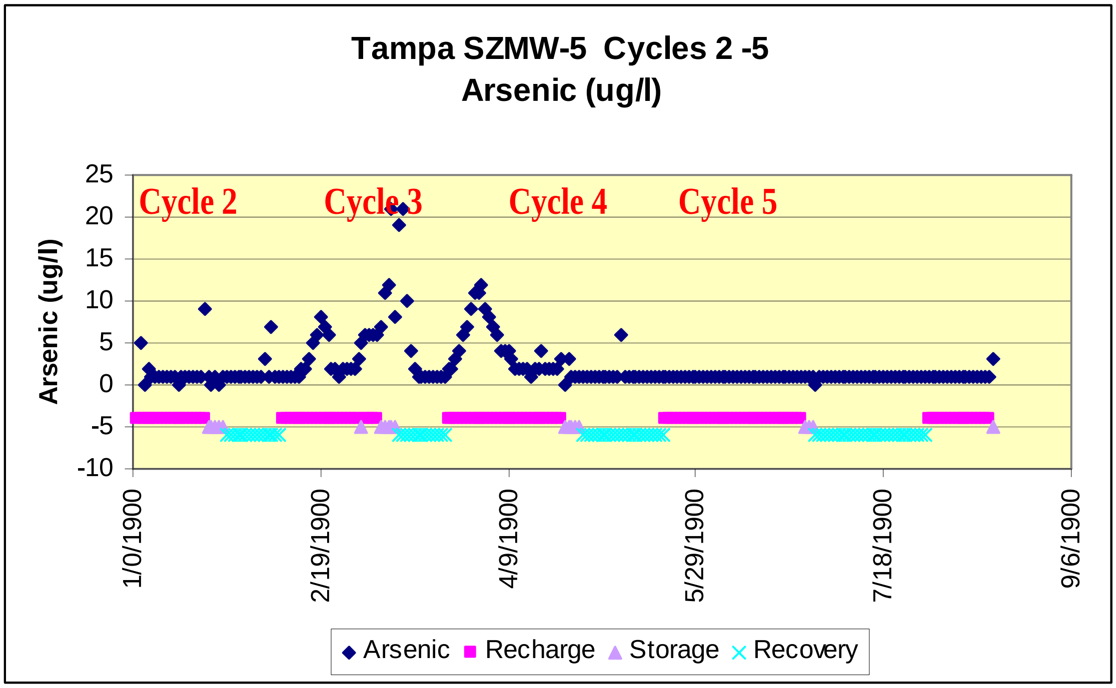


Figure 36 Tampa SZMW-5 Cycles 2 – 5 Arsenic

Figure 37 shows the variability in arsenic concentrations during Cycles 1 through 5 for storage zone monitor wells SZMW-1, SZMW-4 and SZMW-5, shown together. Well SZMW-1 is near well ASR-1; well SZMW-4 is near well ASR-2 and well SZMW-5 is at the southern property boundary, as shown on **Figure 20**. Since 2003, concentrations appear to be generally declining with time, probably as a result of successive operating cycles at about the same volume.

Well SZMW-4 and adjacent well ASR-2 were selected for more detailed consideration of iron concentrations and their potential impact upon arsenic concentrations. Iron concentrations at SZMW-4 during ASR-2 recharge periods from 2001 to 2005 ranged from 60 to 170 µg/l, showing a slight increase during this time. During four successive annual recovery periods total iron concentrations at SZMW-4 steadily increased from an average of 130 µg/l to 540 µg/l. Within each recovery period iron concentrations were variable, generally showing a slight decreasing trend from beginning to end. Arsenic concentrations in SZMW-4 declined from an early peak of 24 µg/l to 3 µg/l as iron concentrations increased with successive cycles.

As shown on **Figure 22**, peak arsenic concentrations at the adjacent well ASR-2 declined from 40 to 10 µg/l during this same period. Total iron concentrations at ASR-2 during recharge periods from 2001 to 2005 ranged from <10 µg/l to 150 µg/l. These are average values for each recharge period. During recovery the iron concentrations were variable, ranging from 220 to 630 µg/l. These are average values for each recovery period.

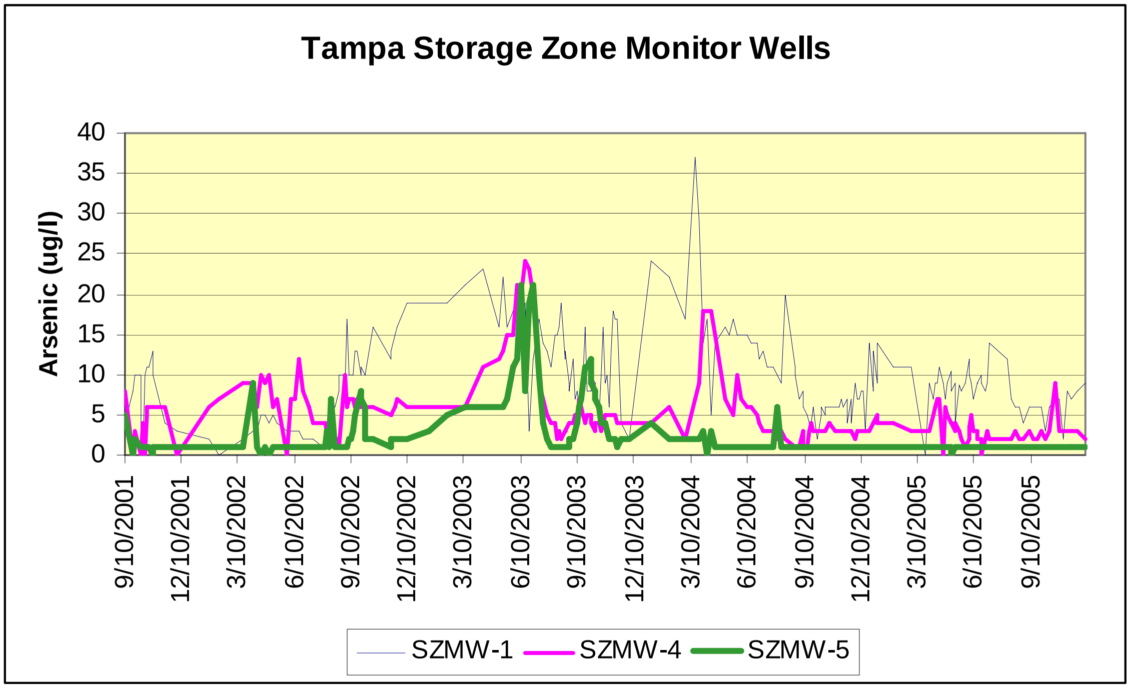


Figure 37 Tampa Storage Zone Monitor Wells, Cycle 5, Arsenic Concentrations

Within each recovery period there was no clear trend of increasing or decreasing iron concentrations from beginning to end. Iron concentrations during recovery are higher than in the recharge water.

Summary Analysis of Tampa ASR Wellfield Results

Analysis of data from this wellfield is complicated by the proximity of the wells to each other and the occurrence of upconing of brackish water during extended recovery from some wells. Nevertheless certain observations are possible.

Wells ASR-2 and ASR-8 maintained generally positive but small cumulative storage volumes during the period of analysis, ranging from -23 to +191 MG. Arsenic concentrations in these wells declined to peak concentrations of 11 and 22 μg/l, respectively, during the fifth cycle. Further cycles at approximately the same storage and recovery volumes can reasonably be expected to further reduce arsenic concentrations, possibly to acceptable levels, so that pretreatment or retreatment is not required for these wells. Alternatively a larger buffer zone could be provided in each of these wells. This may expedite achievement of acceptable arsenic concentrations in the recovered water.

Wells ASR-1 and ASR-5 maintained generally negative cumulative storage volumes, ranging from +74 to -281 MG respectively at the end of Cycle 5. Peak arsenic concentrations during Cycle 5 were 20 and 48 μg/l, respectively. However ASR-1 has been in operation for a much longer period than the remaining wells, with several more operating cycles completed since 1996. Consequently to the extent that cyclic operation of the ASR well contributes toward purging arsenic from the aquifer, independent of buffer zone formation, arsenic concentrations would tend to be reduced for this well compared to other wells completed more recently. Had ASR-1 begun testing at the same time as ASR-5 and experienced the same recharge and recovery cumulative volumes in 2002 through 2005, it is likely that higher arsenic concentrations would have been observed in this well.

Wells ASR-3, ASR-4, ASR-6 and ASR-7 had intermediate levels of cumulative storage volume, alternating between positive and negative values and never forming an effective buffer zone. Arsenic concentrations generally declined with successive cycles however peak values were 34, 37, 25 and 52 μg/l, respectively. These are generally intermediate levels of arsenic concentration compared to wells with consistently positive or consistently negative cumulative storage volumes.

Storage zone monitor wells located approximately 150 to 190 feet from the adjacent ASR wells experienced an initial increase in arsenic concentrations, however this generally declined close to or within acceptable levels during the first four cycles. Higher arsenic concentrations were noted during recharge and storage periods while most samples during recovery periods had acceptable arsenic concentrations. No significant correlation was found between arsenic concentration and either pH or ORP.

Cycle 5 extended from August 19, 2004, to July 2005. Recovery occurred from the end of March to near the end of June 2005. **Figure 38** shows the cumulative storage volume during Cycle 5 recovery for each of the eight wells, and the associated arsenic concentrations. For each data pair, arsenic concentration was selected for the closest water quality sample to the end of the month when the cumulative storage volume was recorded. Most arsenic samples were collected within two to three days of the end of the month. During this recovery period the cumulative volume stored in the Rome Avenue ASR wellfield declined from 1,021 MG to 83 MG. Some wells had more water stored at the beginning of the recovery period than other wells. It is apparent that, for each well, as the cumulative storage volume decreases, the arsenic concentration in the recovered water tends to increase. When comparing one well to another, as the initial storage volume decreases the peak arsenic concentration during recovery increases. Conversely, this implies that increasing the initial storage volume would decrease recovered water arsenic concentrations at the Tampa ASR wellfield. A linear regression equation is shown on the figure, with an R^2 value of 0.75. This is a significant relationship, suggesting that on average for the Tampa wellfield, providing a buffer zone of 94 million gallons in storage at each well, or a total of 751 MG, would ensure that recovered water quality would not exceed an arsenic concentration of 10 µg/l. This could be achieved at one time, by storing at least this volume of water and leaving it underground at the end of recovery, or it could be accomplished over a period of several years, during each of which the same volume stored would be recovered. However due to mixing in the aquifer a buffer zone will be eventually formed anyway.

The relationship shown in **Figure 38** is more likely to be a log-normal distribution, reflecting the exponential nature of most of the physical, geochemical and microbial processes believed to be occurring around the ASR wells. Hydraulic gradient declines exponentially with increasing distance from the well, affecting velocity through the flow paths in the aquifer and also affecting the number of pore volume flushes at different distances from the well. Geochemical gradients are also maximized near the well, driven by declines in oxidation reduction potential as recharge water mixes with ambient groundwater and minerals in the aquifer. The associated surface reactions (sorption, desorption) should be logarithmic. A linear relationship would not fit the model very well. Microbial activity would also be exponential rather than linear. Complete understanding of these processes is lacking. Accordingly, a least-squares linear fit to the data is provided, as follows:

$Y = 23.042-0.139X$

Where Y = arsenic concentration (µg/l)
X = cumulative storage volume (million gallons)

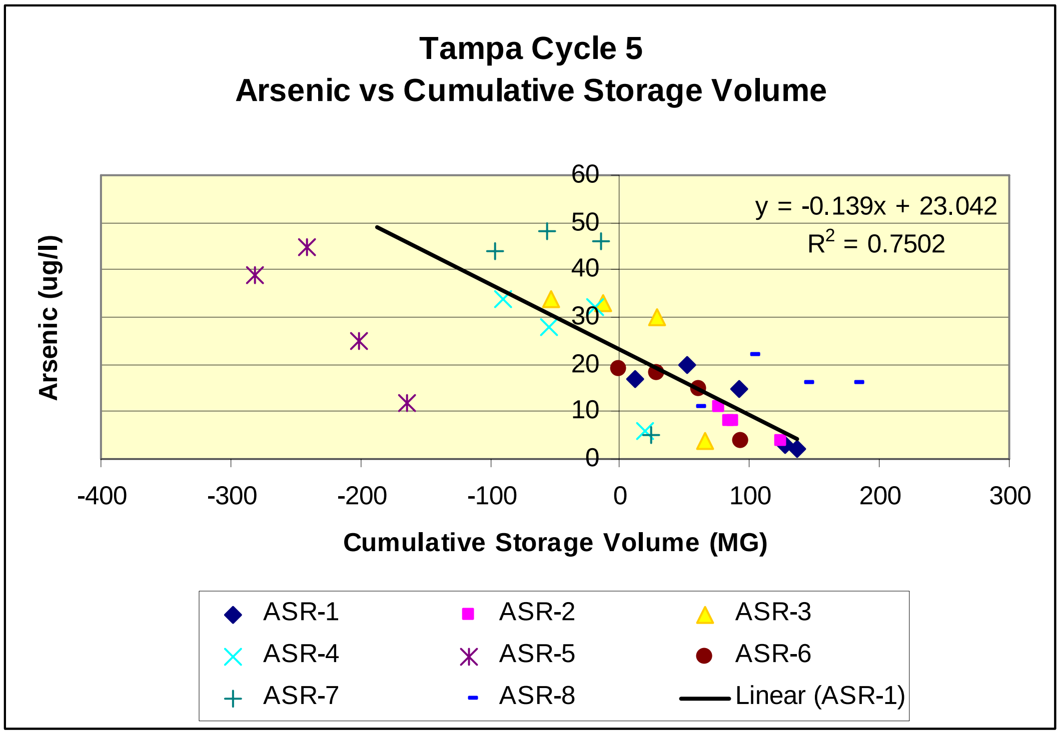


Figure 38 Tampa ASR Wells, Cycle 5, Arsenic Concentration vs. Cumulative Storage Volume

With a nominal wellfield production capacity of 10 MGD, the suggested buffer zone volume equates to 75 MG/ MGD of recovery capacity, or 110 days. This may be added to the design recovery duration of 90 days for the Tampa ASR wellfield, yielding a Target Storage Volume of 165 days. This is within the range of normal Florida experience for Target Storage Volume (TSV) requirements at ASR wells, which is between 50 to 350 days.

Typically the TSV would be formed prior to starting cycle testing, storing available water during wet times of the year when supplies are plentiful and water demand is low. At such times the marginal cost of water production is relatively low, comprising just power, chemicals and residuals disposal. Typical marginal costs for water production during such periods are in the range of $0.10 to $0.50/kgal. Alternatively the TSV can be formed over a period of several years, during each of which approximately the same volume stored is recovered. However in each year a small portion of the stored water remains underground, mixing with the surrounding ambient groundwater and very slowly forming a buffer zone around the well. Whichever approach is selected, the end result is probably the same in terms of arsenic attenuation. However initial formation of the TSV is usually a much more rapid and cost-effective solution to the challenge of arsenic mobilization and attenuation.

Well ASR-3 was selected from **Figure 38** as being representative of a "middle of the range" well in terms of long term cumulative storage volume during Cycle 5. To a greater extent than any of the other wells, the cumulative storage volume for this well remained fairly steady during the four cycles, providing an opportunity to evaluate arsenic attenuation with time (or with successive, approximately equal volume cycles), and with little change in cumulative storage volume from one cycle to the next. For this well the analysis was performed using data from all four cycles (2002 to 2005) to determine whether arsenic concentrations were declining with successive operating cycles, independent of the cumulative stored water volume. **Figure 39** shows the results. It is the same as **Figure 23** but with a trend line added. The R^2 value for the linear trend line is 0.34. Average arsenic concentration in each cycle declined from 80 µg/l in Cycle 2 to 20 µg/l in Cycle 5, or about 27 µg/l per cycle.

Additional analyses were conducted for selected constituents of interest in order to gain an improved understanding of arsenic mobilization and attenuation. These included sulfate, hydrogen sulfide, iron and ORP.

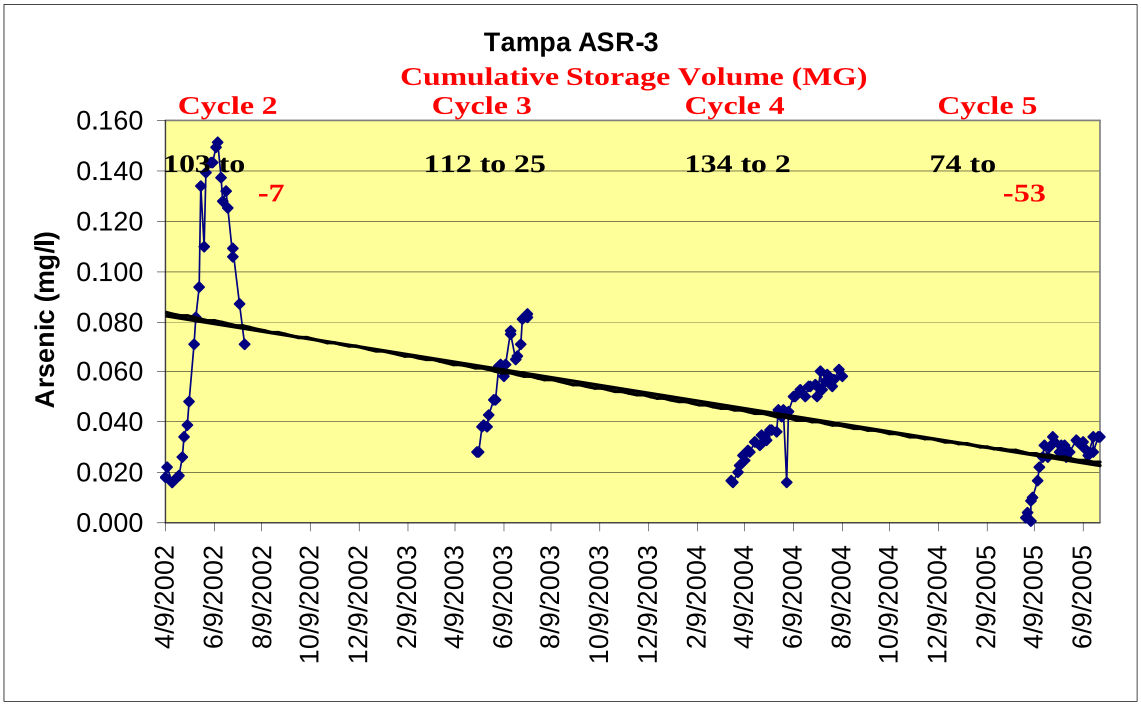


Figure 39 Tampa ASR-3, Arsenic Attenuation With Successive Cycles At Approximately The Same Volume Stored and Recovered During Each Cycle

Sulfate

Minor variability in sulfate concentrations occurs at all eight wells, but no trends are apparent with successive cycles at each well or with increasing recovery duration in each cycle. At ASR-1 sulfate concentrations declined slightly during each cycle, from typical values of 74 to 136 mg/l at the beginning of recovery to 64 to 98 mg/l at the end of recovery. For all other wells sulfate concentrations vary generally from about 50 to 250 mg/l, showing no apparent pattern. Wells 7 and 8 have relatively higher, and possibly increasing sulfate concentrations with time. These differences complicate analysis of sulfate concentrations caused by pyrite dissolution. However background sulfate concentration in the aquifer is in the range of 3 to 36 mg/l while in the recharge water it is about 50 mg/l, so the measured sulfate concentrations suggest pyrite oxidation and the associated release of sulfate.

The increasing TDS concentration during recovery for this wellfield is due to increasing chloride concentrations, not due to increasing sulfate concentrations. This suggests that upconing may be from an underlying aquifer (Avon Park formation) experiencing lateral salt water intrusion rather than vertical movement from deeper formations.

