

Geochemical Modeling of an Aquifer Storage and Recovery Project in Union County, Arkansas

By

Ni Zhu

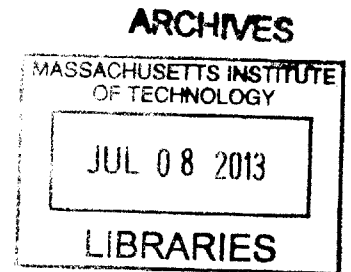
B.ENG. (Honors) of Environmental Science and Engineering
National University of Singapore, 2012

SUBMITTED TO THE DEPARTMENT OF CIVIL AND ENVIRONMENTAL
ENGINEERING IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF ENGINEERING IN CIVIL AND ENVIRONMENTAL ENGINEERING
AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2013

©2013 Ni Zhu. All rights reserved



The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part in any medium now known or hereafter created.

Signature of Author: _____

Department of Civil and Environmental Engineering
May 22, 2013

Certified by: _____

David E. Langseth
Senior Lecturer of Civil and Environmental Engineering
Thesis Supervisor

Accepted by: _____

Heidi M. Nepf
Chair, Committee for Graduate Students

Geochemical Modeling of an Aquifer storage and recovery Project in Union County, Arkansas

By

Ni Zhu

Submitted to the Department of Civil and Environmental Engineering on May 20, 2013 in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Civil and Environmental Engineering

Abstract

The Sparta aquifer in Union County, Arkansas has served as an important potable water supply to the public and industrial sectors in the area. However, increasing water demand and sustained heavy pumping from the aquifer has resulted in the formation of major cones of depression in the area. Union County has been declared as one of the five “critical groundwater areas” in Arkansas due to rapid water level declines, salt water intrusion and overall withdrawals exceeding the rate of natural recharge. To mitigate the adverse impacts of a depleted aquifer, Aquifer Storage and Recovery (ASR) by well injection at the center of the cone of depression is evaluated to address the issue. ASR is the injection of potable water into an aquifer for storage and recovery for use when needed. One important aspect in successful design and operation of ASR systems is to assess the potential geochemical reactions between the injected water and the local aquifer water, which are typically of very distinctive compositions and environmental conditions. The goal of this paper is to use the geochemical modeling software PHREEQC to simulate the scenario of injecting partially treated surface water from Ouachita River into the Sparta aquifer at the city of El Dorado. Key reactions modeled include the initial mixing of the two waters in the proximal zone, surface exchange reactions of the major cations, iron precipitation/dissolution reactions and the oxidizing potential of the injection water. Results from the modeling indicate that reducing the oxygen content of the injection water to enhance geochemical compatibility with the anoxic aquifer water would be beneficial. Arsenic dissolution or attenuation could occur depending on the mixing ratio of injection water to groundwater. Oxidation of ferrous ions is modeled to illustrate the oxidizing potential of the mixed water in the aquifer and the potential of iron precipitation is assessed.

Thesis Supervisor: Dr. David Langseth

Title: Senior Lecturer of Civil and Environmental Engineering

Acknowledgements

This thesis is the culmination of my academic experience at MIT, but more than that, it is also the epitome of unparalleled mentorship, camaraderie and friendship. I feel deeply indebted to the tremendous help and support I have received along the journey.

First of all, I would like to give my greatest gratitude to my advisor, Dr David Langseth, for being such an extraordinary mentor. I would not be able to complete the thesis without his sagacious advice and unwavering support. I consider it an honor to be mentored by him.

I would also like to thank my colleague, Rob Sowby, for generously sharing his knowledge and encouragement at difficult times.

Special thanks goes to Sherrel Johnson and Robert Reynolds, from the Union County Water Conservation Board, for the warm hospitality in guiding our geological trip to the Sparta Outcrops. Immense gratitude also goes to the USGS staff, John Czarnecki, Brian Clark and Tony Schrader for sharing their technical expertise. I would also like to thank Michael Stratton, Operations Manager of Union Power Station for sharing the important data information.

This thesis would not have been possible without the consistent guidance of Dr Eric Adams, direct of the M.Eng Program, and Lauren McLean and Zhandos Orazalin for their technical assistance in installing the software.

Last but not least, my heartfelt gratitude goes to my M.Eng colleagues, whom I have walked through this challenging journey together, and my dear friends in my Christian fellowship for their prayers and love.

Contents

Abstract.....	3
Acknowledgements.....	5
LIST OF FIGURES	8
LIST OF TABLES.....	11
1. Introduction of the Sparta Aquifer	13
1.1 Water use in the Sparta aquifer	16
1.2 Effects of pumping.....	17
1.3 Current aquifer recovery project	19
2 Literature Review	23
2.1 Fundamentals of ASR	23
2.2 Permitting and regulatory work regarding ASR.....	28
2.3 Injection water alternatives and pretreatment	29
2.4 Mixing geochemistry.....	39
2.5 Key contaminants of Concern	41
2.6 Recovery of stored water.....	44
2.7 Geochemical Modeling	46
3. Methodology	47
3.1 Water quality of injection water and the Sparta aquifer water	47
3.1.1 Injection water.....	47
3.1.2 Water quality of the Sparta aquifer	50
3.2 Geochemical modeling - PHREEQC.....	52
4 Results and Analysis	53
4.1 Initial Mixing Model.....	53
4.2 Transport of major cations with equilibrium-phases, exchange and surface reaction.	59
4.3 Speciation of ferrous/ferric oxide.....	64
5. Conclusion	69
APPENDIX A	77
APPENDIX B	78
APPENDIX C	79
APPENDIX D.....	80
APPENDIX E	81
APPENDIX F.....	84

LIST OF FIGURES

FIGURE 1 MAP OF THE MISSISSIPPI EMBAYMENT (USGS, 2013).....	13
FIGURE 2 EXTENT OF SPARTA AQUIFER WITHIN THE MISSISSIPPI EMBAYMENT REGIONAL AQUIFER SYSTEM (MCKEE AND HAYS, 2004).....	14
FIGURE 3 A SCHEMATIC REPRESENTATION OF THE WEST-EAST CROSS SECTION OF THE SUBSURFACE OF THE MISSISSIPPI EMBAYMENT AQUIFER SYSTEM (MCKEE AND HAYS, 2004).....	15
FIGURE 4 CONCEPTUALIZED HYDROGEOLOGIC SECTION OF THE SPARTA AQUIFER IN SOUTHERN ARKANSAS (MCKEE AND HAYS, 2004).....	16
FIGURE 5 GROUND WATER USES IN ARKANSAS COUNTRY FOR THE SPARTA AND ALLUVIAL AQUIFERS FROM 1965 TO 2000 (MCKEE AND HAYS, 2004).....	17
FIGURE 6 CROSS-SECTION OF A WELL IN THE SPARTA AQUIFER, WITH OBSERVED POTENTIOMETRIC SURFACE IN 1997 AND SIMULATED POTENTIOMETRIC SURFACE IN 2027 (MCKEE AND HAYS, 2004).....	18
FIGURE 7 LOCATIONS OF THE MONITORING WELLS IN THE SPARTA AQUIFER RECOVERY PROJECT (FREIWALD AND JOHNSON, 2007).....	20
FIGURE 8 HYDROGRAPH SHOWING WATER LEVELS FOR U.S. GEOLOGICAL SURVEY REAL-TIME WELLS AND INDUSTRIAL CONVERSION TO SURFACE-WATER SUPPLIES (FREIWALD AND JOHNSON, 2007).....	21
FIGURE 9 SPECIFIC CONDUCTANCE AND CHLORIDE CONCENTRATION RESULTS FOR U.S. GEOLOGICAL SURVEY WATER-QUALITY MONITORING WELLS (FREIWALD AND JOHNSON, 2007).....	22
FIGURE 10 GEOGRAPHIC DISTRIBUTION OF ASR WELLS IN THE US BY EPA REGIONS (FROM US EPA, 2009).....	24
FIGURE 11 GRAPHICAL REPRESENTATION OF A TYPICAL ASR WELL (PYNE, 2003).....	27
FIGURE 12 RECOVERY EFFICIENCY OF ASR WELL (SHENG <i>ET AL.</i> , 2007).....	45
FIGURE 13 TREATMENT TRAIN OF OUACHITA RIVER WATER CLARIFICATION FACILITY AND POTENTIAL POINTS OF WATER WITHDRAWAL FOR RECHARGE.....	48
FIGURE 14 LOWER OUACHITA - SMACKOVER WATERSHED -- HUC 080400201.....	50
FIGURE 15 A CROSS-SECTIONAL VIEW OF THE ASR SYSTEM (PYNE, 2007).....	54
FIGURE 16 RADAR CHART REPRESENTATION OF THE MAJOR IONIC COMPOSITIONS IN THE RECHARGE WATER, GROUNDWATER AND MIXTURE WITH 10% OF INJECTION WATER.....	57
FIGURE 17 RADAR CHART REPRESENTATION OF THE MAJOR IONIC COMPOSITIONS IN THE RECHARGE WATER, GROUNDWATER AND MIXTURE WITH 50% OF INJECTION WATER.....	58
FIGURE 18 RADAR CHART REPRESENTATION OF THE MAJOR IONIC COMPOSITIONS IN THE RECHARGE WATER, GROUNDWATER AND MIXTURE WITH 90% OF INJECTION WATER.....	58
FIGURE 19 TRANSPORT AND SPECIATION OF MAJOR CATIONS CA, NA AND AS IN THE AQUIFER WITH 10% INJECTION WATER.....	60
FIGURE 20 TRANSPORT AND SPECIATION OF MAJOR CATIONS CA, NA AND AS IN THE AQUIFER WITH 50% INJECTION WATER.....	61
FIGURE 21 TRANSPORT AND SPECIATION OF MAJOR CATIONS CA, NA AND AS IN THE AQUIFER WITH 90% INJECTION WATER.....	61

FIGURE 22 SPECIATION OF FERROUS/FERRIC CATIONS IN THE AQUIFER WITH 10% INJECTION WATER.....67

FIGURE 23 SPECIATION OF FERROUS/FERRIC CATIONS IN THE AQUIFER WITH 50% INJECTION WATER.....68

FIGURE 24 SPECIATION OF FERROUS/FERRIC CATIONS IN THE AQUIFER WITH 90% INJECTION WATER.....68

LIST OF TABLES

TABLE 1 STRATIGRAPHIC CORRELATION OF THE SOUTHERN PARTS OF ARKANSAS (HOSMAN & WEISS, 1991).....	15
TABLE 2 OPERATING STATUS OF AR AND ASR WELLS IN THE US AS OF FEBRUARY 2009(US EPA, 2009).....	24
TABLE 3 SELECTED CONSTITUENTS IN SOURCE WATERS AND RELATIVE CONCERN (COMMITTEE ON GROUND WATER RECHARGE, NATIONAL RESEARCH COUNCIL, 1994).....	31
TABLE 4 CONSTITUENT CONCENTRATIONS FOR SECONDARY TREATED MUNICIPAL WASTEWATER (TREWEEK, 1985; CROOK, 1992).....	33
TABLE 5 ACHIEVABLE TREATMENT PERFORMANCE FOR KEY WATER QUALITY PARAMETERS WITH VARIOUS COMBINATIONS OF ADVANCED WASTEWATER TREATMENT UNITS (METCALF & EDDY, INC., 1991).....	34
TABLE 6 CONCENTRATION OF POLLUTANTS IN MEDIAN STRENGTH STORM WATER FOR DIFFERENT LAND USE (U.S. EPA, 1983).....	36
TABLE 7 KEY WATER QUALITY PARAMETERS OF PARTIALLY TREATED WATER FROM OUACHITA WATER CLARIFICATION FACILITY.....	49
TABLE 8 CHARACTERISTICS OF SPARTA WATER QUALITY AT EL DORADO.....	51
TABLE 9 COMPOSITIONS OF INJECTION WATER, AQUIFER AND MIXED WATER IN EQUILIBRIUM WITH AQUIFER PHASES FOR THE SPECIFIED INJECTION RATIO.....	56

1. Introduction of the Sparta Aquifer

The Sparta aquifer (Figure 2) is a subsurface geological formation consisting mainly of fine to medium unconsolidated sand, interbedded with silt, clay and lignite. It is located within the Mississippi Embayment Aquifer System (Figure 1) and extends over parts of eight states, Texas, Louisiana, Arkansas, Tennessee, Mississippi, Missouri, Alabama and Kentucky (McKee and Hays, 2004). The aquifer is exposed at the surface at the west and east

boundaries of the embayment, where recharge occurs through the exposed outcrops. Consequently, direction of natural water flow in the aquifer is from the topographically high outcrop area down to the central axis of the basin and then upwards toward the ground surface as illustrated schematically in Figure 3.

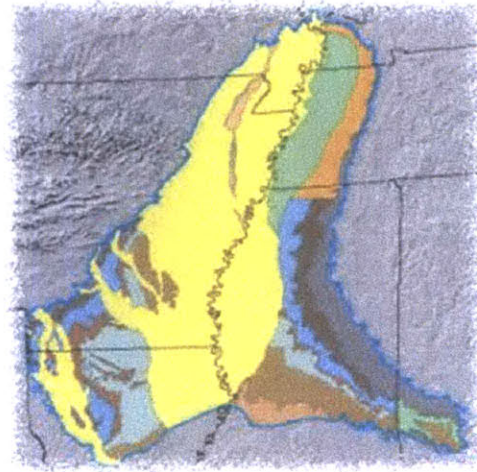


Figure 1 Map of the Mississippi Embayment (USGS, 2013)

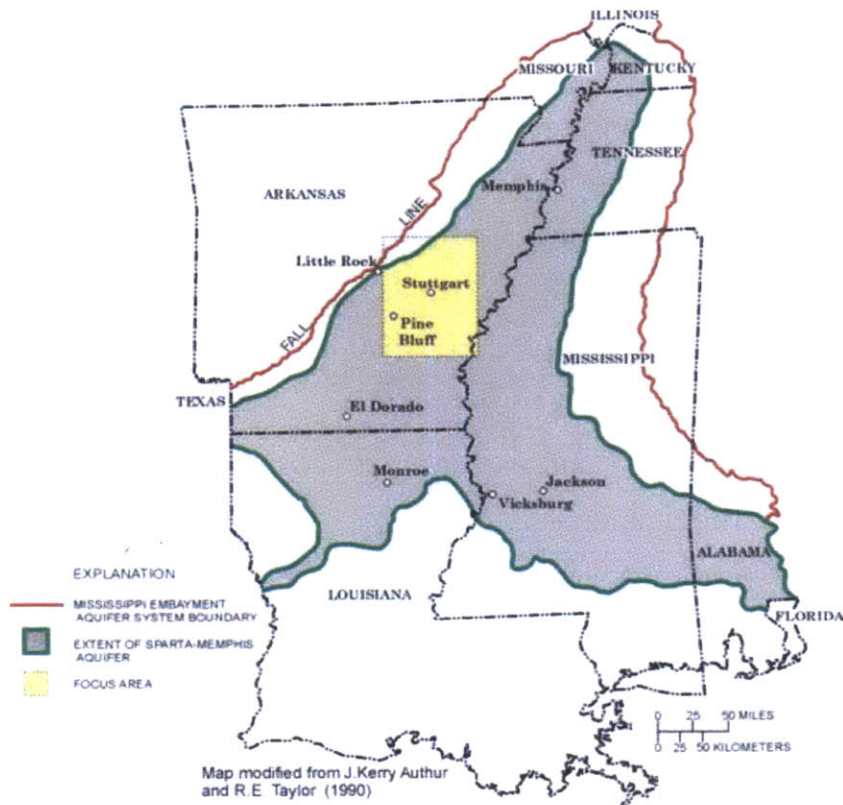


Figure 2 Extent of Sparta aquifer within the Mississippi Embayment Regional Aquifer System (McKee and Hays, 2004)