Hydrogen Sulfide

Analysis of the Tampa data set is complicated by several factors, as discussed previously. Among these is the known upconing of brackish water during recovery. Although no data was obtained regarding hydrogen sulfide concentrations during recovery, anecdotal field observations apparently have noted a hydrogen sulfide odor in the blended water from all wells during ASR recovery. This is probably unique among ASR wellfields in the United States, about half of which have ambient concentrations of hydrogen sulfide. This usually disappears after one or at most two operating cycles. If documented through future sampling and analysis it would suggest that recovery occurs from deeper portions of the storage zone that perhaps receive little or no water during ASR recharge periods, which appears unlikely. Alternatively it may be due to pyrite oxidation processes occurring at this site. Sulfate and sulfide comprise one of the oxidation-reduction couples that affect arsenic speciation, mobilization and attenuation so the continuing occurrence of hydrogen sulfide in the recovered water may be related to arsenic concentrations at this site. Whatever the cause of the continuing presence of hydrogen sulfide in the recovered water, this site is not typical of ASR wellfields. Conclusions regarding arsenic mobilization and attenuation based upon the Tampa data set therefore need to be considered with caution.

Iron

Data is only available for total iron, not dissolved iron concentrations. Recharge water total iron concentration typically ranges from 0.01 to 0.07 mg/l. Ambient groundwater background concentrations range from <0.05 to 0.085 mg/l at the eight wells. Recovered water total iron concentrations showed no particular pattern during each cycle at each well, ranging from 0.02 to about 0.70 mg/l, averaging about 0.24 mg/l. The source of the elevated iron concentrations is most likely from the oxidation of pyrite, which releases both iron and arsenic.

Oxidation Reduction Potential (ORP)

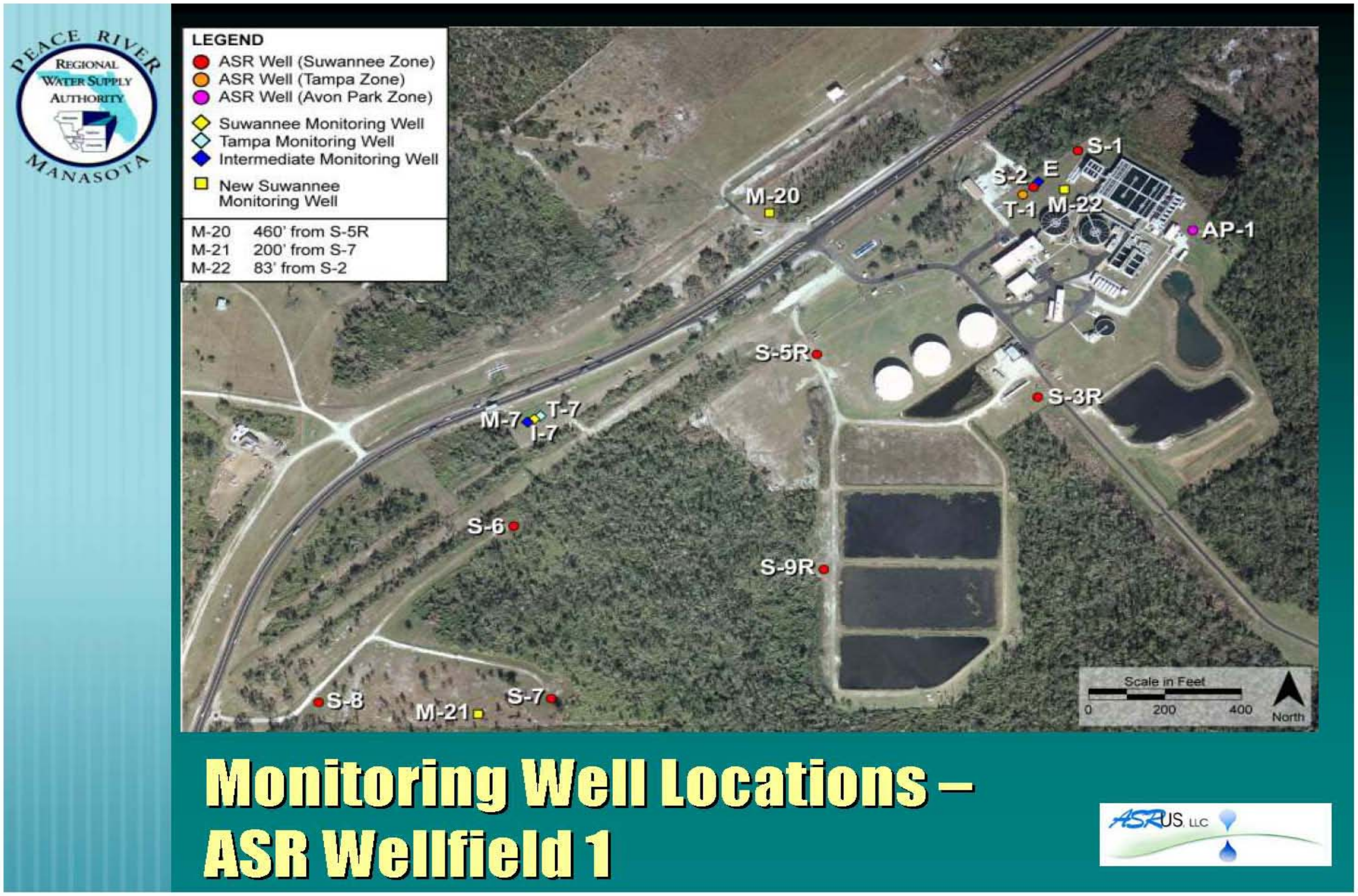
ORP was generally negative and generally declined during the recovery period for each cycle at each well. Well ASR-2 is reasonably representative, with ORP concentrations declining from -45 to -198 mv at the beginning and end of recovery in 2002; -109 to -123 mv in 2003; -118 to -245 mv in 2004; and -60 to -212 mv in 2005. No trends are evident regarding changing ORP values in successive cycles at each well.

4.0 Peace River/Manasota Regional Water Supply Authority

The Peace River ASR site stores drinking water in two confined limestone artesian aquifers, each of which contains groundwater with TDS concentrations between about 700 and 1100 mg/l. The two storage zones are the Tampa formation at approximately 400 to 500 ft deep and the Suwannee formation at approximately 600 to 900 ft deep, both within the upper Floridan aquifer. Combining both wellfields there are twenty one operational ASR wells, of which 20 are in the Suwannee formation and one in the Tampa formation. Three Suwannee wells in Wellfield One are currently out of service due to arsenic concentrations slightly above 10 µg/l. In addition, there are several monitor wells in the Tampa and Suwannee formations throughout the wellfield, and also one ASR test well in the underlying Avon Park formation at an approximate depth of 1100 to 1300 feet which has never been placed into operation beyond limited cycle testing in the middle 1990's, primarily due to insufficient water to complete the test program for this high capacity well.

ASR facilities have been operational since 1985 and have been expanded in four phases to their current combined recovery capacity of about 17 MGD. The first three phases of construction, including nine operational ASR wells, are all at one site, Wellfield One, while the fourth phase is located at a second site, Wellfield Two, about a mile away to the northwest and includes 12 ASR wells. For purposes of this analysis, the ASR wellfields are considered separately since the first three phases (Wellfield One, or "old wellfield") have been in operation since 1984, 1987 and 1995, respectively, while the fourth phase (Wellfield Two, or "new wellfield") was only constructed in 2002. Typical recovery yields range from 0.4 to 1.3 MGD per well. **Figures 40 and 41** show locations of wells in each of these wellfields.

Spacing of wells in Wellfield 1 varies between about 600 and 1000 feet while in Wellfield 2 the well spacing is about 300 feet. Well spacing is pertinent since it affects the stored water volume and time required so that the stored water bubbles around each well in the wellfield coalesce, thereby tending to smooth out variations in recovered water quality. Larger spacing reduces hydraulic interference between wells, thereby reducing changes in water levels and pressures during recharge and recovery. However larger spacing requires greater time and storage volume in order to achieve coalescence of the stored water bubbles around each of the wells, thereby moderating changes in recovered water quality.



LEGEND
- ● ASR Well (Suwannee Zone)
- ● ASR Well (Tampa Zone)
- ● ASR Well (Avon Park Zone)
- ◆ Suwannee Monitoring Well
- ◇ Tampa Monitoring Well
- ◆ Intermediate Monitoring Well
- ☐ New Suwannee Monitoring Well

M-20	460' from S-5R
M-21	200' from S-7
M-22	83' from S-2

Monitoring Well Locations – ASR Wellfield 1

Figure 40 Peace River Wellfield 1 - Old Wellfield (courtesy of Mark McNeal/ASRus)

Aquifer hydraulic characteristics have been estimated for each storage interval, based upon several aquifer performance tests and subsequent estimates prepared to support groundwater modeling, as presented in documents supporting the Authority's Water Use Permit application:

			Wellfield 1	Wellfield 2
Suwannee formation:	Transmissivity, gpd/ft	-	37,400	44,900
	Storativity	-	1×10^{-4}	$3.1\text{x}10^{-4}$
	Leakance, /day			
	Above	-	1.1×10^{-4}	
	Below	-	5×10^{-3}	
	Thickness, ft	-	320	
Tampa formation:	Transmissivity, gpd/ft	-	36,700	no wells
	Storativity	-	4.2×10^{-5}	
	Leakance, /day			
	Above	-	1.34×10^{-5}	
	Below	-	1.1×10^{-4}	
	Thickness, ft	-	240	

Baseline ambient water quality characteristics for each interval were determined during initial testing and development for each of these wells, prior to ASR recharge. Water quality in the two aquifers is similar. Some typical constituent values, based primarily upon February 2001 data from Wellfield 2, are as follows:

TDS - 700 to 1070 mg/l
Sulfate - 226 to 412 mg/l
Chloride - 161 to 328 mg/l
pH - 7.3 to 8.1
Iron - Below Detection Limit to 35 μg/l
Arsenic - Below Detection Limit

Background arsenic was also below the detection limit of 1 μg/l in seven monitor wells.

ASR cycle testing has been limited by the availability of water for recharge and by the regulatory requirement to recover most of the stored water, thereby inhibiting the ability to build a buffer zone.

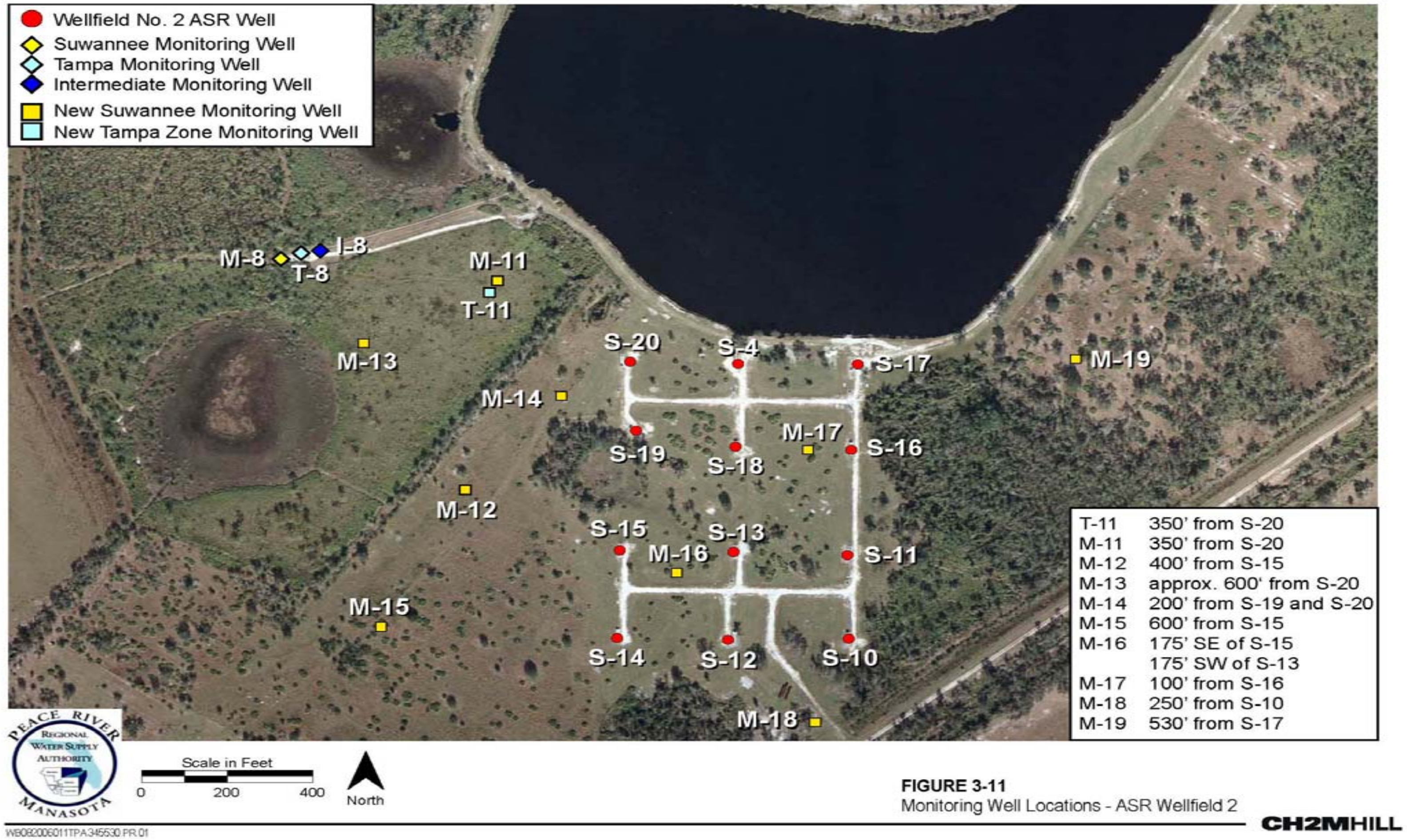


Figure 41 Peace River Wellfield 2, New Wellfield (courtesy of CH2M HILL)

4.1 Peace River - Old Wellfield (Wellfield One)

The “old” wellfield began operations in 1985 and includes eight wells in the Suwannee formation and one well in the Tampa formation, a total of nine operating wells. Data from two cycles, Spring 2004 and Spring 2006, were analyzed for arsenic mobilization and attenuation during recovery. Negligible recovery occurred from this wellfield in Spring 2005. It is helpful to understand the operational history of this wellfield so that arsenic concentrations can be better understood. This is shown on **Figure 42.**

A goal for this wellfield prior to about 1997 was to achieve a Target Storage Volume (TSV) of 2.6 billion gallons (BG), of which 1.3 BG would have been the buffer zone and 1.3 BG would have been available for recovery. Estimated TSV for this wellfield was 350 days, reflecting the very large storage volume required in order to ensure a reliable water supply during an extended drought on the Peace River, duration of which might be as long as about six months. However, a significant portion of the water stored since 1985 was recovered during 1996 and 1997, initially as a stress test for the ASR wellfield (1996) and then to help meet demands during a severe drought (1997). With steadily increasing demands and limited water treatment capacity, the opportunity for recharge declined while the need for recovery increased. In December 1999 cumulative storage volume reached a maximum volume of 2.4 BG. All but 500 MG of the stored water was then recovered by Spring 2002. Recharge then began again. Total cumulative storage volume reached 2.3 BG by February 2006, declining to 1.8 BG by July 2006 at the end of an extended recovery period.

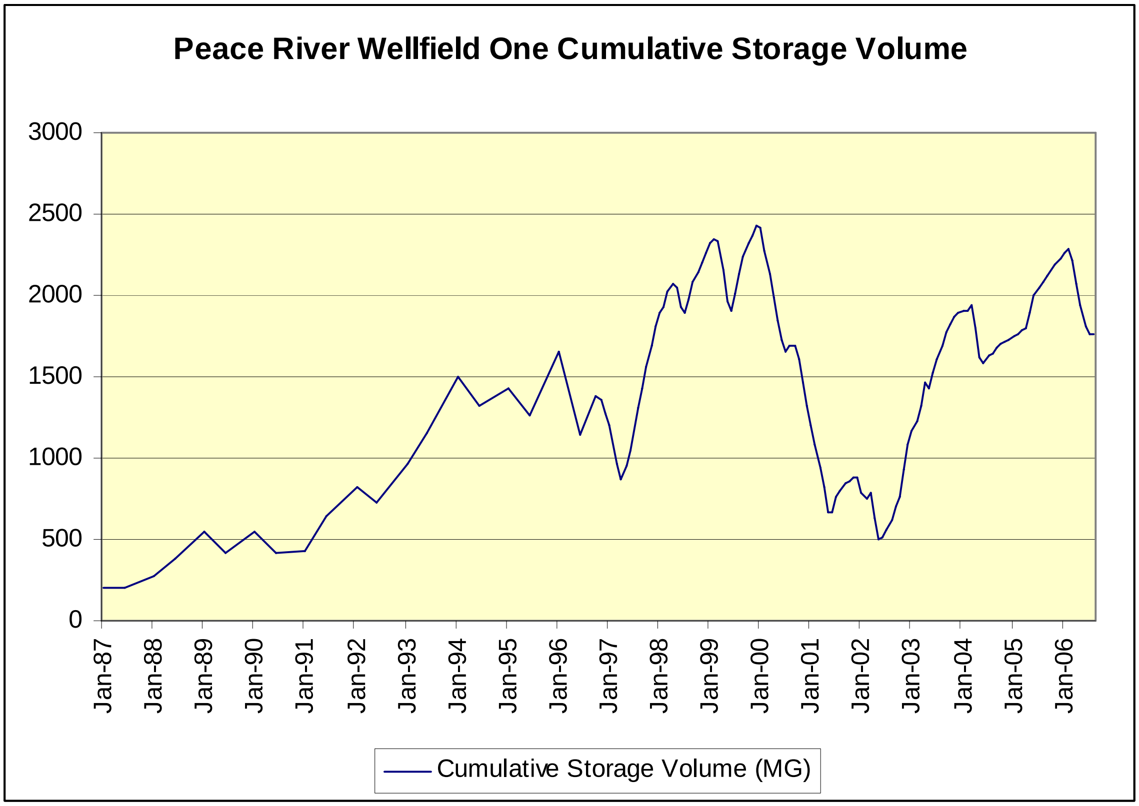


Figure 42 Peace River Wellfield One Cumulative Storage Volume

None of the original ASR wells in Wellfield One experienced any elevated arsenic values above 10 µg/l during the 2004 or 2006 recovery periods except for a single value of 13 µg/l at Well S-6. The next highest value at this well was 4 µg/l and the two values immediately prior to and immediately following this peak value were 1 µg/l. Peak arsenic values for these wells in 2006 ranged from 4 to 9 µg/l. Three of the wells (S-3R, S-5R and S-9R) were modified during 1998 to seal off high production intervals near the base of the Suwannee formation. Two of these three wells have experienced elevated arsenic concentrations, probably associated with relatively low cumulative storage volumes.

Table 3 shows the peak arsenic concentrations during the 2004 and 2006 Spring recovery periods and the associated cumulative storage volumes for each of these wells at the beginning of each recovery period. Peak flow rates were determined for each of the wells during the period of record. The estimated baseline TSV of 350 MG per MGD of recovery capacity for this wellfield (ie: 350 days) was utilized in conjunction with the peak flow rates in order to estimate the TSV for each well. Also shown are the cumulative storage volumes for each well as a percentage of the TSV.

For Peace River, TDS values at the end of Cycle 4 recovery for the original wells during July 2006 ranged from 464 to 676 mg/l, except for Well S-8, which recorded 844 mg/l. Well S-8 has always been unique since it penetrates a cavern that is 80 ft from top to bottom and has always had poor ASR recovery efficiency characteristics.

Table 3
Peace River Old Wellfield - Peak Arsenic Concentrations vs. % Target Storage Volume

Well	Peak Recovery Rate (MGD)	TSV (MG)	2004 Cum. Vol Mar-04 (MG)	2004 % TSV	2004 Peak As Conc. (µg/l)	2006 Cum. Vol Mar-06 (MG)	2006 % TSV	2006 Peak As Conc. (µg/l)
S-1	0.36	126	309	245	2	387	307	7
S-2	1.06	371	335	90	7	383	103	9
S-6	0.74	259	299	115	13 **	369	142	4
S-7	0.89	312	158	51	8	210	67	5
S-8	1.01	354	168	48	3	224	63	7
T-1	0.69	242	242	100	2	305	126	4
S3R *	0.59	207	93	45	19	94	46	*
S5R	0.92	322	95	30	7	123	38	12
S9R *	0.94	329	236	72	41	195	59	*
Total	**7.2**	**2520**	**1935**	**77**		**2290**	**91**	

* shut down due to elevated arsenic concentrations in recovered water

** values prior to and immediately following this were 1 ug/l

It has recently been used more as a production well, blending more brackish water with fresher water from other ASR wells. This range (464 to 676 mg/l, averaging 531 mg/l) may be compared with TDS concentrations recorded for the new wellfield, one mile away, which were 548 to 1,360 mg/l, averaging 893 mg/l.