The Sparta aquifer is considered as an excellent medium for water storage for several attractive hydrogeologic characteristics specific to the Sparta sand. The thickness of the sand increases from 100 feet near the outcrops up to 1000 feet in the central axis (Payne, 1968). The aquifer is underlain by the Cane River Formation and overlain by the Cook Mountain Formation (Table 1). Both of those formations are made up of low-permeability, fine-grained and clay-rich materials, making the Sparta layer a zone of confined flow. The confining layers provide protection to the Sparta aquifer, thus decreasing its vulnerability. In Arkansas, the Sparta aquifer is located from 300 to 700 feet below the land surface with thickness ranging from 500 to 800 feet (McKee and Hays, 2004). Hydraulic conductivity for Sparta aquifer typically ranges from 10 to 200 feet per day (ft/d) with an average of about 70 ft/d in the Mississippi embayment (Hosman *et al.*, 1968). More specifically, at our study area, Union County, the Sparta sand layer can be further distinguished into three units, from the top to the bottom, the white sand, the green sand unit and the El Dorado sand unit (Figure 4) (Hays, 2000). Most of the pumping occurs in the lower El Dorado sand unit.

Albin (1964) reported that the formation of Cook Mountain formation is mainly silt, sand, and lignite and clay and determined that the Sparta sand consists about 95% of quartz [SiO₂] and the mineral compositions of the Sparta sand was found to be comparable to that of the Cook Mountain Formations. Besides quartz, the aquifer consists of the small percentage of biotite, muscovite, coal, and trace amounts of glauconite.

Table 1 Stratigraphic correlation of the southern parts of Arkansas (Hosman & Weiss, 1991)

Group	Formations in the southern part of Arkansas
Jackson Claiborne	Undifferentiated
	Cockfield Formation
	Cook Mountain Formation
	Sparta Sand
	Cane River Formation
	Carrizo Sand
Wilcox	Undifferentiated

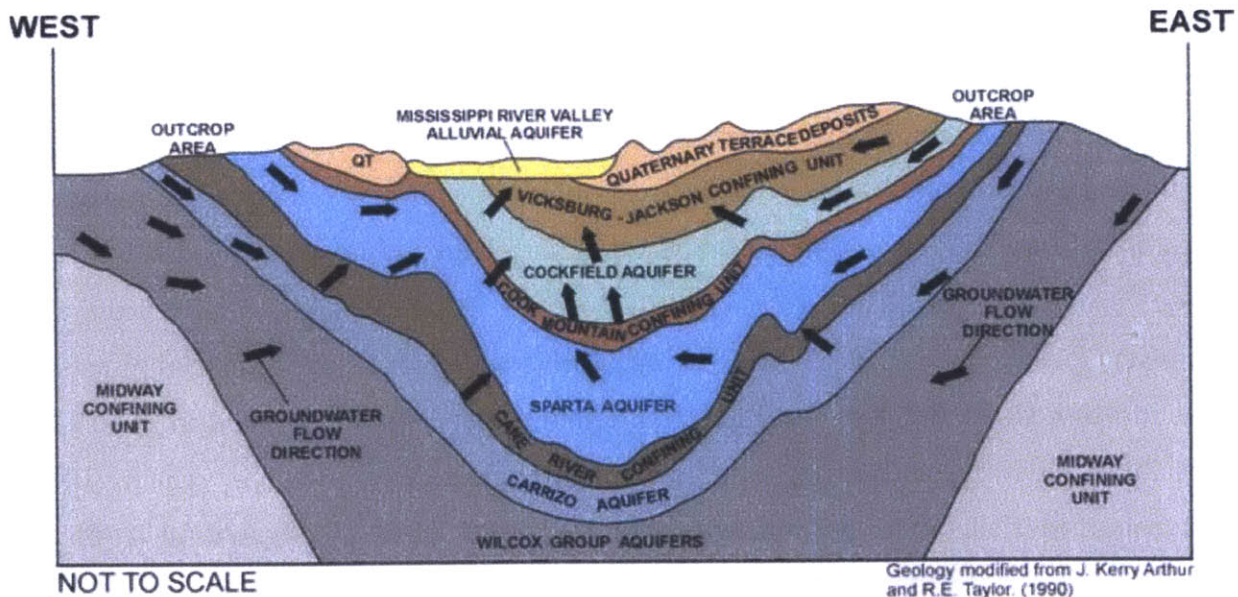


Figure 3 A schematic representation of the west-east cross section of the subsurface of the Mississippi Embayment Aquifer System (McKee and Hays, 2004).

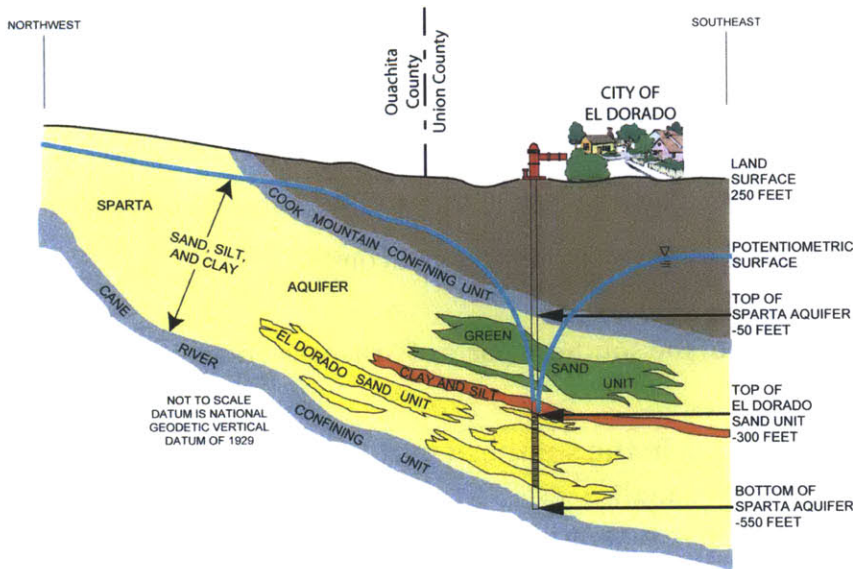


Figure 4 Conceptualized hydrogeologic section of the Sparta aquifer in Southern Arkansas (McKee and Hays, 2004)

1.1 Water use in the Sparta aquifer

The Sparta aquifer has served as an important source of high quality water to major water consumers including municipalities, industries, and as a supplement source to the alluvial aquifer for irrigation in the region. In our study area, Union County, Arkansas, the Sparta aquifer was used to supply all water for industrial and municipal uses before 2004 (Freiwald and Johnson, 2007). Many cities and communities in the southeastern Arkansas used the Sparta aquifer as the primary source of water for public supply, with minimal treatment provided (McKee and Hays, 2004). However, issues of high salinity, iron, and manganese concentrations have limited the use of this water for some industrial purposes at some location (Hosman *et al.*, 1968). Since industrial development started in the 1920s through 2000, the water withdrawal rate from the Sparta aquifer has been increasing. USGS (2004) reported that water withdrawal rate increased from 17 Mgal/d in 1965 to approximately 471 Mgal/d in 2000. (Figure 5).

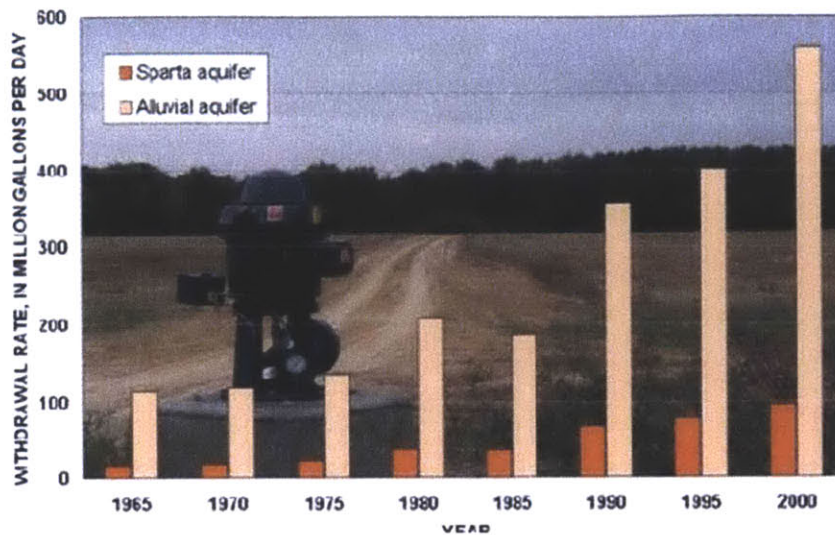


Figure 5 Ground water uses in Arkansas County for the Sparta and alluvial aquifers from 1965 to 2000 (McKee and Hays, 2004).

1.2 Effects of pumping

The long-term heavy pumping from the Sparta aquifer has yielded damaging impacts on the aquifer, including declining water levels, reduced aquifer yield, and water quality degradation in some locations (Hays *et al.*, 1998). It is noted by Freeze and Cherry (1979) that sustained heavy pumping could even lead to potential irreversible compaction of the geological matrix. The impacts can be broadly categorized into hydrodynamic impacts and water quality issues.

1) Hydrodynamics

Groundwater flows down a potentiometric gradient. Pumping causes depletion of water in the vicinity of the well, creating a cone of depression in the potentiometric surface (Figure 6) which alters the direction of groundwater flow. For more detailed discussion on the hydrological impacts of pumping in the aquifer, please refer to Sowby (2013).

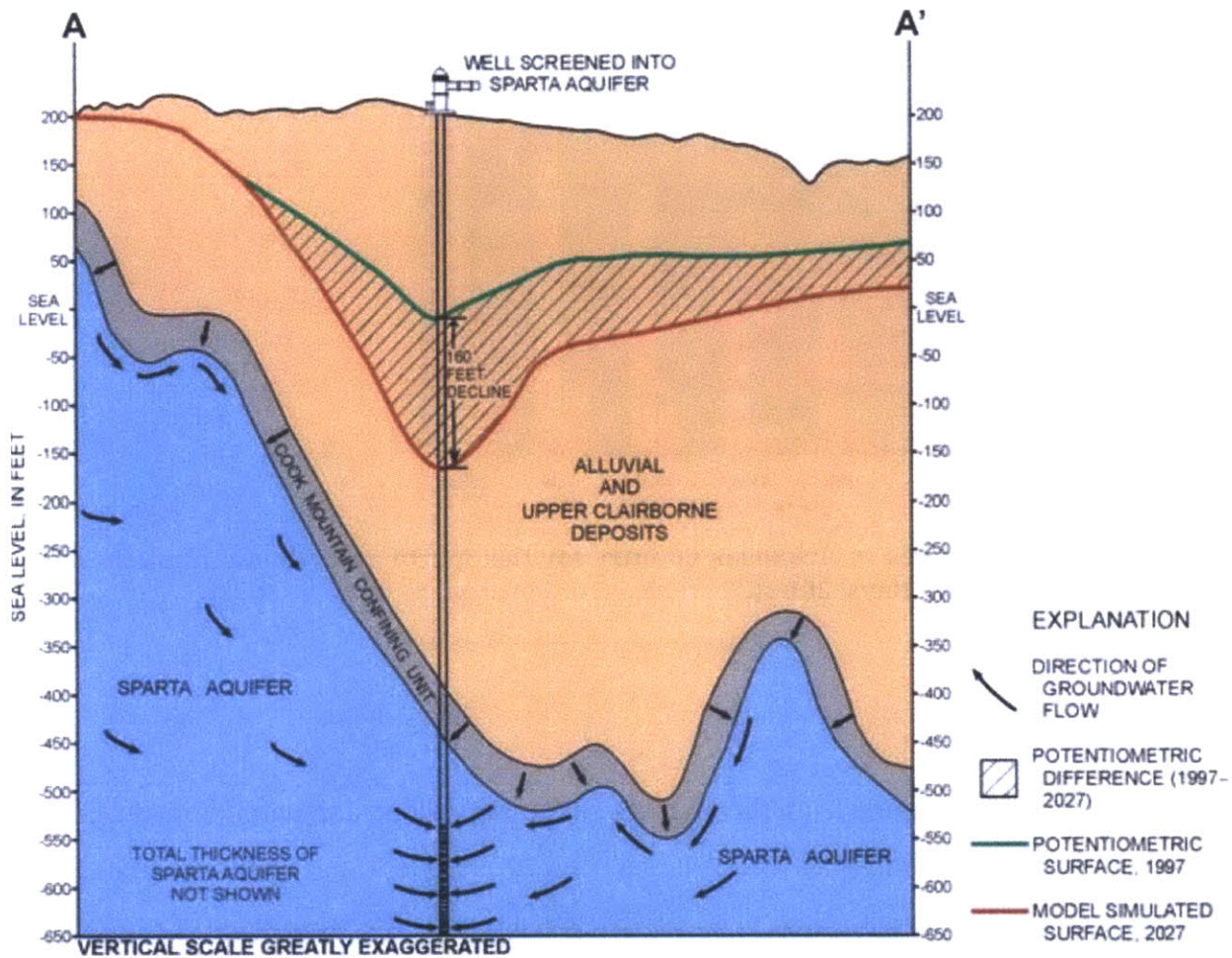


Figure 6 Cross-section of a well in the Sparta aquifer, with observed potentiometric surface in 1997 and simulated potentiometric surface in 2027 (McKee and Hays, 2004)

2) Water quality

Deteriorating water quality is associated with declining water table in the aquifer (Scheiderer and Freiwald, 2006). As freshwater is pumped out the system, ambient water containing saltwater or underlying water with higher salinity can flow into the porous medium to replace the withdrawn water (Scheiderer and Freiwald, 2006). Broom (1984) reports that chloride concentrations in Union County Sparta aquifer wells have been increasing.

The declining water table and degrading water quality in the Sparta aquifer pose a grave concern for long-term sustainability of the groundwater resource in the region. In

1996, the Arkansas Natural Resources Commission designated five counties as “Critical Ground-Water Area” – Bradley, Calhoun, Columbia, Ouachita, and Union, based on the criteria 1) water levels in wells must be above the top of the aquifer formation; or 2) the rate of decline in water levels in wells must not be more than 1 foot per year over a 5-year period. Since then, extensive efforts have been proposed to restore the groundwater budget. From basic mass balance principles, a balanced water budget requires the change in storage equal to the difference of the amount of water entering and leaving the system. Hence, to increase the water storage, the change could come from 1) injecting more water into the aquifer system (natural or artificial recharge); or 2) reducing water withdrawal from the system (Alley *et al.*, 1999).

One approach to optimize the utilization of ground water resources is aquifer storage and recharge (ASR) through well-injection. The aim of this paper is to investigate certain aspects of the viability of injecting surface water to the critical area of cone of depression in the Sparta aquifer for storage and potential withdrawal when needed through ASR wells. The focus of this project is to evaluate potential sources of injection water and the necessary treatment techniques needed to protect the pristine subsurface aqueous and geologic environment. Most importantly, the geochemical compatibility between the two waters and the potential for reuse of the stored water are investigated.