The primary difference between the two wellfields is the well spacing, which varies but is typically 600 to 1000 feet in the old wellfield and is 300 feet in the new wellfield. Interference between the wells of the new wellfield may be creating greater drawdowns and therefore increased potential for upconing from the underlying Avon Park formation during extended recovery periods. Storing water in one or two ASR wells in the Avon Park formation beneath the new wellfield would probably help to manage this operational issue so that upconing would occur with fresh water, not brackish water. Yield of individual Avon Park wells is estimated at 3 to 5 MGD and they could be constructed as part of the next ASR wellfield expansion. This is pertinent to solution of current arsenic issues since it is hypothesized that variable salinity may inhibit subsurface microbial activity close to the ASR wells, affecting natural processes that alter the pH of the aquifer matrix in the proximal zone, very close to the well, and thereby potentially affecting the speciation and mobilization of arsenic.

Three wells in the old wellfield, S-3R, S-5R and S-9R, have been modified to plug back these wells so that they no longer penetrate to the bottom of the Suwannee formation. These modifications were performed in 1998. During cycle testing performed in 2004 and 2005, peak arsenic concentrations in these wells were 19, 12 and 41 ug/l, respectively. Cumulative storage volumes during recovery declined from 86 to 75 MG for Well S-3R, 72 to 37 MG for Well S-5R, and 212 to 176 MG for Well S-9R. Wells S-3R and S-9R were removed from service in April 2005 due to their elevated arsenic concentrations. It appears that a small increase in buffer zone volume for Well S-3R would probably enable this well to re-enter service. Well S-9R has a larger buffer zone already, and also a relatively high arsenic concentration, so this well may require more effort and time to restore its operational viability.

4.2 Peace River - New Wellfield

Wellfield 2, the "new" wellfield, began operations in June 2002 and includes 12 wells in the Suwannee formation. These are numbered S-10 through S-20 plus S-4, which was constructed about 1985. Five ASR cycles have been conducted to date. The first was a baseline cycle in July 2002 with one week recharge followed by one week recovery. The last four were annual cycles with recovery durations of 67, 63, 45 and 95 days. These are referred to as Cycles 1 through 4. Cumulative storage volumes for each of the wells, and for the entire wellfield are shown on **Figure 43**. Peak arsenic concentrations for each well through the end of the 2006 Spring recovery period are shown on **Figures 44, 45 and 46**, along with tables showing the associated cumulative storage volumes. Volumes are reported at the end of each month whereas recharge and recovery periods, and associated approximately twice-weekly water quality samples, were scheduled at other times. So it was necessary to estimate cumulative volumes through interpolation, assuming steady flow rate for each well. A more-detailed analysis for each of these new wells follows.

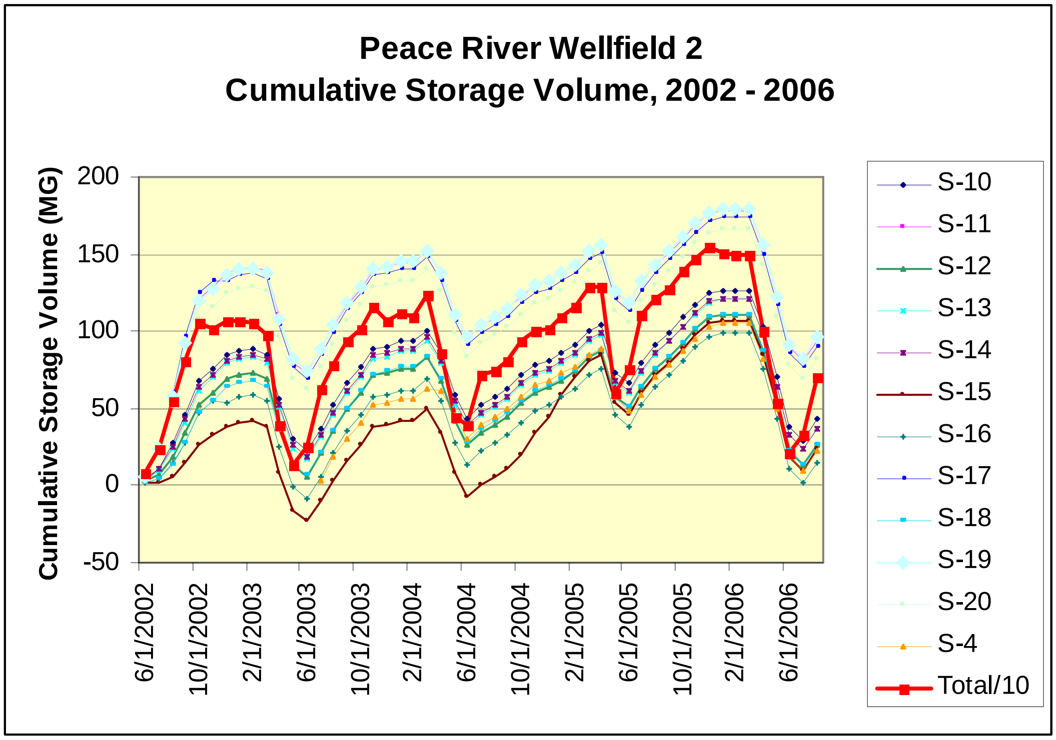


Figure 43 Peace River Wellfield 2 Cumulative Storage Volumes

Data are available for all constituents shown on Table 2. ORP data for the new wells are available since May 2005, beginning midway during Cycle 3 recovery.

Well S-10

For the first three cycles, approximately equal volumes were stored and recovered during each cycle, with a slight increase in cumulative storage volume to help build a small portion of the buffer zone required for proper operation of this ASR well. During the fourth cycle the same volume was stored but a larger volume was recovered, reflecting drier than normal conditions during Spring 2006. As a result the small buffer zone that had been formed was then mostly recovered, resulting in elevated arsenic concentrations. Arsenic concentrations are shown on **Figure 44**. These are related to TDS and cumulative storage volume as follows:

Well S-10			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	11 to 89	540 to 828	0
1	5 to 96 to 89	280 to 744	85 to 30
2	15 to 81	420 to 656	100 to 44
3	2 to 61	320 to 584	104 to 66
4	9 to 162 to 61	324 to 788	127 to 30

To aid with understanding of this table, and the subsequent similar tables, the following explanation is offered. During Cycle 2 recovery arsenic concentrations started at 5 µg/l, increased to 96 µg/l and then declined to 89 µg/l. TDS concentrations increased steadily from 280 to 744 mg/l while the cumulative storage volume declined from 85 MG to 30 MG, indicating recovery of 55 MG.

It is pertinent to note the steady improvement in the TDS concentration of the recovered water at the end of the first three cycles, reflecting progressive development of the buffer zone from one cycle to the next. Based upon prior work at the Peace River site, the TSV has been estimated at 350 MG/ MGD of recovery capacity, or 350 days. This estimate was developed based upon consideration of TDS values, not arsenic values, and reflects the long durations when the source of supply may not be available for diversion during extreme droughts. Well S-10 averaged about 0.9 MGD recovery rate during the four recovery cycles, so the TSV for this well would be 315 MG (350 days x 0.9 MGD). The cumulative storage volume achieved at the beginning of Cycle 4 was 127 MG, or 40% of the TSV for this well.

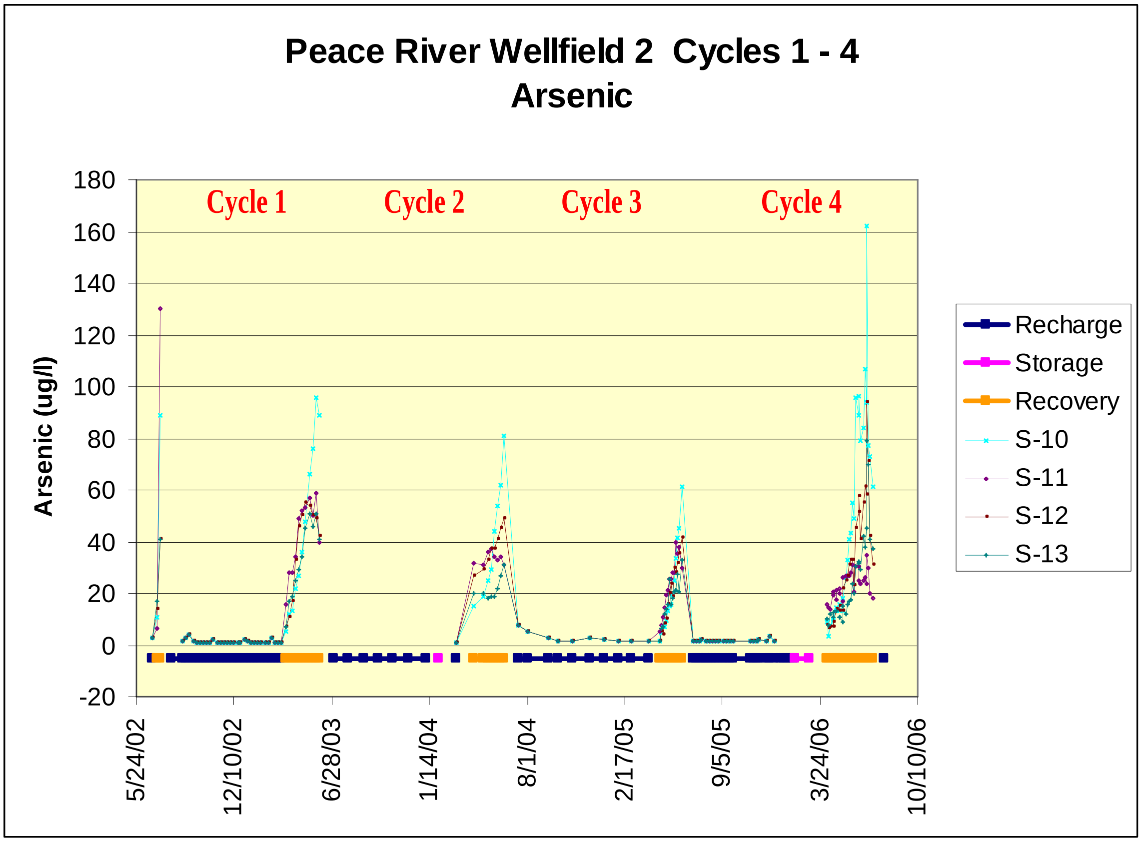


Figure 44 Peace River Wellfield 2 Arsenic at Wells S-10 to S-13

Arsenic concentrations for this well are quite high, but declined during the first three cycles. Review of the Cycle 4 data indicates that acceptable arsenic concentrations were maintained for two weeks after the beginning of the 95 day recovery period. This was approximately the same duration as in Cycle 3 but longer than for Cycles 1 and 2.

With continued formation and maintenance of the buffer zone, the duration of arsenic and TDS recovery at acceptable concentrations should increase so long as the buffer zone is not recovered. If the buffer zone is recovered, high arsenic and TDS concentrations may reasonably be expected. As indicated previously, the buffer zone comprises about half of the TSV. If the stored water volume is at only 40% of the TSV and approximately half of this comprises the buffer zone, then the volume that should be recoverable with acceptable TDS concentration should be about 64 MG. Acceptable TDS concentration at Peace River is about 700 mg/l, based upon prior investigations at this site and FDEP regulatory criteria for secondary drinking water standards. (One secondary constituent is allowed to exceed the standards, but generally not two). It appears that, for this well, the estimated TSV is approximately correct based upon results to date. However the arsenic concentration in the recovered water is still higher than might be expected based upon conservative constituents, indicating that subsurface geochemical and microbial reactions may be significant and have not yet attained equilibrium. Arsenic concentrations should continue to decline, and the duration of acceptable arsenic concentrations in the recovered water should increase as the total volume stored approaches the TSV.

Well S-11			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	7 to 130	524 to 740	0
1	16 to 59 to 40	328 to 960	142 to 73
2	32 to 37 to 31	484 to 836	151 to 95
3	5 to 40 to 30	332 to 764	158 to 118
4	16 to 35 to 18	340 to 1,236	178 to 81

As shown in **Figure 44**, peak arsenic concentrations declined with successive cycles even though the cumulative storage volume was reduced at the end of the fourth cycle. Average recovery flow rate was 1.0 MGD so the TSV for this well would be about 350 MG. The volume stored ranged between 21 and 34% of the TSV.

Of considerable interest is the high TDS concentration in the recovered water at the end of Cycle 4. This is higher than the ambient TDS of the storage zone, which is within a range of 844 to 1,070 mg/l for all of the wells. For this well the background TDS concentration was 936 mg/l prior to ASR operations. The results suggest that upconing of brackish water from the underlying Avon Park formation may be occurring during extended recovery periods at this well. TDS concentration at the top of the Avon Park formation is about 2,700 mg/l, as measured at well AP-1 at the Peace River Water Treatment Plant.

Well S-12			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	14 to 41	476 to 864	0
1	7 to 55 to 42	284 to 744	73 to 6
2	27 to 49	428 to 612	83 to 26
3	2 to 42	332 to 544	89 to 51
4	8 to 94 to 31	312 to 652	111 to 13

The variation in peak arsenic concentrations is shown in **Figure 44**, showing a small decline during the first three cycles, associated with a steady increase in the cumulative storage volume. During Cycles 3 and 4 acceptable arsenic concentrations in the ASR well were maintained during the first two weeks of recovery, which is an improvement over Cycles 1 and 2. However much higher peak arsenic concentrations were observed toward the end of the fourth cycle, following which the concentrations declined substantially. The rapid change from the peak concentration to the much lower concentration at the end of recovery suggests either desorption of arsenic that had sorbed onto the limestone matrix or onto ferric hydroxide close to the well during early cycles, ion exchange or other reactions as more brackish water entered the storage zone during the extended recovery period.

The fourth cycle was longer duration than the previous cycles, recovering a much greater volume of water, some of which was drawn from a portion of the storage zone that had not been previously developed. Whether this small buffer zone that had been developed during the earlier cycles actually contained arsenic mobilized and displaced laterally during the earlier cycles, or whether water from the buffer zone caused a water quality shift close to the well that released the stored arsenic is unknown. Most likely the arsenic that had been mobilized and then reprecipitated never moved more than a few feet or tens of feet from the ASR well. However, the buffer zone extended much further. Water quality changes in the aquifer pore space around the well, caused by changes in recovered water quality as the buffer zone was pulled toward the well, may have released the arsenic due to desorption, ion exchange or other processes.

Average flow rate from this well during the four cycles was 0.94 MGD, corresponding to a TSV of 330 MG. Cumulative storage volume ranged from 2 to 34% of the TSV.

Well S-13			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	17 to 4	476 to 864	0
1	7 to 51 to 41	292 to 804	85 to 17
2	20 to 31	460 to 676	94 to 37
3	2 to 33	336 to 592	99 to 53
4	10 to 79 to 37	316 to 732	121 to 23

Average flow rate during recovery for the four cycles was 1.0 MGD. Consequently the TSV for this well is estimated at 350 MG. Cumulative storage volume ranged from 5 to 35% of the TSV. Essentially the same pattern in recovered water quality is evident for this well as for Well S-12 so the same comments apply. Arsenic concentrations are shown on **Figure 44**.

Well S-14			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	7 to 52	448 to 752	0
1	3 to 114 to 88	272 to 664	85 to 16
2	13 to 77 to 73	408 to 580	96 to 39
3	1 to 58	312 to 536	99 to 54
4	10 to 111 to 65	312 to 644	121 to 23

Average well production rate was 1.0 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 350 MG. During the four cycles the cumulative storage volume ranged from 5 to 35% of the TSV.

Following the pattern of several other wells in this wellfield, TDS and peak arsenic concentrations declined during the first three successive cycles, showing an increase during Cycle 4 associated with the long recovery period. Also, the arsenic concentrations within Cycle 4 showed a substantial increase followed by a substantial decrease. This is consistent with each of the other wells, perhaps providing insight into the possible desorption or ion exchange processes occurring close to the well, and the proximity of the "stored" arsenic. Arsenic results are shown in **Figure 44**.

Well S-15

Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	13	492 to 756	0
1	1 to 66 to 30	272 to 648	43 to -23
2	20 to 89 to 80	372 to 532	49 to -8
3	1 to 33	304 to 396	86 to 46
4	6 to 187	312 to 548	107 to 10

Average well production rate was 1.0 MGD during the four recovery periods. Consequently the TSV for this ell is estimated at 350 MG. During the four cycles the cumulative storage volume ranged from 0 to 31% of the TSV. Although approximately the same volumes of water were recovered in each of the cycles as for the other wells in the wellfield, the cumulative stored volume was less. As a result over-recovery occurred and no buffer zone was formed in this well. Peak arsenic concentrations are among the highest in the wellfield at this well, probably related to the lack of any buffer zone. Arsenic values are shown in **Figure 45**.

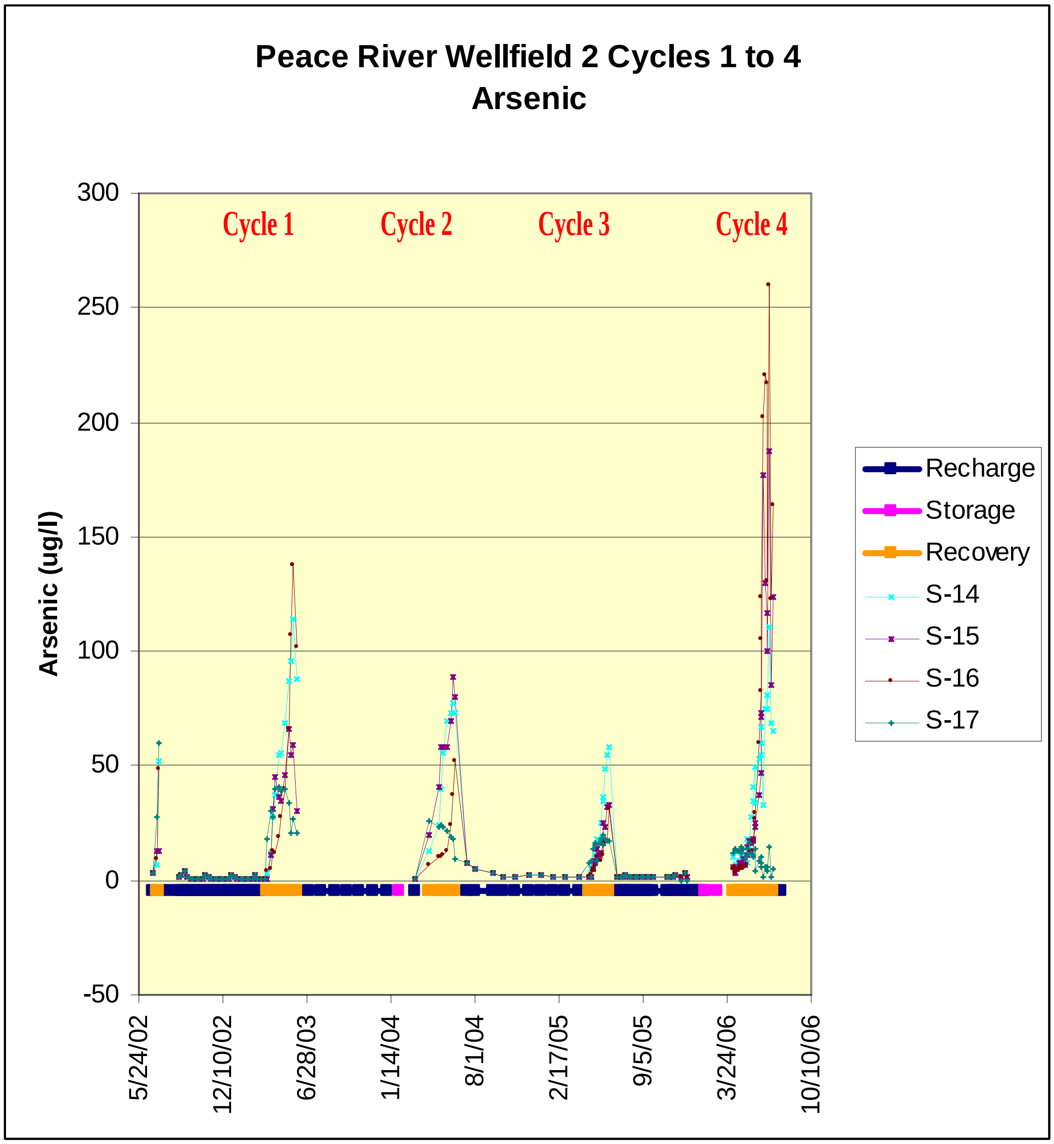


Figure 45 Peace River Wellfield 2 Cycles 1 to 4 Arsenic

Well S-16			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	9 to 49	448 to 760	0
1	4 to 138 to 102	260 to 704	60 to -8
2	7 to 52	360 to 552	69 to 14
3	1 to 31	288 to 496	78 to 39
4	5 to 260	324 to 700	99 to 2

Average well production rate was 0.94 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 330 MG. During the four cycles the cumulative storage volume ranged from 0 to 28% of the TSV. As with Well S-15, no buffer zone was formed in this well. Peak arsenic concentrations are the highest in the wellfield, as shown in **Figure 45**.

Well S-17			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	28 to 60	552 to 748	0
1	18 to 41 to 21	432 to 948	138 to 70
2	26 to 9	532 to 924	148 to 91
3	8 to 20 to 17	460 to 796	152 to 113
4	12 to 16 to 5	448 to 1,360	174 to 77

Average well production rate was 0.95 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 330 MG. During the four cycles the cumulative storage volume ranged from 21 to 53% of the TSV. Peak arsenic concentrations are among the lowest in the wellfield and show a declining trend with successive cycles. This is probably related to the cumulative storage volume which is among the highest in the wellfield, similar to S-11. Results are shown in **Figure 45**. Also, the TDS of the recovered water at the end of Cycle 4 recovery was substantially above the background concentration of 968 mg/l for this well, suggesting upflow from the underlying Avon Park formation under the influence of extended recovery. This is similar to S-11.

Well S-18			
Cycle	Range of Concentrations Arsenic (µg/l)	 TDS (mg/l)	Cumulative Storage Volume (MG)
Baseline	9 to 34	480 to 828	0
1	1 to 87 to 63	284 to 672	68 to 7
2	18 to 38	412 to 720	84 to 28
3	1 to 29 to 24	320 to 552	89 to 45
4	8 to 86 to 58	328 to 752	111 to 14

Average well production rate was 0.95 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 330 MG. During the four cycles the cumulative storage volume ranged from 2 to 34% of the TSV. TDS generally declined with successive cycles at steadily increasing volumes, indicating a flushing out of the storage zone prior to Cycle 4. Peak arsenic concentrations declined during the first three cycles, however when almost all of the small buffer zone was recovered at the end of Cycle 4, arsenic concentrations reverted to their original high levels. Arsenic concentrations are shown in **Figure 46**.

Well S-19			
Cycle	Range of Concentrations		Cumulative Storage Volume (MG)
	Arsenic (µg/l)	TDS (mg/l)	
Baseline	10 to 23	576 to 936	0
1	5 to 53 to 15	348 to 828	142 to 73
2	23 to 10	568 to 904	152 to 96
3	3 to 19 to 14	408 to 644	158 to 119
4	12 to 29 to 8	424 to 964	179 to 83

Average well production rate was 0.95 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 330 MG. During the four cycles the cumulative storage volume ranged from 22 to 54% of the TSV, which is among the highest values in the wellfield. Arsenic concentrations generally declined with successive cycles and were among the lowest in the wellfield during Cycle 4. Also during Cycle 4, TDS concentrations exceeded background levels at the end of the extended recovery period, suggesting the possibility of upconing from the Avon Park Formation. Peak TDS concentrations at the end of recovery did not decline with successive cycles as might otherwise have been expected.

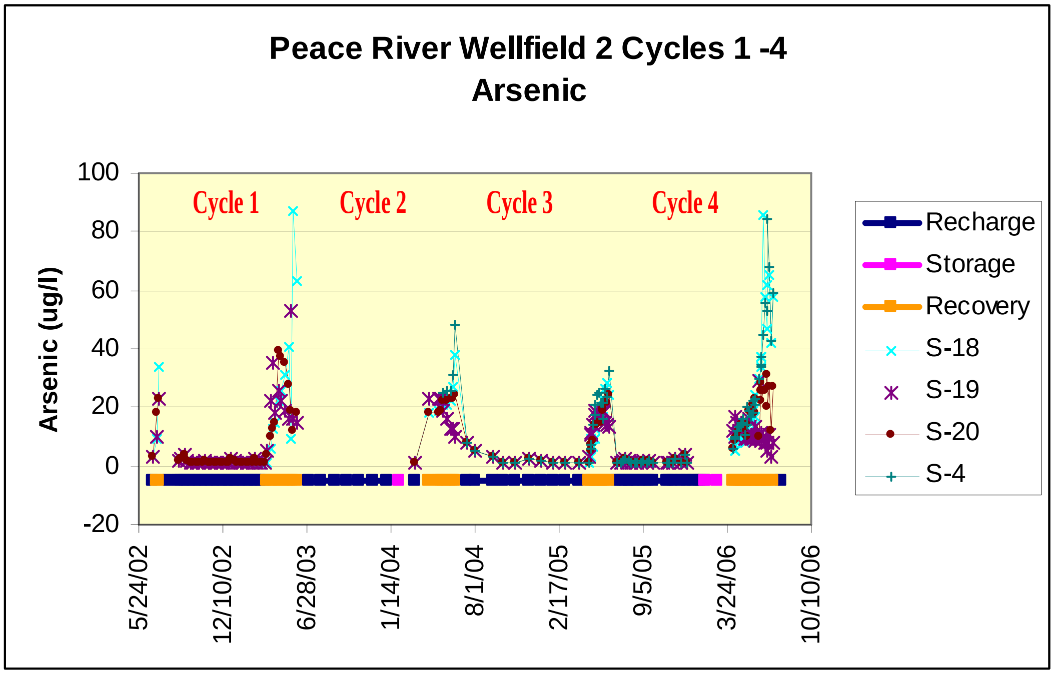


Figure 46 Peace River Wellfield 2 Cycles 1 to 4 Arsenic

Well S-20			
Cycle	Range of Concentrations		Cumulative Storage Volume (MG)
	Arsenic (µg/l)	TDS (mg/l)	
Baseline	18 to 23	500 to 780	0
1	4 to 39 to 18	304 to 856	129 to 62
2	18 to 24	453 to 660	140 to 84
3	1 to 24	340 to 732	145 to 100
4	6 to 31 to 27	336 to 840	166 to 69

Average well production rate was 0.98 MGD during the four recovery periods. Consequently the TSV for this well is estimated at 350 MG. During the four cycles the cumulative storage volume ranged from 18 to 47% of the TSV, which is among the highest values in the wellfield. Peak arsenic concentrations were among the lowest in the wellfield but showed only slight reduction during the four cycles, as shown in **Figure 46**. At the end of Cycles 1 and 4 the TDS concentration exceeded the background level of 780 mg/l. This, combined with the lack of any clear reduction in TDS concentration with successive cycles, and even though a good percentage of the buffer zone was formed during the four cycles, suggests that upconing may also be a factor at this well, affecting recovered water quality and perhaps inhibiting arsenic attenuation.

Well S-4			
Cycle	Range of Concentrations		Cumulative Storage Volume (MG)
	Arsenic (µg/l)	TDS (mg/l)	
2	25 to 48	376 to 660	63 to 30
3	1 to 32	340 to 600	90 to 43
4	6 to 84 to 59	336 to 744	105 to 10

Cycle testing at this well did not begin until Spring 2004. Moderately high arsenic concentrations showing little attenuation are probably related to the absence of a buffer zone at this site. Estimating a typical well yield of 1 MGD, and a TSV of 350 MG, the cumulative storage volume ranged from 3 to 30% of the TSV. Arsenic concentrations are shown in **Figure 46**.

Other Water Quality Constituent Analyses

Two wells were selected for more detailed analysis of selected constituents, including total iron and sulfate. No data is available for dissolved iron or for hydrogen sulfide. The two wells are S-16 and S-17, which yielded the highest (260 µg/l) and lowest (16 µg/l) arsenic concentrations in Wellfield Two, respectively, during 2006 (Cycle 4).

Total iron concentration of the recharge water is generally less than 29 µg/l with a maximum of 132 µg/l. In the storage aquifer ambient concentrations are generally less than 35 µg/l. In the recovered water concentrations were often high for the initial sample at the beginning of recovery, suggesting either incomplete flushing of the well casing prior to sample collection or that iron concentrations are high close to the well. Subsequent samples showed lower but generally increasing concentrations. For Well S-16, recovered water total iron concentrations averaged 14, 35, <36 and 45 µg/l in 2003 to 2006, respectively. These are all low iron concentrations. For Well S-17, total iron concentrations averaged 129, 222, 176 and 217 ug/l, respectively, in 2003 to 2006. A strong inverse relationship is evident between total iron concentration and arsenic concentration at these two wells.

Sulfate concentrations in the recharge water generally range from 102 to 132 mg/l with a maximum of 203 mg/l. In the ambient groundwater it is about 226 to 412 mg/l in Wellfield Two. Sulfate concentrations in the recovered water from Well S-16 increased from the beginning to the end of recovery in each cycle but did not increase with successive cycles. The 2004 recovery period is typical, ranging from 148 to 184 mg/l at the beginning and end, respectively. For Well S-17, the same patterns are evident, with 2004 sulfate concentrations increasing from 182 to 237 mg/l. No significant differences are evident between sulfate concentrations and associated patterns at these two wells. However, for both wells, increasing sulfate concentrations during recovery generally coincided with increasing arsenic concentrations, which are shown in **Figure 42**.

Data pairs for arsenic and total iron for all wells in Wellfield 2 were evaluated to determine whether any significant linear relationship exists. A weak relationship is evident, as follows:

$Y = 0.77\,X + 33 \qquad (R^2 = 0.37)$

where Y = Total Iron (ug/l)
X = Arsenic (ug/l)

This analysis was conducted since visual observation of the data suggested that total iron concentrations generally increased with increasing recovery, similar to TDS.

pH was observed to decline during recovery while arsenic increases in concentration, as discussed previously. A relationship between arsenic and pH was evaluated, combining data pairs from all wells. This yielded the following linear equation with a more significant value for R^2:

$Y = -38X + 320 \qquad (R^2 = 0.61)$

where Y = pH
X = Arsenic (ug/l)

Arsenic and ORP data were evaluated for Wellfield 2, utilizing about 300 data pairs from 10 ASR wells obtained during May to December 2005. Data was sorted into recharge and recovery, as shown on **Figure 47**. No storage period data was obtained. A possible relationship is evident from the analysis of recovery data however with a variance (R^2) of 0.249 the assumed linear relationship shown on the figure is insignificant. The relationship is

$Y=-7.323X +329.5$

Where X = arsenic (ug/l)
Y = ORP (mv)

Peace River Storage Zone Monitor Wells

Twenty-eight monitor wells have been constructed at these two wellfields, including 11 added during 2005. Four of these 28 wells are in the Tampa Formation while most of the remainder are in the Suwannee Formation, the principal ASR storage zone. The Tampa Formation monitor wells have shown no increase in arsenic concentrations above low background levels.

Sixteen monitor wells provide data regarding arsenic concentrations in the Suwannee Formation. Most of these are constructed at a distance of approximately 150 feet from the nearest ASR well, although the radial distances range from 90 to 450 feet. During 2005 all but two of these monitor wells showed no elevation of arsenic concentrations above background levels. Peak arsenic concentrations generally ranged between 2 and 6 µg/l. A single sample at Well M-8 showed 18 µg/l. Well M-16 showed elevated arsenic concentrations near the beginning of recharge, including a peak arsenic concentration of 17 µg/l after one month of recharge, then declined to below 1 µg/l during the remainder of the recharge period.

During the 2006 extended recovery period, seven of these monitor wells showed an increase in arsenic concentrations compared to 2005. Of these, six were elevated above 10 µg/l. Wells M-8, M-14, M-15, M-16, M-17 and M-22 showed highly variable arsenic concentrations, most of which were acceptable but with peaks of 12, 31, 22, 20, 17 and 38 µg/l, respectively.

The extensive monitor well data suggest that arsenic mobilization at this site during recharge does not extend far from the ASR wells. In almost all cases this lateral distance is less than 150 feet. It may be less than 90 feet, which is the closest lateral distance of a monitor well showing no elevation in arsenic concentration. That monitor well is close to Well S-2, which began operations in 1985. However during ASR recovery increased arsenic concentrations are evident at the same monitor wells. As described above, 2006 recovery operations at this site pulled back in a significant portion of the buffer zone surrounding each of these wells. It is hypothesized that the change in water quality caused mobilization of arsenic that would otherwise have remained attached to the aquifer matrix. It is therefore appropriate to consider what changes in water quality may have occurred that could contribute to a change in arsenic speciation or may have impacted microbial or geochemical processes occurring around the ASR wells.

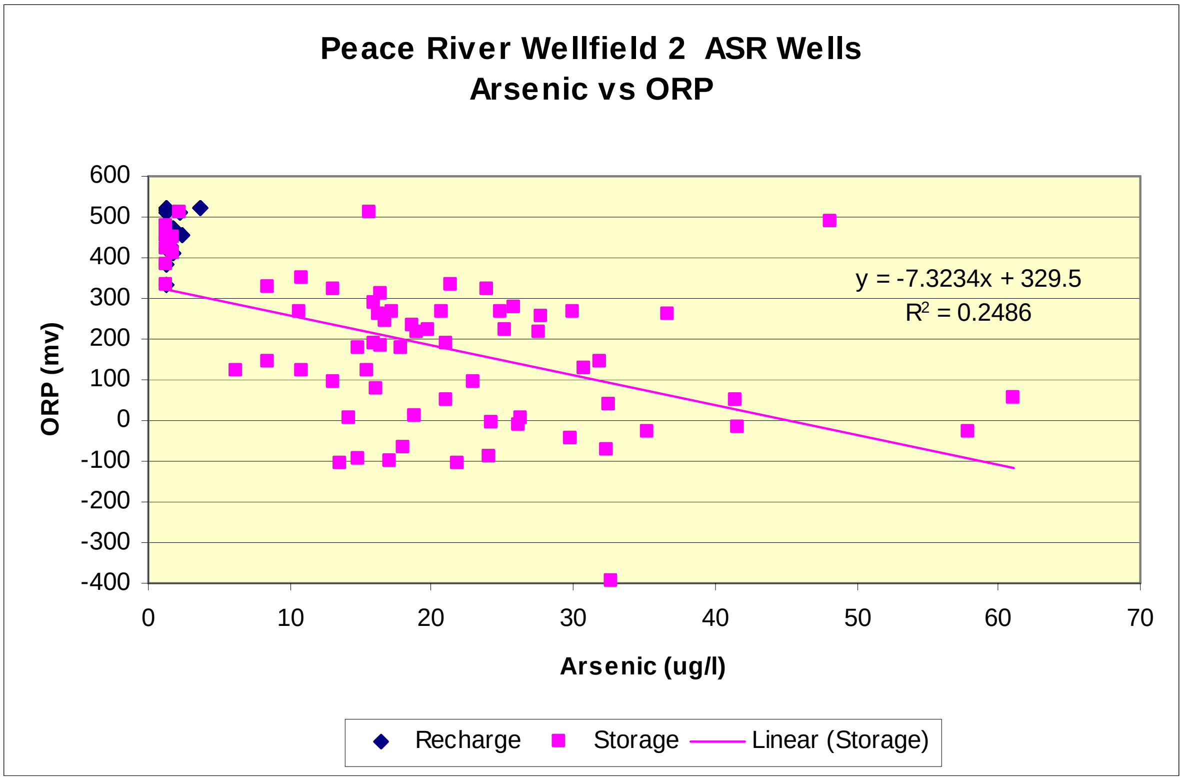


Figure 47 Peace River Wellfield 2, Arsenic vs. ORP

During the recharge period extending from May 26, 2005, to February 24, 2006, average ORP of the water sampled at Well M-22 was +100 mv while the average pH was 8.0. During the recovery period from March 2 to July 27, 2006, the average ORP of the water sampled declined to +87 mv and average pH increased slightly to 8.1. For Well M-14, the average ORP of the water sampled was +260 mv during recharge while the average pH was 8.2. During the recovery period the average ORP had declined to -208 mv and the pH had declined to 7.8. These are the two monitor wells showing the greatest variability in results and also the highest peak arsenic concentrations. They may be compared, for example, with M-20, which had a stable arsenic concentration of less than 2 µg/l during this recharge and recovery period. Average ORP and pH during recharge were -196 mv and 7.6, respectively, while during recovery these values were -264 mv and 7.5. No clear pattern is evident from this brief analysis of ORP and pH data.

The changes in TDS concentrations for these three wells from the end of recharge to the end of recovery were also considered, as follows:

M-14	292 to 760 mg/l	(initial sample after construction – 468 mg/l)
M-20	752 to 740 mg/l	(initial sample after construction – 704 mg/l)
M-22	328 to 352 mg/l	(initial sample after construction – 304 mg/l)

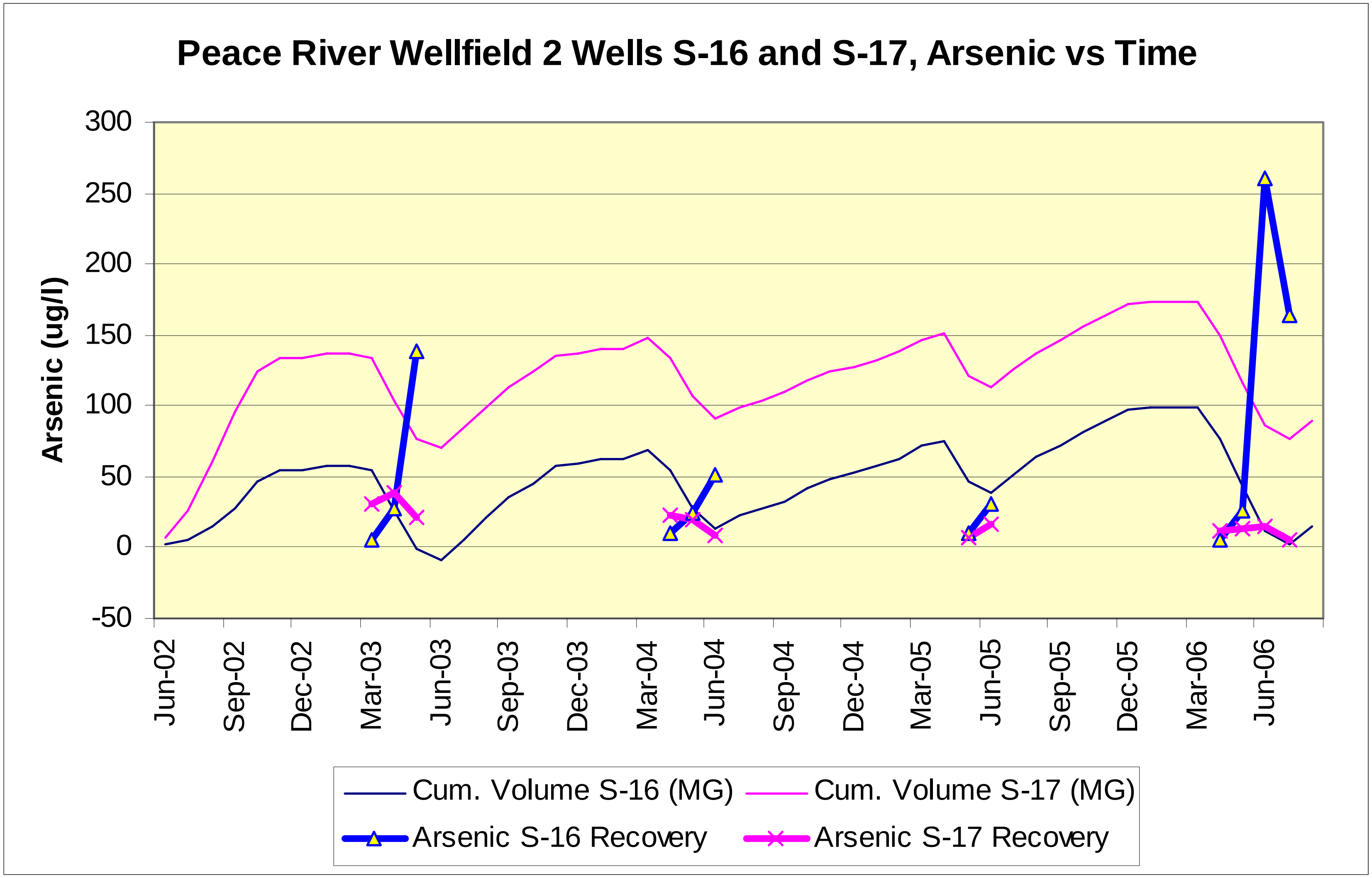


Figure 48 Peace River Wellfield 2 Wells S-16 and S-17, Arsenic vs Time

Wells M-14 and M-22 underwent a significant water quality change during this period or had already experienced such a change prior to the period of analysis due to operations at nearby ASR wells. Well M-22 was obviously located in an area of the wellfield that had been purged of ambient groundwater during prior ASR operations. In contrast, Well M-20 was apparently in an area that had not been purged of ambient groundwater and experienced little change in TDS concentration during the sampling period. Well M-20 is about 500 ft from Well S-5R, constructed about 1989, and 600 ft from Well S-1, which has been operational since 1985.