1.3 Current aquifer recovery project

In 1999, the Union County Water Conservation Board was formed to coordinate groundwater conservation measures among the different stakeholders. Since it was set up, the Board has been actively promoting groundwater conservation, water re-use and most prominently, initiated an alternative surface water supply project, the Ouachita River Alternative Water Supply Project to provide water for the three largest industrial users in Union Counties (Johnson, 2006). Since implementation of a clarification plant with a production capacity of 30 MGD/d, the stress on ground water has been greatly alleviated. This relief allows the aquifer to recover gradually through natural mechanisms. To assess the effects of conservation and alternative supply efforts on water level and water quality,

continuous real-time water-level data from eight USGS monitoring wells (Figure 8) in southern Arkansas are monitored and reported at www.ucwcb.org. Periodic water quality data is also provided on the website.

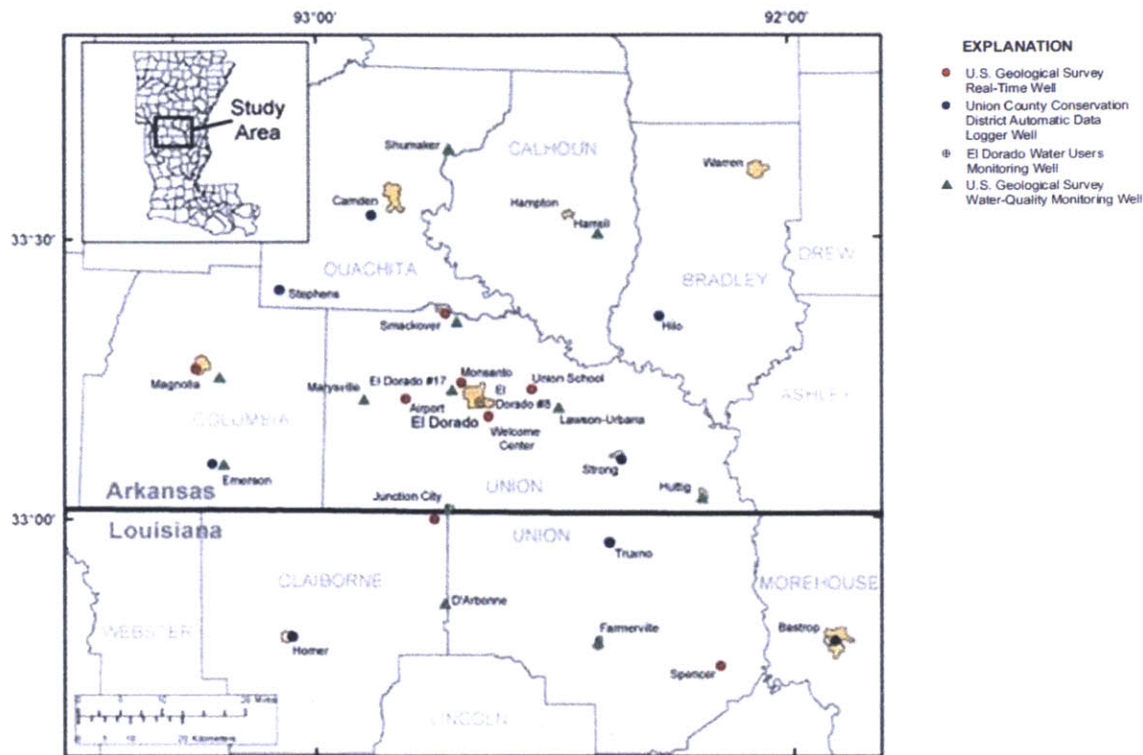


Figure 7 Locations of the monitoring wells in the Sparta Aquifer Recovery Project (Freiwald and Johnson, 2007)

Since the operation of the alternative supply project, results from real-time well monitoring data confirms that water levels in the Sparta aquifer have been rising and simulation results further confirms that water quality should improve and stabilize. Figure 8 illustrates the rise in ground water level since the beginning of the alternative supply project in October 2004. While all the eight monitoring wells responded with a positive result in the aquifer water budget, more noticeable water-level rise is observed at the Monsanto well (49.0 ft) and the welcome Center well (36.1 ft). The smallest rise (1.6 ft) was observed at Spencer, Louisiana.

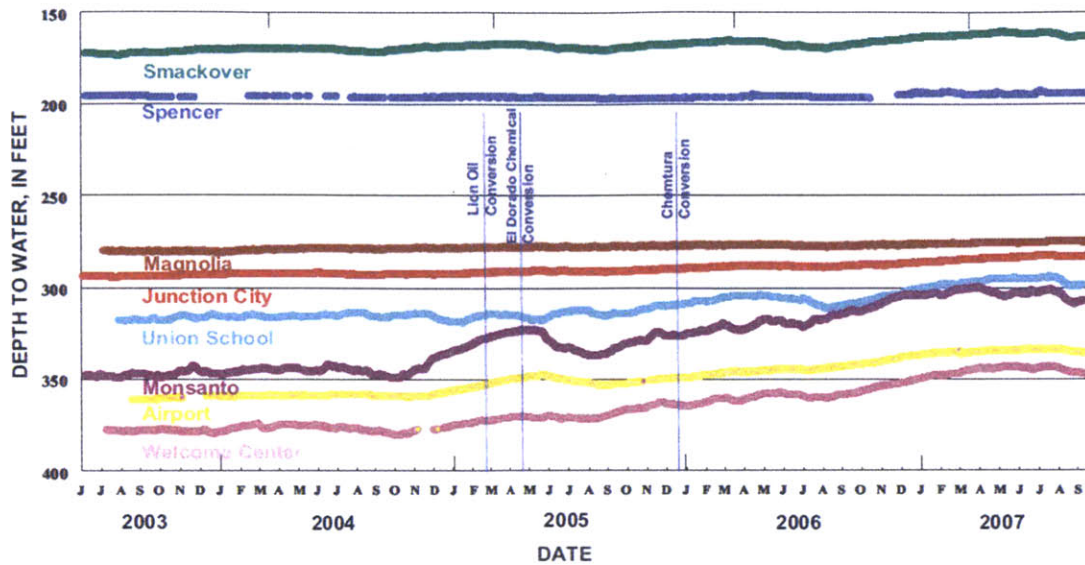


Figure 8 Hydrograph showing water levels for U.S. Geological Survey real-time wells and industrial conversion to surface-water supplies (Freiwald and Johnson, 2007)

Water quality samples collected between 2003 and 2007 measured the specific conductance and chloride concentration as indicators of the salinity intrusion. Results shown in Figure 9 indicated that while chloride concentration generally showed no major changes, specific conductance displayed an initial drop in El Dorado, Lawson-Urbana, D'Arbonne and Huttig, Arkansas. The highest maximum and average specific conductance and chloride concentration were observed at wells located in the southeastern part of the study area, such as Farmerville, Louisiana and Huttig, with an average specific conductance greater than 1150 uS/cm and average chloride concentration greater than 175 mg/l, which is in compliance with EPA's National Secondary Drinking Water Regulation for chloride concentration in public water supply, 250 mg/l.