Summary Analysis of Peace River ASR Wellfield Results

For the twelve wells in the new wellfield, the two wells with the lowest peak arsenic concentrations during Cycle 4 were also the wells with the highest percentage of the estimated TSV for this site, indicating formation of a significant portion of the buffer zone. The two wells with the highest peak arsenic concentrations during Cycle 4 had cumulative storage volumes as a percentage of the TSV that were the lowest and third lowest for the site. As shown in the various figures, considerable scatter exists in the data, reflecting normal variability in field measurements and also undoubtedly the existence of other factors that influence arsenic concentrations besides cumulative storage volume. Nevertheless an inverse relationship is evident between peak arsenic concentration and the cumulative storage volume as a percentage of the TSV for this site. **Figure 48** shows this clearly for wells S-16 and S-17, which had the highest and lowest arsenic concentrations during the 2006 recovery period.

For the six active ASR wells in the old wellfield, arsenic concentrations are acceptable, probably benefiting from prior operations at this site that developed the storage zone to a storage capacity greater than that achieved prior to the Spring 2006 recovery period.

Storage zone monitor wells indicate that arsenic mobilization generally does not extend more than about 150 feet from the ASR wells during recharge. During recovery, subsurface arsenic mobilization processes apparently desorb or otherwise mobilize the arsenic, causing highly variable concentrations, most of which are acceptably low but a few are elevated. Further research will be required to shed light on these subsurface processes which are complex and not well understood.

Considering both Peace River data sets, plus the Tampa and Bradenton experience, a slightly revised hypothetical model may be postulated. The TSV concept, developed to achieve high recovery efficiency as rapidly as possible in brackish aquifers, is adaptable for achieving acceptable (ie: 10 µg/l) arsenic concentrations even though arsenic is clearly not a conservative constituent. Operational experience at Peace River in both wellfields, and at other wellfield sites, suggests that arsenic concentrations reach acceptable levels within a few cycles of operation at approximately the same storage volume. Alternatively the same outcome may be achieved by forming the buffer zone at one time, prior to beginning operational cycles, as shown for Bradenton. However the portion of the aquifer that is developed through this process is limited to approximately half of the cumulative stored water volume while the remaining half is associated with the arsenic buffer zone.

It is unknown where the arsenic accumulates, having been mobilized close to the ASR well during recharge and then moved laterally away from the well. As discussed elsewhere in this report, there are several indications that the mobilized arsenic does not move very far from the well, perhaps within a few tens of feet, and certainly not as far as the stored water. When the buffer zone is maintained, arsenic is observed at monitor wells ranging from 90 to about 150 ft from the nearest ASR well and is not observed at monitor wells greater than about 200 ft. Arsenic is probably adsorbed on amorphous iron oxides where it remains unless the sorption sites are lost. For these Florida ASR wells, desorption is commonly observed when the buffer zone is pulled back close to the well. Subsequent storage and recovery operations within this radius around the ASR well help to create a stable geochemical environment at a sufficient distance away from the ASR well so that arsenic is not remobilized during recovery. However, if the buffer zone is recovered, arsenic is remobilized. Further research is needed to investigate the complex interplay of physical, geochemical and microbial mechanisms that occur close to the ASR well during recharge and recovery.

It would be appropriate to reevaluate the previously-estimated TSV for the Peace River ASR wellfields. The previous estimate, 350 days, was prepared more than 10 years ago based upon operational data from the old wellfield plus consideration of variability in water supply, water demand and water quality. It has been used as a reference point for this analysis.

5.0 Manatee County

This was the first Florida ASR wellfield, funded by the Southwest Florida Water Management District and Manatee County. The successful project received a major national award in 1984, galvanizing development of the ASR technology globally in subsequent years.

The storage zone at this site is a confined, limestone artesian aquifer. Six ASR wells have been constructed in the Suwannee formation within the upper Floridan aquifer, utilizing both the upper and lower production intervals of this formation. Typical wells are cased to 400 feet and open hole to 700 feet.

Two ASR wells, B1 and B2, were constructed in 1982, cycle tested and placed into operation in 1983. Combined recharge capacity is currently about 4 MGD while recovery capacity is about 5 MGD. The remaining four wells, B3 through B6, were constructed in 2001 and two of them have some preliminary cycle testing data, however none of these four wells have yet been placed into operation. Cycle testing for the last four wells is planned following construction of an additional monitoring well, renewal of the construction permit, and further well development for two of the more recent ASR wells.

As part of the initial ASR test program, several monitor wells were constructed. The first of these, Well A, is open hole into the top of the Avon Park formation which underlies the storage zone at a depth of 1,000 feet. The second monitor well, Well C1, is constructed with 2" PVC, screened and gravel-packed in the upper Suwannee formation with a screened interval from 469 to 479 feet. The third monitor well, Well C2, is constructed in the lower Suwannee formation, also screened and gravel-packed from 662 to 672 feet. All three of these monitor wells are located in a cluster 330 feet from Well B1 and 739 feet from Well B2.

Aquifer hydraulic characteristics are generally as follows:

Transmissivity - 299,000 gpd/ft
Storativity - 1.5 x 10^{-4}
Leakance - 2.8 x 10^{-4}/day

Ambient groundwater quality was defined from a sample collected December 8, 1982, plus other samples, as follows:

Conductivity - 558 mS/cm
Sulfide - 0.84 to 2.57 mg/l
Iron - 30 µg/l
Sulfate - 138 mg/l
T. Alkalinity - 138 mg/l
TDS - 340 mg/l

No analysis was obtained in 1982 for background arsenic concentration although many other constituents were analyzed.

Source water for the ASR wells is surface water from Lake Manatee, treated at a conventional coagulation-filtration surface water treatment plant. Treated surface water is supplemented and blended with water from a wellfield, treated with lime-softening.

During cycle testing of ASR well B1 in 1983, nine ASR cycles were conducted. Extensive water quality data were obtained on both the recharge water and the recovered water, focusing on the issues of greatest interest at the time which were trihalomethanes, gross alpha radiation and radium in addition to conventional anions and cations of interest, plus dissolution of limestone during storage. However no data are available to indicate sampling and analysis for arsenic concentrations during recovery at the end of cycle testing. Priority pollutant scans were conducted on the recharge water, but not on the recovered water.

On September 27, 1982, a sample was pumped from the well for priority pollutant analysis. This followed completion of Cycle 1, a small cycle to verify operational performance of wellhead facilities, but was prior to Cycles 2 through 9, which constituted the cycle testing program. The analytical results for this sample include a determination for arsenic at 0.1 µg/l. Total iron concentration was 78 µg/l. A sample dated August 19, 1982, of the recharge water (treated drinking water) indicated less than 2 µg/l arsenic concentration.

Total recharge through December 2005 was 1,358 MG while total recovery was 862 MG, leaving a net cumulative storage volume of 496 MG. Due to regulatory constraints, no recharge or recovery has occurred at Well B1 since February 2003 or at any of the four new wells since May 2003. During the last three years it is believed likely that the stored water has probably moved away from Well B1 due to groundwater production from nearby wells in the same aquifer. This is indicated by the re-occurrence of hydrogen sulfide in samples pumped from the well, indicating ambient groundwater instead of treated drinking water.

For Well B2, cumulative net recharge has been 521 MG while recovery has totaled 424 MG, leaving a net storage volume of 97 MG. Negligible recharge and recovery has occurred in the four new wells to date. Ending storage volumes range from -16 to 11 MG.

Since October 2000, 85 samples have been collected from four ASR wells during recovery and also from the monitor wells and the recharge water. These samples have been analyzed to determine their arsenic concentration. Recharge water and Avon Park monitor well samples have shown consistently below 2 µg/l arsenic concentration. For Well B1, which has been in operation since 1983, concentrations have ranged from less than 2 µg/l to 6 µg/l. For Well B2, which has also been in operation since 1983, arsenic concentrations have ranged from 7 to 11 µg/l. For Well B3, which is not yet operational but has gone through a single ASR test cycle, arsenic concentrations ranged from 5 to 20 μg/l. For Well B4, which is also not yet operational but has gone through a single ASR test cycle, arsenic concentrations have ranged from 10 to 26 μg/l. Of perhaps greater significance is that arsenic concentrations increased steadily during the first ASR recovery cycle for Wells B3 and B4 whereas for Wells B1 and B2, which have been in operation for over 20 years, there was no increase in arsenic concentration during recovery for the same operating cycle. Significant differences between the wells include the cumulative volume in storage and the duration of operations.

All recovered water from the ASR wells is disinfected and blended with much greater quantities of treated drinking water from the water treatment plant prior to distribution.

Analysis of data from the monitor wells indicates that since October 2000, the upper Suwannee monitor well, Well C, has indicated arsenic concentrations of less than 2 to 5 μg/l. No data have been obtained for the Lower Suwannee Monitor Well. The Avon Park and Hawthorn Monitor Wells have both indicated arsenic concentrations of less than 2 μg/l.

Total iron concentrations in the recharge water typically range between 0.01 and 0.09 mg/l while the background ambient groundwater concentration was 0 – .03 mg/l. For Well B-1, recovered water total iron concentrations between May 2000 and February 2003 ranged from zero to 0.23 mg/l, with higher values tending toward the beginning of recovery. Average concentration was 0.04 mg/l. For well B-2 the range was 0.03 to 0.11 mg/l with an average of 0.04 mg/l. No recovery total iron data was available for the four new wells.

Sulfate concentration in the recharge water ranges from 66 to 121 mg/l while in the ambient groundwater it was 138 mg/l. During May 2000 to February 2003 recovery periods sulfate concentration at well B-1 ranged 97 to 129 mg/l. A very small increase in sulfate concentration was evident between recharge periods and associated recovery periods for each cycle, typically between 10 and 20 mg/l. These were probably associated with a slight increase in arsenic concentration, such as from <2.0 to 5 μg/l.

The iron and sulfate data suggest that pyrite reactivity at this well has attenuated.

Summary Analysis of Manatee Potable ASR Wellfield Results

Based on available data, arsenic does not appear to be a significant problem at this site for wells placed into operation in 1983. Of the 28 recent analyses for these wells, results range from less than 2 μg/l to 11 μg/l and all but three of these samples are 10 μg/l or less. For new wells at this site it appears probable that arsenic concentrations during recovery will achieve drinking water standards of 10 μg/l after a few operating cycles at about the same volume. Alternatively a buffer zone may be formed in each of these wells initially, enabling their subsequent operation without producing elevated arsenic concentrations.

For the first cycle at two new wells, conducted in April and May 2003, arsenic concentrations have ranged from 5 μg/l up to 20 and 26 μg/l, respectively. It appears that arsenic concentrations in the recovered water at this site attenuate to acceptable levels after at least one cycle and probably two or three cycles.

Arsenic concentrations also attenuate with distance from the ASR well, as measured at the storage zone monitor well C1, for which all values were less than 5 μg/l. The radial distance to the monitor well is 330 feet from Well B1.

6.0 Englewood Water District

The South Regional Wastewater Treatment Plant, owned and operated by the Englewood Water District, is located in northwest Charlotte County, Florida. This facility, consisting of twin advanced secondary treatment units, produces 2.2 mgd of reclaimed water and has recently been expanded to 3 mgd production capacity. Reclaimed water was initially stored in on-site reuse ponds before being distributed for non-agricultural irrigation of city property and golf courses.

The South Regional WWTP is a complete mix activated sludge process domestic wastewater treatment plant. The facility consists of flow equalization, influent screening, aeration, secondary clarification, filtration, chlorination, and aerobic holding and dewatering of residuals with centrifuges. Facilities include one ASR well, cased with carbon steel casing, and three adjacent observation wells, one of which is in the storage zone, one in an overlying aquifer and one in the surficial aquifer.

The Englewood Water District began investigating ASR feasibility in December 1997 and applied to the Florida Department of Environmental Protection (FDEP) and the Southwest Florida Water Management District (SWFWMD) for their ASR test well construction permits in March, 1998. An ASR test well construction permit was issued by the FDEP in June, 1999, and well construction permits were issued by the SWFWMD in January 2000. Construction of the ASR test well system and monitoring network was initiated in January 2000 and was completed in April 2000. A comprehensive engineering report was submitted to FDEP in July 2000 requesting authorization to commence ASR cycle testing. Englewood Water District received authorization to cycle test, which was initiated in July 2001 and is currently ongoing.

The following well facilities were constructed at the South Regional Wastewater Treatment Plant: one Class V ASR test injection well (TPW-1), one 6-inch PVC-cased, storage zone monitoring well (SZMW, approximately 400 feet from the ASR well, cased from 510 to 700 ft), one 6-inch intermediate monitoring well (IMW, approximately 2,200 feet from the ASR well, cased from 280 – 320 ft), and one 6-inch shallow monitoring well (SMW, approximately 150 feet from the ASR well, cased from 170 to 205 ft). The basic ASR well design consisted of a 16-inch diameter injection well to a depth of 700 feet and cased to 507 feet. The pilot hole for this well was drilled to 808 ft and then backfilled to 700 ft.

During testing, the native water quality in the storage zone was found to be very poor. Below 300 feet in depth, the concentration of background total dissolved solids (TDS) was estimated to be greater than 10,000 mg/L. The background TDS concentration in the reclaimed water ASR well (storage zone) was determined to be approximately 20,000 mg/L. The exceptionally poor water quality led to problems during drilling (i.e., no acceptable location was available to discharge the saltwater produced from the borehole) thus resulting in closed-circulation drilling throughout most of the process.

ASR cycle testing was initiated in July 2001 at recharge rates ranging from 0.25–1.0 mgd. All water recharged met primary and secondary drinking water standards with the exception of color, which required a Water Quality Criteria Exemption (WQCE) from FDEP. Recharge of the well is continuing on an as-needed basis. Initial recovery cycles were completed during the early part of the cycle testing program. Additional recharge and recovery cycles are underway, to be followed by applying for a reclaimed water ASR well operating permit.

At least 650 million gallons (MG) have been recharged to date, with limited recovery due to low demand for reclaimed water plus extended wet weather conditions. This is a net recharge volume, including reductions in storage occurring during recovery periods. Four ASR test cycles were conducted between 2001 and 2003, recovering a total of about 120 MG. Recharge then continued from 2003 until 2004. As demand for reclaimed water increases in the Englewood Water District (EWD) service area, it is anticipated that less water will flow to the ASR well and more water will be recovered.

The ASR storage zone is at a depth of 512–700 feet and is constructed in the upper Floridan Aquifer System (FAS), which is a limestone, artesian aquifer. The ambient groundwater quality in this aquifer is brackish, with a total dissolved solids (TDS) concentration of about 19,350 mg/L in the ASR well and 22,100 in the storage zone monitor well 400 feet away, as measured upon completion of well construction and baseline testing. Aquifer transmissivity, based on step-drawdown pumping tests, is estimated at 35,000 gpd/ft. Static water level is 5 feet above land surface.

Arsenic is not deemed to be a significant issue at this site since the storage zone TDS concentration exceeds 10,000 mg/l. Consequently this aquifer is not considered by FDEP to represent a potential underground source of drinking water. Nevertheless monthly data reports are provided to FDEP containing some data of interest to this analysis of arsenic mobilization and attenuation. Data from April to July 2006 were evaluated, during which time total cumulative storage volume declined from 651 to 618 MG and then increased to 645 MG.

Recharge occurred at variable average daily rates up to about 1.5 MGD. Recovery occurred at rates of 0.7 to 1.0 MGD, however recovered water quality is reported (McNeal 2006, personal communication) to be better when recovery rates are below about 0.5 MGD. Wellhead pressure ranges between about 6 and 51 psi, depending upon whether recharge is occurring or not. Land surface elevation is about 10 ft above mean sea level (msl). Displacement of brackish water with fresh water in the ASR well causes static wellhead pressure to rise from close to land surface to about 14 ft above land surface.

Pressure response at SZMW-1 400 ft away during injection is less than 1 psi. Water quality response at SZMW-1 is also minimal, with conductivity declining from 29,200 to 23,600 µmhos/cm while at the ASR well the recharge water conductivity varied between 934 and 3,070 umhos/cm. Similarly, chloride concentration declined from 10,400 to 8,050 mg/l at the SZMW, and TDS declined from 19,033 to 15,567 mg/l. Whether due to aquifer anisotropy or density stratification, it appears that little hydraulic communication occurs between the ASR well and the SZMW at this site.

Pressure response at the shallow monitor well, SMW-1, was less than 0.8 psi at the maximum recharge rate, suggesting little hydraulic communication between ASR-1 and SMW-1. The two producing intervals are separated by the Lower Hawthorn aquifer, which was not monitored at this site.

Throughout this recharge and recovery period arsenic concentrations were below 4 ug/l in all monitor wells. At the ASR well arsenic concentrations remained less than 6 µg/l. No data are available regarding ORP, however pH of the recharge water varied between 7.0 and 7.7 while at the SZMW it varied between 7.0 and 7.3.

7.0 Punta Gorda

Treated drinking water is stored at this site in the lower producing zone of the Suwannee Formation in the upper Floridan aquifer. This is a confined, limestone artesian aquifer containing brackish water. The storage zone occurs at depths of about 764 to 933 feet.

In September 1997 Well ASR-1 was originally cased to 700 ft and drilled to a depth of 1043 ft. It was then plugged back to 764 ft to isolate just the top of the Suwannee formation (700 to 764 ft), which provided about 25% of the flow to the well prior to plugging back. A lower flow zone in the Suwannee Formation from 800 to 950 ft provided about 60% of the flow to the well. ASR Wells 2, 3 and 4 were constructed in 2001, plus three monitor wells. All of these wells were constructed in the lower Suwannnee formation. One of the three monitor wells is in the storage zone 100 ft from ASR Well 1 and in the direction of Well ASR-2, which is the next closest well. However monitor well MW-1 is in a cavern so flushing characteristics tend to be dampened. Well ASR-2 is not in use since it produces excessive sand.

Storage zone hydraulic characteristics were determined from pumping tests following construction of Well ASR-1. A transmissivity of about 10,000 gpd/ft was estimated based upon a single well pumping test since there were no monitor wells available at the time. However this is for the upper Suwannee Formation. No test information has been developed for the lower Suwannee Formation which constitutes the current storage zone at this site.

Baseline ambient groundwater quality was determined 10/19/95 and from subsequent samples, as follows:

Arsenic - ND to <2.2 µg/l
TDS - 1918 – 2000 mg/l
Chloride - 850 – 860 mg/l
Sulfate - 300 - 373 mg/l
pH - 7.2
Iron - 137 µg/l
Alkalinity - 100 mg/l

A baseline sample was collected from Well ASR-1 for metals on June 28, 1999, indicating 7.96 µg/l for arsenic and 153 µg/l for iron. It is unknown what prior recharge or acidization activities may have occurred in this well, if any, between 1995 and June 28, 1999. This sample would have been after the well was reconstructed.