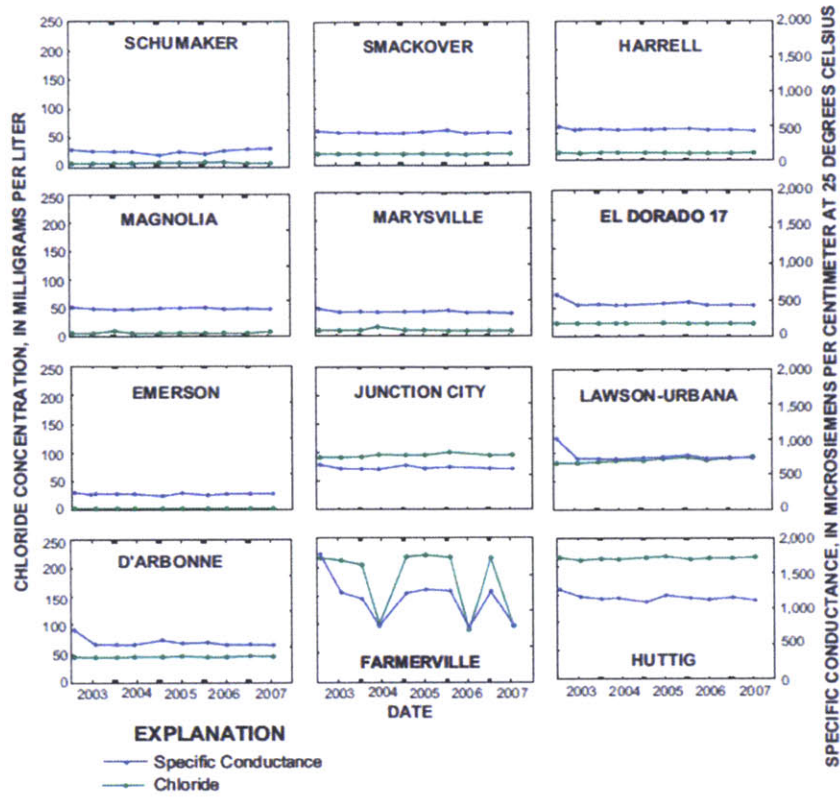


Figure 9 Specific conductance and chloride concentration results for U.S. Geological Survey water-quality monitoring wells (Freiwald and Johnson, 2007).

2 Literature Review

2.1 Fundamentals of ASR

The term “aquifer storage and recharge” was coined by David G. Pyne in 1983 when the first ASR scheme was proposed at Manatee county, Florida. Since then, this technology has become a mainstream option for water resource management in many parts of the United States, as well as worldwide. According to U.S. Environmental Protection Agency (2009), ASR is defined as a specific type of artificial aquifer recharge with two objectives, 1) enhancing ground water budget and 2) recovering the stored water either using the same well or pairing injection wells with recovery wells in the vicinity. Typically, the recovered water is used for drinking water, irrigation, industrial water supplies, and even ecosystem restoration projects to preserve the health of the ground water environment. In recent years, ASR has emerged as a popular innovative water resource management strategy as development put on increasing pressures on available freshwater resources. ASR can provide a cost-effective way to manage and store periodically available flow with minimal impact on land use requirement. This is achieved by controlling the timing and duration of the injection activity during periods of high flow or low demand and recover during dry periods or high demand. Hence, for many water suppliers and regulators, ASR is emerging as a compelling strategy to manage current and future water demands. According to U.S. EPA (2012), ASR has been widely accepted and implemented in the Southeast, Southwest and Western states as a reliable supply of portable water throughout the year or the treatment cycle. Fewer ASR wells are found in the Northeastern and Midwestern states, due to the relatively abundant sources of drinking water supply. As of February 2009, there were 542 functional ASR well in the US. Most of the wells are located in the west coastal zone as illustrated in Figure 10. While most of the ASR wells are well managed and operational, over a third of the AR wells are plugged and abandoned as shown in Table 2.

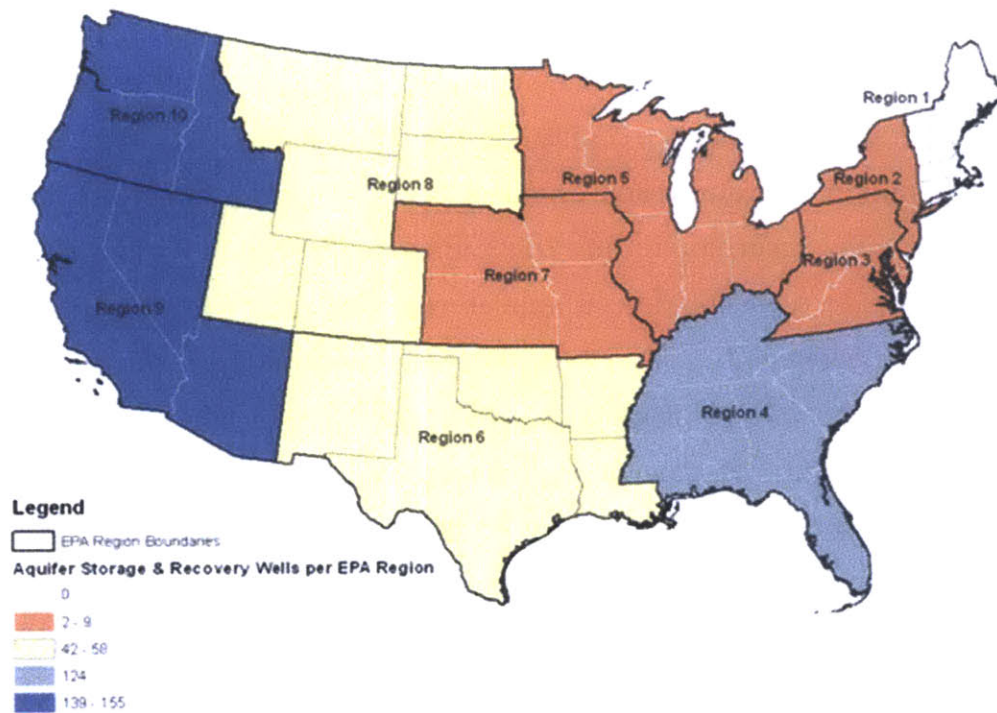


Figure 10 Geographic distribution of ASR wells in the US by EPA regions (From US EPA, 2009)

Table 2 Operating status of AR and ASR wells in the US as of February 2009(US EPA, 2009)

Well Type	Operational	Non-operational	Plugged
ASR	542	14	65
AR	661	0	375
Total	1203	14	440

Pyne (1995) briefly discussed 22 ASR applications. Although ASR system is typically designed for one primary purpose, one or more secondary objectives could be incorporated to achieve multiple objectives. Some typical ASR applications that have been implemented in the U.S and overseas are briefly discussed below.

➤ Seasonal Storage

This is the most common objective of operating ASR wells. The aquifer is used to store seasonally available water, such as peak river flows, storm water, or excess precipitation, and pumped out when water is needed. Water quality could also be used as a criterion in designing the storage and recovery cycle. Water could be stored when quality is the best to minimize treatments needed to produce injection water meeting the regulations. In our study area, Arkansas, flow in the nearby Ouachita River is comparative high and displays little seasonal variation (Sowby, 2013), making it a reliable year-round source.

➤ Long-term Storage

Impacts of human-induced climate change on the hydrological cycle and water resources are receiving increasing attention recently. A comprehensive study of the impacts of climate change on groundwater is conducted by the World Bank Group (Clifton *et al.*, 2010). In the report, it is highlighted that increased global temperatures are expected to change the rainfall patterns, leading to increases in the intensity and frequency of extreme storm events. Increased evaporation rates and risk of flooding and drought would adversely affect the attractiveness of using surface water bodies for water storage. Furthermore, reliance on groundwater is likely to increase due to growing development and increasing population. In considerations of the changing hydrological patterns and the vulnerability of surface water to the potential changes, aquifers are deemed to have greater capacity to store excess water, to reduce evaporation and to preserve water quality (Clifton *et al.*, 2010). Storage and recovery cycles can be designed to store water during wet years or when the treatment or distribution facilities have the spare capacity to produce water of high quality at relatively low cost. Recovery is flexible depending on the climate and demand for expanded water supply. This type of storage is also known as “water banking”.

➤ Replenish groundwater budget

Declining water tables in aquifers are becoming an increasingly frequent concern in groundwater management (Clifton *et al.*, 2010). ASR could be incorporated as part of a groundwater management plan with recharge phases used to help alleviate pumping stress. If recharged water is not fully recovered, net accumulation could still contribute to a positive change in the aquifer water budget.