All wells at this site currently recharge with water that is pretreated with hydrochloric acid to slightly reduce pH. This steadily increases yield and compensates for any well plugging.

Cycle 1

Cycle 1 recharge was conducted July 23 to July 28, 1998, on Well ASR-1. Recovery began July 29 and continued to August 7. No information has been made available regarding recharge and recovery rates and volumes, however it is known that specific capacity was deemed to be very low. Recharge TDS varied from 290 to 493 mg/l while recovery TDS increased steadily from 454 to 1710 mg/l. Iron concentration was 5 µg/l in the recharge water, 260 µg/l near the end of the first day in the recovered water, and 137 µg/l after 10 days of recovery. Arsenic concentrations during recovery were at the minimum detection limit of 3 µg/l for the first day, increased to a peak of 37 µg/l on the fifth day and then declined to 13 µg/l on the ninth day.

Cycle 2

Cycle 2 was attempted however it encountered increased plugging and low flow problems, with flows declining from 200 to 10 gpm. No data have been provided for that cycle. Well 1 was then reconstructed to case out the upper Suwannee and utilize only the lower Suwannee flow zone from 764 to 933 ft. Data have not been provided regarding further testing of this well prior to February 2003, which is presumed to have included Cycles 2 and 3.

Data are included in FGS Report of Investigation No. 83 regarding Cycles 1A and 2A on Well ASR-1, conducted after reconstruction of the well. Cycle 1A occurred between about June 29 and August 8, 1999, while Cycle 2A occurred between about August 18 and September 7. Arsenic concentrations peaked at 50 µg/l in Cycle 1A and 20 µg/l in Cycle 2A. Iron concentrations peaked at about 400 µg/l in each cycle, compared to ambient groundwater concentrations of about 170 µg/l. A higher initial iron concentration of 500 µg/l occurred at the beginning of Cycle 2A recovery.

Cycle 3

A large cycle was conducted during 2001 on the reconstructed Well 1. No data have been provided for that cycle, which returned very little water. At the end of this cycle, there was a cumulative volume in storage of 210 MG in Well 1.

Cycle 4

Wells 3 and 4 and associated monitor wells were then constructed. Cycle test 4 was initiated at Well ASR-1 beginning July 31, 2002. Recharge continued to February 3, 2003, storing 155 MG of treated drinking water. Well ASR-3 began recharge November 19 and totaled 30 MG stored prior to February 3, 2003. Well ASR-4 began recharge November 21 and totaled 33 MG stored prior to February 3.

Recharge rates in the three wells during this cycle were as follows:

	Average Monthly Rate (gpm)	Daily Range (gpm)	
		Maximum	Minimum
Well ASR-1	572 - 944	1163	300
Well ASR-3	551 – 676	1168	286
Well ASR-4	536 – 630	1050	297

Recovery from all three wells began March 4, 2003, and continued to March 24. Recovery rates averaged 539, 753 and 741 gpm in the three wells, respectively. Recovery volumes were 10, 13 and 13 MG, respectively. Samples collected from the three ASR wells on March 11, approximately mid-way during recovery, had arsenic concentrations of <1, 8 and 2 μg/l, respectively. Monitor well samples had arsenic concentrations of 6, <1 and 4 μg/l, respectively.

For the three monitor wells, total iron concentrations were <6, <6 and 19 μg/l, respectively. Sulfate concentrations were 156, 210 and 210 mg/l. TDS concentrations were 752, 1860 and 1,960 mg/l, respectively, indicating that probably only MW-1 had been reached during ASR storage on this and previous test cycles.

Upon completion of Cycle 4, net cumulative storage volumes were 355 MG for Well ASR-1, and 17 and 20 MG for Wells ASR-3 and ASR-4, respectively.

Cycle 5

Recharge on Cycle 5 commenced June 16, 2003, for Wells ASR-3 and ASR-4. Well ASR-1 was not recharged due to its low recovery efficiency. Recharge ended October 19 with 101 MG stored in Well ASR-3 and 97 MG in Well ASR-4, for a combined total recharge volume of 198 MG.

Average monthly recharge rates ranged from 603 to 786 gpm in Well ASR-3 and from 587 to 777 gpm in Well ASR-4. This is a higher average recharge rate than for the previous cycle.

A sample collected on November 25, 2003, after 37 days of storage indicated arsenic concentrations of 15 and 7 μg/l in Wells ASR-3 and ASR-4, respectively. Total iron was 376 and 326 μg/l. Sulfate concentration was 127 and 128 mg/l.

Cycle 5 recovery from both wells commenced April 2, 2004, and continued until June 8, and possibly later. Well ASR-3 recovered 43 MG while Well ASR-4 recovered 49 MG. Weekly water quality samples are available from all wells for April and May but have not been obtained for June.

Assuming completion of Cycle 5 recovery on June 8, net cumulative volumes remaining in storage at the end of the cycle were 75 and 68 MG, respectively, for Wells ASR-3 and ASR-4.

It is important to note that the substantial increase in storage volume between Cycles 4 and 5 would have initiated geochemical reactions in the storage zone in Cycle 5 for portions of the aquifer not previously impacted during Cycle 4. Consequently it is reasonable to expect little or no attenuation of arsenic concentrations between the two cycles since they were not anywhere near the same volume.

Dissolved oxygen concentrations shown in the data set are not representative of field conditions and are therefore not referenced above.

Weekly samples during Cycle 5 recovery were analyzed for arsenic and several other constituents. Arsenic concentrations varied as follows:

	Arsenic (µg/l)	
Month	Well ASR-3	Well ASR-4
April, 2004	1 to 8	3 to 8
May, 2004	11 to 32	2 to 30

Monitor well arsenic concentrations during Cycle 5 recovery were 18 to 24 in Well MW-1 during April, and 1 to 19 µg/l in May. Of some interest is that the May samples began and ended with 1 µg/l while the higher concentrations were in the middle of the month. It is suspected that the one high analytical result for each well during Cycle 5 was probably inaccurate.

Summary Analysis of Punta Gorda ASR Wellfield Results

Arsenic remains problematic at this site, however testing to date has masked any attenuation of arsenic concentrations around the ASR wells since storage volumes have either been very small (Cycles 1 and 2, 1A and 2A) or have been conducted at substantially increasing volumes in two successive cycles (Cycles 4 and 5). It is anticipated that Cycle 6, if conducted at the same approximate volume as Cycle 5, may exhibit arsenic attenuation perhaps comparable to the 60% reduction that was observed between Cycles 1 and 2.

Arsenic concentrations are quite varied in successive samples from the same well during the same month, sometimes showing significant changes. Consideration of blending between ASR wells during recovery at this site would seem appropriate, obtaining composite samples from all ASR wells in addition to individual samples from each ASR well.

Arsenic concentrations in the monitor well MW-1 do not seem to show any clear pattern of attenuation with distance since they are at higher concentrations than the ASR wells during April 2004 and lower concentrations during May 2004. This could be a relic of Cycle 4 testing, which left approximately 20 MG in cumulative storage in each well at the end of recovery.

Storage periods have ranged from less than one day to more than five months. No pattern is evident that storage period increases or decreases arsenic concentrations.

8.0 City of Northport

The only information that has been reviewed regarding this site is that provided by FDEP, supplemented by a Well Completion Report prepared in 2003 by Water Resources Solutions Inc. The storage zone is a brackish limestone artesian aquifer in the Suwannee formation at depths of 583 to 650 feet. The storage zone monitor well is at a distance of 453 feet. Transmissivity of the storage zone was estimated at 25,000 to 50,000 gpd/ft. Background TDS is 3,396 mg/l.

Cycle testing began during October 2004 and has continued since that time. 129 MG have been recharged and 25 MG recovered, yielding a cumulative storage volume of 104 MG. Three cycles have been conducted, of which two have complete recovered water quality data as of December 2005. The first cycle stored and recovered about 10 MG while the second cycle stored 43 MG and recovered 14 MG. The second cycle therefore formed a small portion of the buffer zone. Recharge and recovery flow rates were each about 700 gpm.

During the first recovery cycle, arsenic concentrations climbed from <3 to 87 µg/l while during the second cycle they declined from 460 to 89 µg/l. The storage zone monitor well showed consistently less than 8 µg/l of arsenic, however it also showed little sign of any freshening as a result of ASR operations.

Insufficient information is currently available from this site to draw any useful conclusions regarding arsenic attenuation and associated mechanisms.

9.0 Lee County, Olga Water Treatment Plant ASR Program

This Lee County ASR site stores drinking water in either the Lower Hawthorn formation or at the top of the Suwannee formation of the upper Floridan aquifer, probably the former. This is a confined limestone artesian aquifer containing brackish water.

One ASR well (ASR-1) and two storage zone monitor wells were constructed and began cycle testing in 2001. Well depths range from 850 to 945 ft. Monitor wells OBS-1 and OBS-3 are located 350 and 400 ft from the ASR well. Typical recharge rates are 0.5 to 0.6 MGD while recovery rates are around 0.4 MGD.

The well was acidized prior to initiation of cycle testing. During cycle testing recharge water pH was adjusted downward slightly to within a general range of 6.5 to 7.0. Chlorine concentration in the recharge water was typically about 5 to 6 mg/l, including a free chlorine residual of about 2 mg/l. Recharge water DO typically ranged from 7.6 to 9.0 mg/l.

Aquifer hydraulic characteristics are as follows:

Transmissivity	-	75,000 gpd/ft
Storativity	-	1.6×10^{-4}
Leakance	-	2.3×10^{-1} gpd/ft^3

Specific capacity of the ASR well increased steadily from 14.7 to 27.0 gpm/ft during Cycles 1 and 2 recovery. During Cycle 3 recovery, specific capacity varied between 8.4 and 15.3 gpm/ft, averaging about 11 gpm/ft. A significant drop in specific capacity is evident during Cycle 3.

Specific injectivity generally increased from 20.3 to as high as 42.4 gpm/psi during Cycle 2, or about 9 to 18 gpm/ft, reflecting the effects of continuous light acidization during recharge. During Cycle 3 specific injectivity climbed again from 49 to 97 gpm/psi, or 42 gpm/ft. This is a rather dramatic increase in specific injectivity over the course of three cycles, suggesting that substantial dissolution of limestone is occurring close to the ASR well.

Of interest is the relatively low ratio of specific injectivity to specific capacity for this well, about 61 to 66% in Cycles 1 and 2, declining to about 30% in Cycle 3, which is unusually low for any ASR wells, particularly in Florida.

A preliminary cycle test was conducted with recharge between June 15 and July 2, 2001, followed by recovery from July 9 to 10, 2001. Five MG were recharged and 0.4 MG were recovered. Storage time was 7 days. A sample collected on July 9 near the beginning of recovery showed 3 μg/l arsenic concentration.

Cycle 1 recharge began July 17, 2001 and extended to December 27, 2001, storing 80 MG. The storage period was 123 days following which recovery began April 29, 2002 and continued until June 12, 2002, recovering 19 MG, at which point chloride concentration was 260 mg/l. Cumulative net storage at the end of Cycle 1 was 61 MG.

Cycle 2 recharge began June 24, 2002, and continued until January 28, 2003, storing 129 MG. Water was stored for 98 days, following which 29 MG were recovered between May 7 and July 28, 2003, when chloride concentration reached 202 mg/l. TDS of the recharge water decreased steadily from 462 mg/l near the beginning of recharge to 208 mg/l near the end of recharge. Recharge water sulfate concentration ranged from 73 to 164 mg/l while dissolved oxygen concentration varied from 3.5 mg/l near the beginning to 8.3 mg/l near the end of recharge. Free chlorine residual was generally between 5 and 6 mg/l. Cumulative net recharge at the end of Cycle 2 was 161 MG.

Cycle 3 recharge began July 29, 2003, and ended November 20, 2003. Volume recharged was 58 MG. Water was stored for 180 days, following which recovery began on May 19, 2004. Recovery continued until August 13, 2004, recovering 37 MG. Cumulative net recharge at the end of Cycle 3 was 182 MG.

No information has been made available regarding baseline ambient water quality in the ASR well. This information may be inferred from early samples collected from the two monitor wells prior to initiation of cycle testing, as follows:

Arsenic - BDL (MDL = 3 to 5 µg/l)
Iron - BDL to 0.11 mg/l
Sulfate - 304 to 423 mg/l
TDS - 2030 to 2640 mg/l
Chloride - 940 to 1550 mg/l
Dissolved Oxygen - 1.05 to 1.55 mg/l
pH - 7.2 to 8.7

Weekly arsenic concentrations during Cycle 1 recovery ranged from 8 to 39 µg/l, with no clear pattern except that the highest concentration was at the end of recovery. During this time TDS of the recovered water increased steadily from 560 to 826 mg/l. Iron decreased from 0.14 mg/l to below detection limit. Sulfate increased from 118 to 166 mg/l. Dissolved oxygen decreased from 3.88 to 1.82 mg/l. pH varied between 7.2 and 7.9.

During Cycle 2 recovery, arsenic varied between BDL and 7 µg/l during the first half of the recovery period, then increased to 38 µg/l at the end of recovery. Iron was BDL throughout recovery. TDS increased steadily from 370 to 638 mg/l. Sulfate increased from 103 to 173 mg/l. Dissolved oxygen varied from 1.52 to 3.6 mg/l. pH ranged between 7.2 and 7.7. It appears that the substantially larger storage volume on Cycle 2 compared to Cycle 1 caused geochemical reactions to occur in portions of the storage zone that had not been impacted during the earlier cycle. Arsenic concentrations during recovery were therefore essentially the same as if this was an initial cycle.

Cycle 3 was a smaller volume cycle with a longer storage period. During Cycle 3 recovery, arsenic concentration slowly increased from about 8 to 16 µg/l for the first half of the recovery cycle, and then continued to increase to as high as 66 µg/l when recovery stopped. The increase in arsenic approximately tracked the increase in TDS. TDS concentrations increased from 372 to 606 mg/l. Sulfate levels also increased, but to a lesser degree during the recovery period. The measured amount of dissolved oxygen ranged between 1.6 and 4.1 mg/l, however the data for this parameter are not reliable as it is felt that sampling introduced oxygen into the water. Recovered water pH ranged from 7.9 to 8.1.

Monitor Well Data Analyses

Throughout Cycle 1 recharge, arsenic concentrations were BDL at monitor wells OBS-1 and OBS-3 except for a single hit of 4 µg/l at OBS-3 at the end of recharge. During this time TDS concentrations in the two monitor wells declined from 2,450 to 1,510 mg/l at OBS-1 and from 2,210 to 1,340 mg/l at OBS-3, representing almost a 50% blend of ambient groundwater with recharge water. During recovery from Cycle 1, arsenic concentrations at the two monitor wells were BDL except for the last weekly samples, which were 3 and 7 µg/l.

During Cycles 2 and 3 the arsenic concentrations in both OBS-1 and OBS-3 ranged between BDL and 6.1 µg/l and, for OBS-3, did not follow a particular pattern. For OBS-1 a possible trend of declining arsenic concentrations was apparent during Cycle 3 injection. During Cycles 2 and 3 injection, arsenic was detected in a few recharge samples at levels ranging from 4 to 8 µg/l, however the great majority of the measurements were BDL. For these cycles the monitor wells clearly indicated that the stored water was present since the TDS of the wells had reduced by approximately 50 percent.

Summary Analysis of Olga ASR Wellfield Water Quality Results

Arsenic concentrations were slightly lower during Cycle 2 than during Cycle 1, however they increased during Cycle 3. A freshening of the aquifer around the ASR well was apparent from the TDS concentration comparison between the first two cycles, however no further aquifer freshening occurred between Cycles 2 and 3, even though the cumulative storage volume increased.

Response to ASR cycle testing in the two monitor wells was negligible for arsenic. Despite an approximately 50% blend of recharge water with ambient groundwater, arsenic concentrations ranged from BDL to 7 µg/l. Arsenic appears to attenuate with distance at this site.

Building a buffer zone around the ASR well, which had reached 182 MG by the end of Cycle 3 recovery, may not be pushing the zone of active arsenic dissolution very far away from the ASR well. It is not apparent from the data whether or not a larger buffer zone at this site would adequately address the arsenic issue. Other factors may be important.

Arsenic concentrations at the beginning of recovery were not significantly different for storage times of 7, 123 and 98 days, ranging from BDL to 3 µg/l. However the initial sample after 180 days storage time was 8.1 µg/l. Also, the highest concentration of arsenic in the recovered water from the initial test cycle and the three full ASR cycles was highest at the end of the last cycle, which is contrary to expectations.

It is possible that the open hole interval on this well is not the same at the end of Cycle 3 as it was when the well was constructed. Specific injectivity has climbed substantially due to the continuous acid feed during recharge. Specific capacity also increased significantly from Cycle 1 to Cycle 2 but then declined substantially during Cycle 3 recovery. It is postulated that the open hole may have partially collapsed, either during the Cycle 3 storage period or more likely at the onset of Cycle 3 recovery, causing flow to enter the well from a previously relatively unproductive interval near the base of the casing that perhaps had not received much recharge during earlier ASR operations. Results from this well during Cycle 3 are anomalous and need to be investigated further.

10.0 Lee County, North Reservoir

Treated drinking water is stored in the Arcadia Formation of the upper Floridan aquifer, a confined, limestone artesian aquifer containing brackish water. The ASR well, ASR-1, and one storage zone monitor well, MW-1, are open hole at depths of about 537 to 642 feet. The monitor well is 250 ft from the ASR well. Typical recharge and recovery flow rates are about 0.5 MGD.

Aquifer hydraulic characteristics are as follows:

Transmissivity - 62,000 gpd/ft
Storativity - 3.3×10^{-4}
Leakance - 5.5×10^{-3}/day

Cycle testing began on February 25, 2000 with one small test cycle that was completed on March 18, 2001, storing 6 MG and recovering 0.6 MG, at which point recovery chloride concentration reached 250 mg/l. Storage period on Cycle 1 was 7 days. The first full cycle began July 12, 2001 and continued until May 14, 2002, storing 60 MG and recovering 7 MG, at which point chloride concentration reached 266 mg/l. Storage period was 168 days. Cycle 2 began June 24, 2002, and continued until end of recovery July 31, 2003. 127 MG were stored and 24 MG were recovered, at which point chloride concentration was 272 mg/l. Storage period was 50 days. Cycle 3 began August 5, 2003 and continued until December 29, 2003, storing 104 MG. The storage period was 122 days. Recovery began on May 11 and continued to July 20, 2004, at which point chloride concentration was 254 mg/l. Recovery volume was 18 MG. Cumulative volume in storage at the end of Cycle 3 was 242 MG.

The storage volume increased significantly during each of the first three cycles, from 6 to 60 to 127 MG. Consequently each cycle would be developing portions of the aquifer that had not previously been developed. Any significant improvement in recovery efficiency or in arsenic attenuation would be unexpected until such time as a few approximately equal volume cycles are conducted. The following cycle recharged 104 MG, providing a reasonable opportunity for evaluation of any improvement in recovery efficiency with successive cycles, typically associated with formation of a buffer zone around the ASR well.

Background water quality was determined from monitor well data, as follows:

Arsenic - BDL
Iron - BDL
TDS - 1650 mg/l
Sulfate - 235 mg/l
Chloride - 670 mg/l
Dissolved Oxygen - 0.7 mg/l
pH - 7.6 to 7.7

For the initial test cycle, after a storage period of 7 days, a recovered water sample had an arsenic concentration of 4 µg/l at the end of recovery.

For Cycle 1, recovery arsenic concentrations were 10, 5 and 9 µg/l at the beginning, middle and end of recovery.

For Cycle 2, recovery arsenic concentrations were BDL for the first month of recovery. Subsequent weekly samples ranged between 3 and 9 µg/l.

For Cycle 3, recovery arsenic concentrations ranged between 2.0 and 6.9 µg/l. Iron concentrations ranged between 0.05 and 0.26 mg/l. Sulfate concentrations ranged between 106 and 202 mg/l. pH ranged between 6.8 and 7.9.