➤ Emergency storage

Stored water could also serve as a strategic reserve in case of unpredicted events, such as failure of the primary water supply system, contamination of water resources or natural disaster. This is a particularly attractive concept for places that rely heavily on a single water source.

Target Storage Volume (TSV)

One important design parameter of an ASR system is the capacity available to store water. According to Pyne (2003), stored water typically extends up to 2000 feet away from the point of injection. Three distinctive zones develop around the point of injection, as illustrated in Figure 11. A buffer zone develops outside the storage zone which separates the stored water which is targeted for reuse from the ambient subsurface water, or brackish water in places where saline water intrusion is a concern. Water in the buffer zone is a mixture of injected water and ambient aquifer water. The term “Target Storage Volume (TSV)” is defined as the volume of water in the storage zone and in the buffer zone. The value of TSV for an individual well can vary widely from 10 to 500 million gallons (MG) per million gallons per day (MGD) injected, depending on an inter play of factors such the aquifer geology, gradation and composition of the porous media, local density-driven or heat-driven mixing, and natural mixing along the flow path (Pyne, 1995). Currently, estimation of the TSV is still primarily derived from experience and repeated initial testing. At ASR sites, monitoring wells are set up in the storage zone and in the buffer zone to collect water samples, which are tested to determine if there is any change on water quality and any impact on the intended use of the stored water. These data are used to evaluate the amount of injected water.

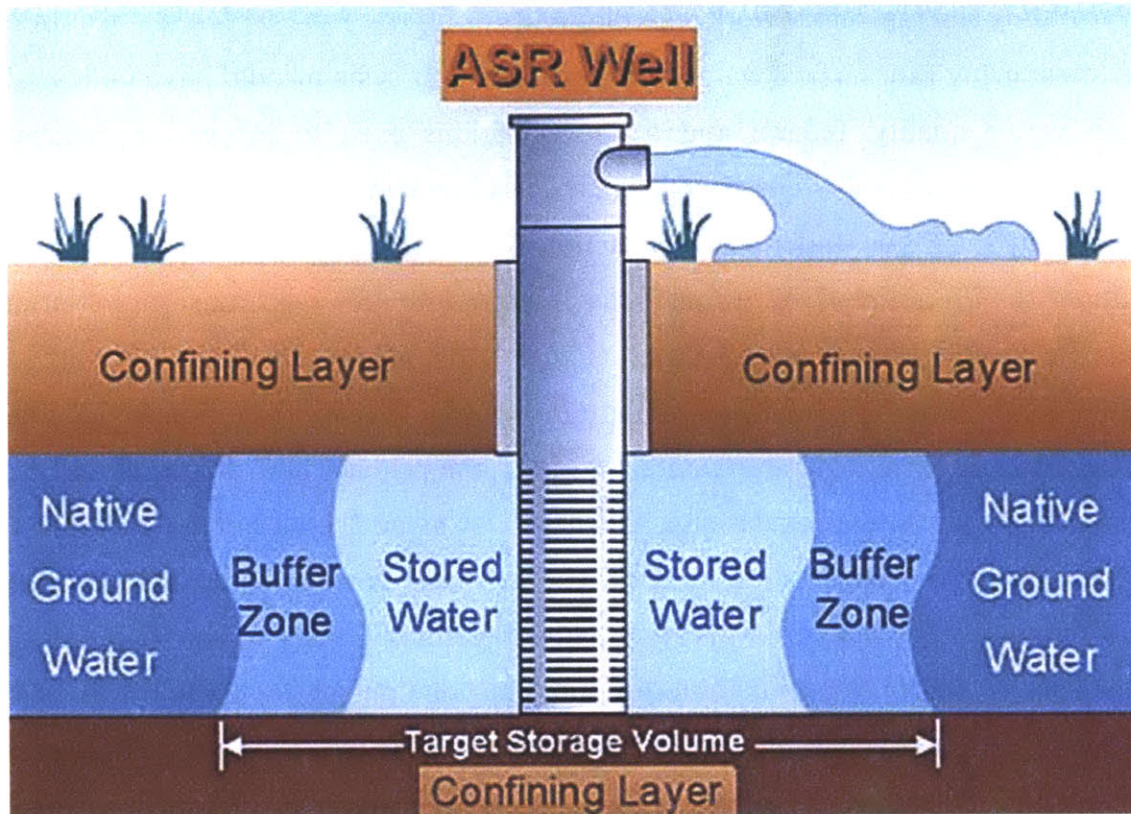


Figure 11 Graphical representation of a typical ASR well (Pyne, 2003)

Injection Hydrology

Injection of freshwater into the depleted aquifer to increase the water table could yield very different local hydrological effects, depending on the injection rate, the duration of the injection, and the hydrogeological characteristics of the aquifer. Injection of water into an aquifer increases the heads locally, in a manner analogous to the decrease in heads that occur during pumping out of well (Maliva and Missimer, 2008). Increase in the water level at the center of the cone of depression is also affected by the location of the injection wells. For more information on the hydrological effects of artificial recharge to the Sparta aquifer, please refer to Sowby (2013).

2.2 Permitting and regulatory work regarding ASR

Because introducing raw surface water into a groundwater system could have undesirable effects on water quality, federal and state regulations exist to protect underground drinking-water sources. ASR wells are designated as Class V injection wells by the EPA and are regulated by the EPA's Underground Injection Control (UIC) program (Bloetscher *et al.*, 2005). Under the UIC regulations, water that is injected into ASR wells must meet National Primary Drinking Water Regulations under the Safe Drinking Water Act (<http://www.water.epa.gov/drink/contaminants/index.efm>) (refer to Appendix A). States with more stringent drinking-water standards may claim primacy and choose to add more requirements beyond EPA's regulations. Arkansas was given the authority to administer the UIC program as a primacy state in 1982. The Arkansas Department of Environmental Quality is the regulatory body to oversee activities regarding Class V wells. The applicable regulations are primarily Arkansas Underground Injection Control (Regulation 17), as well as the Code of Federal Regulations (CFR) Title 40, Parts 144, 145, 146 and 124 (Arkansas Department of Environmental Quality, 2004). The key criteria for injection water are compliance with drinking-water standards and no harming of public health by endangering underground sources of drinking water (USDW) (Arkansas Department of Environmental Quality, 2004).

However, UIC only regulates the quality of the injection water with regard to potential health impacts. No additional regulations are specified for water quality in the storage zone or for the recovered water. If stored water is destined for recovery, in-situ monitoring of the stored water quality and the geochemical interactions of recharged water in the aquifer is required to determine appropriate end-use of the stored water. Traditionally, due to the high quality of water in the Sparta aquifer, it has been used as a primary source of water for industrial, municipal and agricultural uses in southern Arkansas and northern Louisiana (Yeatts, 2004). Depending on the location of the injection wells, specific use of the stored water would be proposed according to the local water demand budgets for different sectors.

While the federal regulations only requires the injected water at the wellheads to meet National Primary Drinking Water Standard prior to recharge, some states have taken

further steps to ensure there is no endangerment of the groundwater environment. When two dissimilar water types, the injected water and the ambient ground water, interact with the aquifer geologic matrix, there could be significant changes to water quality. Recognizing that, some states have developed a “compliance zone” extending up to a few hundred feet away from the well and require the mixed storage water to meet Primary Drinking Water Regulations at the edge of the zone of compliance. In our study area, Union County, Arkansas, currently there is no specific state requirement of water quality compliance in the aquifer. However, as ASR projects becomes a more common practice to address water demands for different purpose, it may be advisable to consider implementing monitoring and compliance regulations of in-situ water quality in the aquifer. Some examples of the current practices in defining the compliance zone are described below (Pyne, 2003),

- In Arizona where water is typically stored in unconsolidated sand aquifers and recovered for drinking water supplies, the State defines a “compliance zone” of 700 feet away from the well and requires recharge water quality to meet drinking water standards as measured at the edge of the compliance zone.
- In Wisconsin where the ASR wells are generally in sandstone aquifers, the compliance zone of radius of 1200 feet is defined.