In the observation well, arsenic concentrations during Cycle 1 recovery were BDL, 3 and 8 µg/l, respectively, at the beginning, middle and end of recovery. During Cycle 2 they ranged from BDL to 7 µg/l, with no clear pattern or trend. During Cycle 3 they ranged from BDL to 6.9 µg/l, with no clear pattern. In the ASR well they also increased to 6.9 ug/l, with an increasing trend during recovery. Chloride concentration during Cycle 3 recovery ranged from 94 to 380 mg/l at the monitor well, confirming that recharge water had reached that distance during the three cycles. At the ASR well it increased from 102 to 154 mg/l. Iron concentration at the monitor well ranged from BDL to 0.13 mg/l. Sulfate concentration increased from 110 to 203 mg/l.

Summary Analysis of North Reservoir ASR Water Quality Results

Arsenic is not a significant issue at this site. Concentrations at the ASR well started out acceptable (below 10 µg/l) and diminished with successive cycles. However the volume of water recovered on each cycle has been a relatively small percentage of the volume stored, achieving only 17% on the third cycle before reaching the target chloride concentration.

The recovery efficiency has not followed a typical pattern and therefore this issue has been investigated further. For example, cycle 3 stored 104 MG compared to 127 MG in Cycle 2, and some improvement in recovery efficiency should have been evident between these two cycles. Instead they were about the same. Two reasons are now considered to have contributed to this. Recently a neighboring property owner has installed an irrigation well that taps the same interval being used for storage. Pumpage from this well is suspected to be moving some of the stored water out of range of recovery from the ASR well. The evidence to support this is that the new irrigation well is experiencing freshening of the water produced.

A second reason identified deals with a contributing flow interval in the ASR well. This zone, in the uppermost part of the open borehole, appears to plug during recharge. When plugging occurs, the more brackish native water is not flushed out. However, when flow is reversed during recovery, this zone contributes a greater portion of the flow to the well, and that portion of the flow is much more brackish due to its not having received flushing during recharge. Both of these issues are currently being addressed in permitting and remedial activities.

Observation well arsenic concentrations were also low, but not significantly different than samples from the ASR well. Attenuation of arsenic concentration with distance is not apparent from this data set, possibly reflecting the generally low concentrations.

Attenuation of arsenic concentration with storage time is not significantly different between storage times of 7 and 168 days.

11.0 Collier County, Marco Lakes

This ASR wellfield stores filtered and disinfected surface water from a limestone quarry next to the Henderson Creek drainage canal. Water is stored in the Arcadia Formation of the Upper Floridan Aquifer. This is a confined artesian sandy limestone aquifer containing brackish groundwater.

Three ASR wells are operational, storing water at depths of 735 to 790 feet. One of these wells was constructed in 1997 after which six initial test cycles were conducted. Two monitor wells were constructed as part of the initial ASR program, one in the storage interval ("Deep Zone Monitor Well") and one in the overlying Mid-Hawthorn aquifer ("Shallow Zone Monitor Well"). In 2001 two additional ASR wells were constructed plus two more monitor wells, one each in the deep and shallow zones. Operating cycles were conducted with all three wells in 2001 and have been repeated annually since then.

Aquifer hydraulic characteristics for the storage zone have been estimated from pumping tests, as follows:

Transmissivity - 75,000 gpd/ft
Storativity - 3×10^{-5}
Leakance - 5×10^{-3} /day

Background ambient groundwater samples were obtained from the completed ASR wells prior to initiation of cycle testing and were tested for Primary and Secondary Drinking Water Standards and other constituents. Selected results were as follows:

Arsenic - BDL (3.2 μg/l)
TDS - 5,800 mg/l
Chloride - 2,700 mg/l
Sulfate - 840 mg/l
pH - 7.43
Color - 4 pcu

Recharge water is treated with pressure filtration and chlorination (3-4 ppm). A pH adjustment is used to lower the pH of the water by 0.5 to 1 pH units prior to injection. Based upon 2002 operating records, typical recharge rates in the three ASR wells are about 1000, 1100 and 750 gpm, respectively, for ASR wells 1, 2 and 3. Specific injectivities during well recharge are 36, 39 and 24 gpm/ft, respectively. Injection pressures range from 36 to 44 psi at the wellhead.

Six cycles were conducted on Well 1 between July 2, 1997 and June 20, 2000. A single sample was analyzed for arsenic on April 3, 2001, indicating a concentration of less than 3 μg/l. This sample was obtained during the recovery portion of Cycle 6 when arsenic was determined to be a problem at other Florida ASR sites.

Cycle 7 recharge, which was the first recharge cycle for all three wells, began on September 1, 2001, and continued until December 11, 2001. During this time 326 MG were recharged into all three wells, distributed as follows: Well 1 – 100 MG; Well 2 – 130 MG; Well 3 – 95 MG. Water was recovered from each well between April 2 and June 25, 2002, until the chloride concentration of water from wells ASR-2 and ASR-3 reached 350 mg/l. Well ASR-1 recovered 55 MG. However, the chloride concentration remained near 250 mg/l. Well ASR-2 recovered 49 MG, and Well ASR-3 recovered 38 MG prior to reaching the site limit of 350 mg/l chlorides. The storage period between recharge and recovery was 112 days.

Cycle 8 recharge for all three wells began on July 22, 2002 and ended December 31, 2002. Total volume injected was 670 MG, distributed as follows: Well ASR-1 – 239 MG; Well ASR-2 – 259 MG; Well ASR-3 – 173 MG. Recovery began May 1, 2003 and continued until August 13, 2003. Total volume recovered was 147 MG, of which 52, 49, and 45 MG were recovered from each of the wells, respectively. Recovery was terminated due to the start of the rainy season. The recovered chloride concentration was only 150 mg/l at the end of this recovery period. Storage period between recharge and recovery was 120 days.

For Well ASR-1, arsenic concentrations have remained below the 10 µg/l level and, in most cases, have been below the detection limit since testing for arsenic began. In 2002, during Cycle 7, water was first recovered from Wells ASR-2 and ASR-3. The historic data for these wells show that in the first year of recovery water recovered from Well ASR-2 had an initial arsenic concentration of 30 µg/l. This level rapidly dropped to 19 µg/l prior to shutting in the well. Approximately 40 MG of water were recovered from this well. The arsenic concentration in Well ASR-3 started at 49 µg/l upon initial recovery, and then dropped to approximately 20 µg/l by the end of this cycle. Approximately 38 MG of water were recovered from this well.

In 2003, during Cycle 8, no arsenic was detected in the recovered water from Well 1. The arsenic concentration in Well 2 started at or below the detection limit and then climbed to 11 µg/l before falling back to below detection limits by the time recovery was concluded for this well. Similarly, the arsenic concentration for Well 3 started at or below the detection limit and then rose to a maximum of 9.5 µg/l. By the time this well was shut-in, arsenic levels were again near or below the detection limit.

Cycle 9 ended in July 2004. Arsenic levels were at or near the detection limit for all water recovered from Well 1 in this cycle. Arsenic levels in Well 2 started out at or below the detection limit and then rose to a high of 8.2 µg/l before falling back to at or below the detection limit prior to ending the cycle. Similar results were obtained for Well 3. In water recovered from Well 3, the arsenic concentration was at or below the detection limit initially, rose to a maximum of 10 µg/l near the middle of recovery, and then fell back to near the detection limit at the end of recovery.

Monitoring well DZ-1 is completed in the storage zone at a lateral distance of 375 feet from Well 1. Measured arsenic concentrations in this well have remained less than 3 µg/l. Water quality response for other constituents suggests that fresh water reached this monitoring well during the cycle testing. Arsenic concentrations have essentially remained below the detection limit in all of the other three monitoring wells. There is no indication that the injected water has reached any of these other wells, which are at distances of 750 to 2,750 feet.

Summary Analysis of Marco Lakes ASR Wellfield Water Quality Results

The data for this site show that the arsenic concentration in recovered water approached the previous limit of 50 µg/l for the first ASR cycle in the new wells, but concentrations in subsequent cycles for these wells has, with a few exceptions, remained below the current limit of 10 µg/l.

The maximum arsenic concentrations in the recovered water appear within the geographic boundary described by the recovered water as indicated by the rise and fall of the arsenic levels during recovery and by the lack of detection of arsenic in the ASR zone monitoring well, DZ-1, which is located within 375 feet of Well 1. The data suggest that the arsenic remains within a band that is less than 375 feet surrounding these wells.

12.0 Collier County, Corkscrew

The Corkscrew ASR wellfield stores treated drinking water in the mid-Hawthorn Formation, a confined artesian limestone aquifer at depths of 253 to 397 ft. Typical storage zone thickness at individual wells is 50 to 70 ft. Five ASR wells are in operation, ASR-1 through ASR-5. Three monitor wells are constructed in the storage zone, two at distances of 250 ft from each of two ASR wells and one at 450 ft. from a third ASR well. Two other storage zone monitor wells are located too far from the ASR wellfield to be useful for geochemical monitoring purposes. Typical well recharge rates with all five wells in operation are 0.8 to 0.9 MGD while recovery rates are 1.4 to 1.8 MGD.

Based on several pumping tests on different wells, aquifer hydraulic characteristics are as follows:

Transmissivity - 15,000 to 45,000 gpd/ft
Storativity - 4 x10^{-5}
Leakance - 3 x 10^{-4}/day

Five ASR cycles were conducted prior to May 2004, the first three on Well ASR-1 and the last two with the expanded wellfield comprising all five wells. The first three cycles occurred in 1995, 1996 and 1997, respectively, storing 1, 31 and 26 MG and recovering 3, 23 and 20 MG. The last two cycles were each approximately one year in duration and occurred between August 2000 and May 2002, storing 95 and 107 MG, respectively, and recovering 82 and 107 MG from all five ASR wells. Chloride concentrations at the end of recovery in each cycle were 44 and 43 mg/l, respectively, essentially the same as background concentrations in the storage zone. Cumulative net storage volume at the end of the second large cycle was 27 MG.

Background water quality in the storage zone can be inferred from samples collected from the monitor wells near the beginning of the 2002 ASR cycle. TDS is estimated at between 254 and 384 mg/l. Hydrogen sulfide was between 0.1 and 1.6 mg/l. pH was between 7.9 and 8.3. Chloride was between 40 and 51 mg/l.

Samples were collected from all ASR and monitor wells on April 2 and April 16, 2001, approximately mid-way through recovery of the first large cycle with all five wells. Duration of the storage period prior to sampling is not known but is probably several months. Arsenic concentrations from the five individual ASR wells in the first sample ranged from less than 3 µg/l to 5 µg/l. In the second sample (April 16) they ranged from 4 to 8 µg/l. Composite samples of the recovered water ranged from 3 to 6 µg/l. In the monitor wells arsenic concentrations were measured only on April 16 and were less than 3 µg/l.

On April 30 and May 14, 2001, toward the end of the recovery period on the first large cycle, additional samples were collected. Arsenic concentrations in the five ASR wells ranged from <3 to 10 µg/l. In the monitor wells, concentrations were all less than 3 µg/l.

On February 13, 2002, a sample was pumped from each of the five ASR wells during the storage period between recharge and recovery, after 79 days of storage. This was during the second large cycle. Arsenic concentrations ranged between less than 3 μg/l and 3 μg/l.

At the beginning of recovery for the second large cycle on March 20, 2002, arsenic concentrations for the five ASR wells ranged from less than 3 to 11 μg/l, with a composite sample averaging 9 μg/l. The storage period at that point had extended for 112 days. On March 27 a composite sample was 17 μg/l. Composite weekly samples during April ranged from 4 to 9 μg/l. Three weekly composite samples collected during May were 17, 6 and 8 μg/l, in that order. Individual ASR wells indicated arsenic concentrations of 17, 10, 4 and 3 μg/l for the last sample when the composite was 8 μg/l. One well was not tested. Monitor well samples during April and May 2002 showed <3 μg/l for arsenic.

Operations have continued since that time. Informally we understand that the cycle ending in Spring 2004 yielded similar results to the previous cycles. Monthly operating records have been reviewed for the period May 2004 to July 2005. Recovery ended from all five ASR wells during mid-May 2004 with each well having recovered between 33 and 36 MG, a total of 171 MG during the previous cycle. At the end of the recovery period arsenic concentration was 7.1 ug/l in the composite recovered water flow from all ASR wells and was non-detect at MW-C, 250 feet away from ASR-1. Corresponding arsenic concentrations at individual ASR wells ranged from 1.2 to 15.6 μg/l. Well ASR-1 had the highest concentration.

Recharge for the next cycle started in mid-July 2004 and continued until the end of January 2005 . No arsenic was detected at the monitor wells. Storage volumes at the five ASR wells were 49, 52, 65, 61 and 64 MG, totaling 290 MG. Recovery began in mid-February and continued until the end of June, recovering 271 MG. Arsenic concentrations in the recovered water increased slowly, reaching 8.8 μg/l at the end of recovery. Individual ASR well arsenic concentrations ranged from 6.2 to 14.2 μg/l at the end of recovery, with ASR-1 having the highest concentration. No arsenic was detected at the monitor wells during recovery. It is pertinent that the storage volume in this cycle was considerably larger than for previous cycles, developing some new portions of the aquifer around each ASR well.

Summary Analysis of Corkscrew ASR Wellfield Water Quality Results

Arsenic does not appear to be a significant issue at this site, at either the ASR wells or the observation wells.

Monitor well arsenic concentrations are consistently lower than ASR well concentrations, typically showing <3 μg/l. It is not easy to differentiate whether or not ASR recharge water is reaching the monitor wells since little differential in water quality occurs for chloride and TDS, which are often used as conservative tracers. The relatively close proximity of the monitor wells and the storage volumes for each of the large cycles suggest that some of the recharge water probably reached the monitor wells. Unless it can be confirmed that recharge water reached the monitor wells, little can be concluded regarding arsenic attenuation with distance, other than that no elevated arsenic concentrations showed up at monitor well distances of 250 feet.

Compositing the samples helps to meet drinking water standards, smoothing out spikes from individual wells.

Since the aquifer is fresh, the need for development of a buffer zone to achieve acceptable recovery efficiency (based on TDS considerations) is not evident. Building a small buffer zone around each well to induce arsenic attenuation is not necessary since water quality meets drinking water standards for arsenic.

Storage periods associated with these cycles were several months' duration. The significance of storage duration as a mechanism for arsenic attenuation, if any, is not evident.

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Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage Recovery Activities

Task 4 - Technical Memorandum
Modeling

Prepared for

Southwest Florida Water Management District

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May 4, 2006

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Task 4 – Modeling

The purpose of Task 4, Modeling, as discussed in the project scope of work, is as follows:

> *Discuss arsenic mobility and attenuation processes under subsurface physical, geochemical and microbial conditions occurring in this region and a reasonable range of scientific assumptions regarding arsenic speciation and microbial activity. Discuss the applicability, input data requirements, strengths and weaknesses of up to three currently available computer models to simulate arsenic mobilization and attenuation trends under a wide range of water quality scenarios.*

4.1. CONCEPTUAL GEOCHEMICAL AND HYDROGEOLOGICAL MODEL FOR AQUIFER STORAGE AND RECOVERY (ASR)

The basis for our conceptual model is a division of the storage zone into 3 distinct sub-zones, the "proximal" zone, the main storage zone and the buffer zone. The extent and relative proportions of these zones vary based upon aquifer characteristics and operational parameters, such as, (1) water quality/composition of the native groundwater, (2) water quality/composition of the injected water, (3) volume injected and recovered and (4) length of storage.

Immediately surrounding the borehole or screened section of the ASR well is the "proximal" zone, where pore flushes are at a maximum. This zone typically extends no more than a few feet to a few tens of feet surrounding the well. This is a zone of potentially high geochemical and microbial reactivity, potentially driven by a high oxygen reduction potential (ORP), possibly high nitrate content, and relatively high dissolved organic carbon (DOC) content of the recharge water. Nutrients such as ammonia and phosphate, and small but important traces of ferric hydroxide may also be present in the recharge water due to pretreatment processes. Water quality gradients in this zone are potentially steep, with ORP typically dropping from positive to negative in a relatively short period of time. pH values also may vary, typically lower near the well and increasing away from the well. Velocities decline as the recharge water moves away from the well into the aquifer, providing some opportunity for settling out of any entrained particulates and sorption of colloids. Microbial metabolism products, corrosion and precipitation products accumulate in this zone. Desorption, adsorption and other processes also occur. A geochemical "rolling front" may occur in this zone, mobilizing metals during each successive cycle and moving them away from the well a short distance during recharge, where they adsorb again. Microbial processes contribute to the mobilization and attenuation of metals and other constituents.

Beyond the "proximal" zone is the main portion of the storage zone further away from the well. In this main portion geochemical and hydraulic gradients are reduced, the number of pore volume flushes during each ASR cycle declines and water quality changes are less pronounced. During the initial ASR operating cycle water quality changes are at a maximum. With successive cycles at approximately the same storage and recovery volumes the storage zone around the well gradually becomes purged of ambient groundwater. Geochemical and microbial reactions tend to be less significant. Typically after about three to six cycles at the same storage volume, the storage zone achieves close to a geochemical and microbial equilibrium. This process is accelerated if a portion of the stored water is left in the well during each of the first few cycles.

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. Depending upon the differences in water quality between the stored water and the ambient groundwater, water quality changes in the buffer zone may be substantial. It is often important to not recover the buffer zone during extended recovery since water quality deterioration may tend to occur rapidly, particularly in brackish storage zones.

During ASR recovery, the first flush of water recovered may contain particulates and biosolids, as discussed above. Depending upon well casing materials of construction, this may last from a few minutes to perhaps two hours. The subsequent water, after a few operating cycles at approximately the same volume, or after formation of the buffer zone, is usually relatively uniform in quality. Due to the long flow path through the aquifer for water recovered toward the end of an extended recovery period, any opportunity for desorption may tend to lead to steadily increasing concentrations of desorbed compounds in the recovered water along the flow path toward the well, reaching a peak concentration and then decreasing as desorption proceeds to completion. Conversely, microbial processes may augment, inhibit or override desorption processes. The science has yet to be developed regarding the complex interplay of microbial and geochemical processes occurring during ASR storage. These processes can be inferred from other investigations and research regarding bank filtration, wastewater treatment and soil aquifer treatment (SAT) processes however there are several unique aspects relating to ASR systems, understanding of which facilitates analysis of ASR water quality data:

- Contact time between the stored water and the aquifer matrix is typically weeks to months for ASR wells compared to hours to days in SAT systems, some bank filtration wells, and wastewater treatment plants.

- Most, but not all, ASR wells are in deep, confined anoxic aquifers under reducing to highly reducing conditions. A few ASR wells are in deep water table aquifers with low level oxidizing conditions. These sites tend to occur in the southwestern United States.

- Flow in ASR wells is, by definition, in two directions, away from the well during recharge and back toward the well during recovery. The lateral reach of the stored water “bubble” typically does not extend more than a few hundred feet from the ASR well.

- Many ASR wells store water in brackish or saline aquifers, or aquifers that have at least one water quality constituent present in the ambient groundwater at concentrations that would require treatment to achieve drinking water standards.

Three models have been selected for consideration as to their likely ability to simulate arsenic mobilization and attenuation during the complex array of geochemical and microbial processes occurring underground during ASR storage. These models are addressed in the following sections.

4.2 EVALUATION OF THE GEOCHEMIST'S WORKBENCH MODELING CODE TOWARDS ASSESSING ARSENIC MOBILITY IN AQUIFER STORAGE AND RECOVERY (ASR) SYSTEMS IN THE UPPER FLORIDAN AQUIFER

The Geochemist's Workbench is a set of interactive software tools for solving problems in aqueous geochemistry, including those encountered in environmental protection and remediation, the petroleum industry, and economic geology. The Professional version of the program consists of a platform of different modules that address the various aspects of geochemical reactions:

1. The module **Rxn** balances chemical reactions and calculates equilibrium constants, temperatures, and equations
2. The module **Act2** generates stability diagrams on activity, Eh, pe, pH, and fugacity axes
3. The module **Tact** generates temperature-activity and temperature-fugacity diagrams
4. The module **SpecE8** computes species distributions, mineral saturation, and gas fugacity in aqueous solutions
5. The module **Aqplot** projects **SpecE8** calculations in a variety of ways, including ternary, Piper, Stiff, Durov, Schoeller, and ion balance diagrams
6. The module **React** traces reaction paths involving fluids, minerals, and gases. **React** can account for kinetic rate laws, isotope fractionation, microbial metabolism and growth, and much more
7. The module **Gtplot** displays the results of **React** simulations
8. The module **X1t** simulates 1D reactive transport
9. The module **X2t** simulates 2D reactive transport

To model arsenic mobility in ASR systems one must consider the source of As (As-rich pyrite), the reactivity of that pyrite with injected water over the storage (reaction) period, and the secondary mineralization and sorption characteristics, which potentially affect released arsenic mobility. A thermodynamic framework for the oxidation of pyrite can be established and a forward reaction model, found in the Geochemist's Workbench (GWB) React code, would be well suited to the task to assess how much pyrite can be oxidized (dissolved) by a certain amount of injection water containing oxygen as the primary oxidant. This can be modeled on a mass basis and/or temporal scale. Incorporation of trace/minor levels of arsenic into pyrite for consideration of this release process could be done with the existing thermodynamic database by either using different masses of pyrite and arsenopyrite or adjusting the reaction to include a specific percentage of As in pyrite based on field results by adjusting the S^{2-} stoichiometry and adding As. Arsenic is present in arsenopyrite and loellingite in the As^{-1} form, which is not available as a basis species in this database (Jones and Nesbitt, 2002; American Mineralogist V87 p 1692-1698). The reaction in the Lawrence Livermore National Laboratory (LLNL) thermodynamic database for arsenopyrite implies a redox reaction between the As^{-1} and S^{-1} in arsenopyrite and represents As and S release as HS- and an equal combination of As^{-3} and As^{5+} to make an equivalent amount of As^0 which then redistributes via equilibrium speciation. An easier way to rewrite this reaction for trace amounts of arsenic in pyrite could be to not consider the electron transfer of As to S to form sulfide. Instead write the reaction of As-rich pyrite by adjusting the arsenic stoichiometry to account for a total As valence of -1 in the mineral, to get the appropriate reaction, which would correspond to basis and redox species in the LLNL database such as:

$$FeS_{1.9}As_{0.1} + 0.1\ H_2O + 0.075\ H^+ = Fe^{2+} + 0.95\ S_2^{2-} + 0.075\ AsH_{3(aq)} + 0.025\ H_2AsO_4^-$$

This approach makes the assumption that the thermodynamic properties of the pyrite will not be changed significantly by the presence of trace/minor arsenic, but at low As levels this should be a reasonable assumption. In fact, given the goals of the modeling experiment, even several order-of-magnitude differences in the equilibrium constant will not make significant differences in the mass calculations as the O_2 equilibrium will be well lower than anything actually measurable and will result in mass changes in nano- to pico-molar ranges. The kinetics of As release from pyrite however, are not as straightforward because As-enriched zones in a crystal of pyrite have the capability to react in a galvanic manner. The As-rich material serves as an anode and is oxidized, while reduction occurs at the more pyritic portion (cathodic) – serving to release more arsenic early in the reaction progress. This could potentially be addressed as well in the GWB, but one would have to play a mass ‘trick’ in which the amount of arsenic in pyrite is distributed by a combination of pure pyrite and arsenopyrite, where the rate constant of arsenopyrite is faster.

In summary, there are 2 methods for representing the arsenic in pyrite at these sites: adding a new reaction for trace As in pyrite, or by using a mass ‘trick’. The former might be preferable in terms of the output, allowing for a more general but potentially more accurate picture of mass balance for iron and arsenic, while the latter is both more simple and more easily configurable to investigate kinetic effects associated with galvanic interactions.

The input of oxygen content or other oxidants into the reactive water is an additional parameter of importance. The equilibrium concentration of oxygen can quite easily be used for these calculations assuming a closed system. It is necessary to model in a closed system because leaving it open would oxidize everything as the calculation constantly re-equilibrates with atmospheric O_2. Other oxidants of concern would have to be input into the database if they are to be considered. Ozone and chloramines in particular are potentially important parameters to consider, and thermodynamic data are available and can be added to the database. It would be prudent here to consider ozone as a source of oxygen rather than a truly direct oxidant, therefore the addition of ozone should be as a dissociation reaction to O_2. To consider ozone as a direct oxidant would require rewriting a host of reactions, and thermodynamically this is not necessary. The kinetics of the argument are again a very different picture and in order to consider kinetic effects additional sets of equations and rate data would have to be added. Since these data are not readily available for all possible reactions some experimental work may be required, particularly for the chloramines.

In a discussion of kinetics of a set of environmental reactions, the role of microorganisms becomes pivotal. Both water and potential energy are available in the ASR system, which is an almost certain guarantee that microorganisms will be taking advantage of that potential energy and accelerating the reactions to some degree. Sterilization reactions in the subsurface may limit microbial activity, but there is little chance this will stop microbes completely. GWB is capable of modeling the microbial component of this system as well, though the effects of sterilization as an inhibition is not represented well in the microbial kinetic models used. Several of the potential kinetic models for microbial respiration are dependant on biomass, which can be set.

Once the initial set of calculations is performed in GWB, the next logical step will be to consider the speciation and secondary mineral formation that could potentially occur. GWB, as other programs, will re-speciate the solution at equilibrium with some set of pH and redox conditions. This can be done in several ways, the most logical would be to model this as a closed reaction path, in effect starting with a concentration of $O_{2(aq)}$ and letting it come to equilibrium, the output of this can also be integrated onto an Eh-pH stability diagram for a graphical picture of system approach to stability.

The formation of secondary minerals during ASR operation could also be of importance, particularly in a flow system where additional oxygen can interact with liberated Fe from pyrite and leading to the precipitation of hydrous ferric oxides (HFO), such as ferrihydrite. Thus a significant component of arsenic mobility in such instances is the sorption of As onto HFO surfaces. GWB can incorporate surface sorption modeling into these calculations to assess both the formation/dissolution of these minerals and the concomittent sorption/release of arsenic from them. Several models of surface complexation can be investigated, including the two-layer surface complexation model (after Dzombak and Morel). The GWB database includes data for HFO surface sites including arsenic sorption, but log K values are only estimates. Thus the best approach here is to choose the most pertinent sorption study model and parameters to tailor the database with, including up-to date data on arsenic sorption parameters. Additionally simple batch adsorption experiments that represent ASR conditions may provide the necessary parameters.

In summary, the GWB set of programs is an effective tool to investigate conceptual models for arsenic release and mobility in ASR systems. In particular the combination with 1D and 2D reactive transport modeling tools in GWB Professional will facilitate the combination of geochemical and hydrogeological parameters to simulate reactions and evolution along a flow path such as: (1) transport by advection, diffusion and dispersion, (2) fixed and evolving flow rates and patterns, (3) saturated and unsaturated flow, (4) permeability constant or varying, (5) flexible boundary conditions on all sides of the domain, (6) heterogeneous domains and initial conditions, and (7) simulate injection and production wells. The graphical interface and ability to overlay forward reaction modeling progress on Eh-pH stability diagrams coupled with speciation and plotting of real sample data will provide a very elegant and simple method of ascertaining model viability in the face of improving sampling, characterization, and understanding of the dynamics of this system. The mass balance calculations, as part of these closed system calculations will provide estimates of arsenic potentially released from pyrite and potential insight on the role of secondary reactions, which may affect As mobility. The incorporation of microbial metabolism, 'tricks' for representing galvanic effects, and some incorporation of ozone into the model additionally make the GWB package a very versatile tool for tackling some more of the details concerning the kinetics of these reactions. Overall a set of models using GWB can address a host of questions, test a number of models based on field and lab experiments, and provide mass balance estimates of arsenic release required for management decisions.

4.3. EVALUATION OF THE EASY LEACHER (EL) MODELING CODE TOWARDS ASSESSING ARSENIC MOBILITY IN AQUIFER STORAGE AND RECOVERY (ASR) SYSTEMS IN THE UPPER FLORIDAN AQUIFER

Easy-Leacher (EL) is a 2D reactive transport code, developed by Stuyfzand (1998, 2005) and set in an EXCEL spreadsheet. It combines chemical principles with empirical rules in an expert system. These rules are based on 30 years of intensive Kiwa research on numerous experimental and productive sites with Artificial Recharge (AR), using (1) either basins or injection wells with remote recovery, and (2) River Bank Filtration (RBF), in the Netherlands, Germany, UK, Sweden, Denmark and Australia. EL is relatively easy to apply (spreadsheet). The leaching of aquifers is important because of high fluxes in AR and RBF systems. In EL, the quality of the input (e.g. river or drinking water), flow and sludge conditions are assumed constant since the start of AR or RBF.

The model is mainly based on:

1. Microsoft's spreadsheet EXCEL for Windows (≥95);
2. the straw approach, which simplifies 3D groundwater flow into a 2D set of maximum 50 flow tubes through a maximum of 10 horizontal aquifer layers;
3. hydrological key parameters (from separately run hydrological models or field data), like travel times of water, fluxes in aquifer layers, and admixing of native groundwater;
4. equilibrium of the Ca-CO_2-H_2O system (if relevant);
5. the chemical mass balance approach and the concept of retardation;
6. first order decay of organic micropollutants,
7. empirical rules for the sequence of reactions, reaction kinetics and behaviour of specific dissolved species, bacteria and viruses.

By including these empirical rules EL can be considered an expert system. Chemical transport is in fact calculated on the basis of pore flushes (time scale), retardation and leach factors (superimposed on the pore flushes), $CaCO_3$ equilibrium (if relevant), mass balancing and many if/else statements (expert rules).

In 2003 a separate EL model was prepared for a Dutch ASR trial system (EL-ASR-2.0; Stuyfzand et al., 2006). The ‘general’ version for AR- and RBF-systems could not be used, because the hydrology and hydrogeochemistry of ASR systems strongly deviate. In ASR-systems flow is not constant, due to alternating periods of injection, storage and recovery by the injection well. And (sub)oxic infiltration water, that became anoxic by redox reactions with the aquifer, may return from the outer, reduced zone of the injected bubble into the oxidized inner zone (close to the ASR well) during backpumping. This return can lead to significant sorption processes, which do not occur during steady flow from an infiltration facility to a separate recovery point at some distance.

The calculations of aquifer leaching and water quality changes during the injection phase of ASR follow the general EL model for all AR- and RBF-systems. The only difference is, however, that the leaching and water quality changes are calculated for 11 points at different distances, for each aquifer layer (max = 4), all of them distributed within the ASR-bubble. The leaching progress during each injection phase is simulated by simply adding up the effects of each phase and neglecting any leaching during storage and any redox reactions with adsorbed or dissolved Fe^{2+}, Mn^{2+} and NH_4^+. During storage the hydrogeochemical reactions are, for the sake of simplicity, limited to (a) the oxidation of pyrite and soil organic material (SOM) where O_2 and NO_3 survived transport in the aquifer, and (b) the dissolution of hydrous ferric oxides (HFO) and siderite (if present). During recovery the water qualities as calculated for the maximum of 44 points are transported back to the ASR well, with the only modification that part of their Fe^{2+}, Mn^{2+} and NH_4^+ concentrations is adsorbed to the oxidized parts of the aquifer around the ASR well to an extent that empirically depends on pH and the number of ASR cycles.

In the current EL-ASR-2.0 model the behavior of arsenic has been matched to experiences with AR in deep anoxic, sandy, pyritiferous aquifers in the Netherlands (Stuyfzand, 1998a, 2001), and with ASR in a similar aquifer at the Herten pilot (Stuyfzand et al., 2006). The main mobilization process on those sites is the oxidation of pyrite, as in Florida. However, ASR operation procedures and geochemical and hydrogeological conditions in Florida differ substantially from those in the Netherlands, thus limiting the use of the EL-ASR-2.0 model in Florida. Particularly the following conditions cannot be accounted for:

1. the infiltration water dissolves gypsum on many sites, thus significantly increasing the sulfate concentration. During backpumping this SO_4^{2-} can desorb the As (probably as arsenate);
2. DOC and PO_4 concentrations in the recharge water in Florida are higher. They compete for sorption sites and thus reduce the fraction of arsenate that will adsorb;

3. Water temperature is higher in Florida. This normally reduces the extent of sorption;
4. Flow is concentrated in karstified zones and along bedding planes and fractures where pyrite contents are higher than in the low primary porosity zones (Price & Pichler, 2006);
5. pH of both the native groundwater and recharge water is somewhat higher. This reduces the tendency of arsenate to adsorb;
6. the addition of oxidants for disinfection. This raises the oxidation rate of pyrite and arsenite, and thus the conversion of immobile As in pyrite into more labile As in ferrihydrite

In addition, complications are expected due to: (a) the formation of an ASR-proximal zone with a raised microbiological activity, (b) the input of HOF (ferric hydroxide) particles deriving from water pretreatment processes, (c) the formation and transport of HOF particles deriving from pyrite oxidation, and (d) the formation of As roll front deposits. Thus, it can be concluded that EL-ASR-2.0, although an extremely powerful model, has significant limitations modeling arsenic behavior during ASR applications in the Upper Floridan aquifer.

4.4. EVALUATION OF THE PHT3D MODELING CODE TOWARDS ASSESSING ARSENIC MOBILITY IN AQUIFER STORAGE AND RECOVERY (ASR) SYSTEMS IN THE UPPER FLORIDAN AQUIFER

The computer code PHT3D couples two existing and widely used computer programs, the solute transport model MT3DMS (Zheng and Wang, 1998) and the USGS geochemical code PHREEQC-2 (Parkhurst and Appelo, 1999). The coupled model forms a powerful and comprehensive three-dimensional reactive multi-component transport model (Prommer et al., 2003), which can handle a broad range of equilibrium and kinetically controlled geochemically reactive processes, including aqueous complexation, redox, mineral precipitation/dissolution, and ion exchange reactions.

Owing to the flexibility of PHREEQC, reaction networks can be defined quickly within a reaction database file, which allows PHT3D to act as a modeling toolbox that can be efficiently used to develop, adapt and apply site-specific and contaminant-specific reactive transport models. PHT3D uses the original PHREEQC database files and format for the definition of the geochemical reactions. Therefore it is possible to append, modify or exchange reaction databases, depending on the modeling task. Readily available databases include (i) the original PHREEQC database (ii) MINTEQ database (iii) WATEQ database and (iv) the LLNL database. The reaction databases contain and define primarily equilibrium reactions while kinetic reactions will in most cases need to be defined by PHT3D model users.

An important feature of the transport solver in PHT3D is that it includes several different numerical solution techniques for simulating advective transport. In particular the particle-tracking based solution schemes can produce results that are essentially free of numerical dispersion in the absence of excessive grid refinement - a common problem among many other models. The transport simulator is fully compatible with MODFLOW. It allows for a wide variety of boundary conditions and features that are needed to build realistic models. A variable density version of PHT3D has been developed recently and is currently evaluated and tested (Langevin et al., 2004; Mao et al., 2006, Bauer-Gottwein et al., 2006; Post and Prommer, 2006). Two graphical user interfaces (PMWIN Pro and Visual Modflow) are currently available to pre- and postprocess PHT3D.

Modeling projects involving PHT3D would normally be carried out in stages of increasing complexity and typically start with preliminary, batch-type model simulations using PHREEQC and flow/nonreactive solute transport modeling with MODFLOW and MT3DMS, respectively. Measured chloride concentrations and/or temperature data might serve as constraints to calibrate the model parameters influencing physical transport processes (see e.g., Prommer and Stuyfzand, 2005; Greskowiak et al., 2006). The PHT3D model was successfully applied to simulate water quality changes and contaminant transport at several managed aquifer recharge sites, including ASR sites:

1. Deep-well injection in Dizon, Netherlands (Prommer and Stuyfzand, 2005)
2. ASR of reclaimed water in Bolivar/South Australia (Greskowiak et al., 2005).
3. Fate of phenazone during artificial recharge in Berlin/Germany (Greskowiak et al., submitted)
4. ASR within a pyritic aquifer, Jandakot/Western Australia (ongoing research)

The key chemical reactions affecting the fate of arsenic are mineral reactions and adsorption/desorption. Both types of reactions as well as the speciation of As in the dissolved phase might be strongly affected by the pH and the redox state of the solution. Both of these key variables can vary significantly in space and time during ASR. A good understanding and detailed, sometimes 3-dimensional simulation of physical transport processes has therefore in previous modeling studies repeatedly shown to be an important ingredient for understanding the evolution of the redox zonation and pH at MAR sites. The initial mobilization of arsenic at the Upper Floridan Aquifer ASR sites is thought to occur as a kinetically-controlled dissolution process. The incorporation of this process requires the definition of a suitable reaction rate expression, similar to previous PHT3D applications, e.g., for pyrite oxidation at the previously discussed deep-well injection site in Dizon, Netherlands (Prommer and Stuyfzand, 2005). Competition with other oxygen consuming processes (e.g., dissolution of other reduced minerals or oxidation of sediment-bound organic matter) will also need to be incorporated through appropriate reaction rate formulations within the PHREEQC/PHT3D database file(s). Reaction rate expressions might also include formulations for growth and decay of microbial groups (see e.g., Prommer et al., 2002, Greskowiak et al., 2005). However, whether such an approach is required and/or can be constrained by measured data will need to be evaluated and decided as part of the actual modeling process.

Adsorption and desorption of arsenic is pH-dependent. To account for this dependency and the competition for sorption sites by other constituents (e.g., by phosphate) a surface complexation model (SCM) approach will most likely be required. A double-layer SCM is available within the PHREEQC framework with default data (constants) being based on the work of Dzombak and Morel (1990). The PHT3D interface to use the PHREEQC SCM has only recently been integrated into PHT3D. Initial benchmark and other test simulations involving As species were successfully carried out. However, the SCM was not yet applied for the interpretation of field-scale data. Application of the SCM capability to ASR sites will ideally incorporate site-specific data that affect the sorption behavior (iron oxide content, batch sorption tests to determine site-specific SCM constants) into the model parameterization process.

4.5. SUMMARY

The two models PHT3D and Geochemist's Workbench Professional (GWB) seem to provide the necessary capabilities to carry out process-based simulations of As mobility during ASR operation. Of the two, GWB is probably better suited for the geochemical modeling, while PHT3D is superior in modeling the hydrogeological aspects such as flow and solute transport. Which of the two is user friendlier is not clear at this time, but GWB is the likely candidate. The geochemical modeling interface of GWB is more intuitive than that of PHREEQC. The Easy Leacher code does not seem to be suited for modeling arsenic behaviour during ASR operations in Florida since arsenic behaviour in Easy Leacher has been simplified to an extent which is useful for various continuous flow systems with artificial recharge but not for the more-complicated ASR systems.

As stated, the ASR system is not a simple one, nor will it be straightforward to fully characterize all occurring parameters and processes. Thus, the models developed with either PHT3D or GWB must be carried out in concert with field and laboratory studies. Only incorporation of field and experimental data into the model can be used to verify our conceptual models of arsenic mobility prior to their use as a truly predictive tool. Good and meaningful model applications and results can normally not be achieved without appropriate effort and in the absence of geochemical and mineralogical data that support the model development and evaluation.

At this time we still lack most of the parameters that are required for a successful modeling effort, such as, quality data for the relevant redox couples (i.e., sulfide/sulfate, arsenite/arsenate, ferrous/ferric iron) and rates for microbial reactions. Only an array of monitor wells spaced closely, stepping away from the ASR well, will provide this information.

Potentially useful data regarding pH variability in the proximal zone close to the ASR well can be readily obtained by frequent sampling, such as every ten minutes, during the first few hours of a recovery period. Only one such test has been conducted to date, at the Bradenton ASR well, indicating a substantial decline in pH around the ASR well at the beginning of recovery. The initial minimum pH of 6.4 at the beginning of recovery increased steadily to a maximum of 7.7 after three hours of pumping, and then declined to around 7.3 with extended pumping for several days. The time required to purge one casing and hole volume was 3.8 minutes. Similar data sets from other ASR wells would be relatively easy to obtain and would shed considerable light on subsurface microbial and geochemical reactions occurring in the ASR storage zone.

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