2.3 Injection water alternatives and pretreatment

Compliance with US EPA regulations on underground injection requires recharge water to meet the National Primary Drinking Water Standard at the point of injection. The list of contaminants includes chemical and microbiological constituents that have specific maximum contaminant levels (MCLs) and /or treatment technology requirement established by the US EPA (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008). Besides the more well-researched chemicals, there is new interest on an emerging category of micro pollutants found in water supply sources, such as endocrine disrupting chemicals found in personal care and pharmaceutical products. For many of the chemicals in this category, analytical methods and relevant

regulating standards have yet to be fully outlined by US EPA (Committee on Sustainable Underground Storage of Recoverable Water, Nation Research Council, 2008). Introduction of the synthetic compounds, which are purely of an anthropogenic origin, into the pristine Sparta aquifer could have uncertain impacts on the microbiota environment (Pyne, 2003).

While the Safe Drinking Water Act provides a straightforward limit on the chemical and biological constituents allowed in the injection water, it only specifies the minimal requirement. Another equally important set of water quality consideration is the geochemical compatibility of the source water and groundwater. Mixing incompatible waters could lead to dysfunctional ASR systems from operational failures such as well cloggings or dissolution of the matrix (Committee on Sustainable Underground Storage of Recoverable Water, Nation Research Council, 2008). In order to analyze that, information on the composition and characteristics of source water, operational method, local aquifer structure and compositions are necessary.

Selection of the specific type of source water for injection depends on both the technical feasibility of meeting the regulatory standards, as well as a holistic assessment of the reliability and availability of the water source, the cost of treatments needed before injection, the intended end use of water and sometimes public acceptance (Asano and Cotruvo, 2004).

National research Council (2008) published a study evaluating the potential of five surface water sources for groundwater recharge (

Table 3). Water stored in the aquifer considered is intended to be recovered for portable use of water. The constituents of concern are determined based on the committee consensus on the selection of contaminants from US EPA regulatory list that could have adverse impacts on the aquifer. From an operational perspective of the ASR facilities, the source water characteristics that are of greater concern include suspended solids, dissolved gases, nutrients, biochemical oxygen demand (BOD), microorganisms, and sodium adsorption ratio (which affects the aquifer permeability) (Committee on Ground Water Recharge, National Research Council, 1994).

Table 3 Selected constituents in source waters and relative concern (Committee on Ground Water Recharge, National Research Council, 1994)

Constituent	Wastewater Treated for Non-potable and Indirect Potable Use	Urban Stormwater Runoff	Surface Waters	Untreated Groundwater	Waters Treated to Drinking Water Standards
Salinity	High	Low to medium	Low or medium	Low	Low
Nutrients (NO ₃ -, etc)	High	Medium	Medium	Medium	Low
Metalloids, including arsenic	Low	Medium to High	Low	Low to medium	Low
Mn, Mo, Fe, Ni, CO, V	Low	Medium	Low	Low to medium	Low
Trace organics	Medium	High	Medium	Low to medium	Low
Total organic carbon (TOC)	Medium	Medium	Medium to high	Low to medium	Low
Disinfection by-products	High	Low	Medium	Low	High
Microorganisms	High	Medium	High	Medium to high	Low

1) Reclaimed wastewater

Characteristics

Comparing the five types of water, reclaimed wastewater is associated with the greatest concern and needs the most extensive pre-treatment before injection. Wastewater usually includes contribution from a diverse source of low-quality waters, from predominantly domestic and industrial sources, to smaller contribution from infiltration into the sewer network and urban storm water overflow. The most prominent concern of using reclaimed wastewater as source water are microbiological contaminants, disinfection by-products (DBP), nutrients and salinity. A typical

treatment train in a full-scale wastewater treatment facility comprises preliminary/primary, secondary, tertiary and advanced treatment.

Treatment Methods

Primary treatment usually refers to the removal of bulk materials and a portion of the coarse suspended solids. Units adopted at this stage include coarse screening, grit removal, sedimentation and sometimes pre-secondary treatment such as pre-aeration, taste and odor control and chemical additions. Typically, 50% of the suspended solids and 30%-40% of organic matters are removed at this stage. Some of the organic nutrients and heavy metal are removed along in the sludge. However, primary treatment has little effect on the soluble contents and the microbiological species presented (Tchobanoglous *et al.*, 2002). While primary effluent alone does not produce water meeting the direct injection regulations, it has been used in recharging through outcrop areas (Carlson *et al.*, 1982; Lance, Rice and Gilbert, 1982; Rice and Bouwer, 1984). High organic contents stimulate microbial activity to enhance the rate of microbial degradation of nutrients and synthetic organic compounds (Lance, Rice and Gilbert, 1982). However, slower hydraulic loading rate is expected due to high suspended solids loadings. It is a common practice that at least secondary treatment and disinfection are needed for reclaimed wastewater before use even as surface-applied recharge.

The aim of secondary treatment is to remove the SS and most of the BOD. The key process involved at this stage is usually an aerobic biological process coupled with a settling tank to separate the clarified effluent. A high performing secondary process could remove up to 95% of BOD, COD, and SS and a significant portion of heavy metals (Water Pollution Control Federation, 1989), but very few dissolved substances are removed by a conventional secondary process. Table 4 illustrates that the secondary effluent still has a significantly high content of dissolved solids, which limits its use as recharge water.

Table 4 Constituent concentrations for secondary treated municipal wastewater (Treweek, 1985; Crook, 1992).

Constituent	Concentration (mg/l)
Calcium	9-84
Potassium	9-108
Magnesium	12-176
Sodium	44-1320
Ammonium	0-501
Chlorine	43-2450
Fluoride	0.2-3.8
Bicarbonate	76-563
Nitrate	0.4-30
Sulfate	1.2-46
Silicon dioxide	14-490
Hardness (as calcium carbonate)	10-76
pH(units)	62-951951
Electrical conductivity	6.3-8.4
Total dissolved solids	423-6570umol/cm
Arsenic	210-4580
Boron	<0.005-0.023
Cadmium	0.3-2.5
Chromium	<0.005-0.22
Copper	<0.001-0.1
Lead 0.003-0.35	0.006-0.053
Molybdenum	0.003-0.35
Mercury	0.001=0.018
Nichol	0.003-0.60
Zinc	0004-0.35
Biochemical oxygen demand	1.5-30
Chemical oxygen demand	40-70
Total suspended solids	10-25

Tertiary treatment traditionally is used to remove excessive nutrients still present in the water after primary and secondary treatments. It is increasingly combined or replaced by one or more advanced treatment processes such as carbon adsorption, nano/microfiltration and reverse osmosis to achieve higher overall water quality. Metcalf & Eddy (1991) evaluated the performance of several sets of options of combining the advanced water treatment processes (Table 5). The options generally yield high quality product water in terms of the parameters evaluated, with best

performance resulting from combining activated sludge tank with filtration and carbon adsorption.

Table 5 Achievable treatment performance for key water quality parameters with various combinations of advanced wastewater treatment units (Metcalf & Eddy, Inc., 1991)

Typical Effluent Quality^b							
Treatment Process^a	SS (mg/l)	BOD₅ (mg/l)	COD (mg/l)	Total N (mg/l)	NH₃-H (mg/l)	PO₄ as P (mg/l)	Turbidity (NTU)
AS+F	4-6	<5-10	30-70	15-35	15-25	4-10	0.3-5
AS+F+CA	<3	<1	5-15	15-30	15-25	4-10	0.3-3
AS/N (single stage)	10-25	5-15	20-45	20-30	1-5	6-10	5-15
MS addition to AS	10-20	10-20	30-70	15-30	15-25	<2	5-10
MS addition to AS+N/D+F	<5-10	<5-10	20-30	3-5	1-2	<1	0.3-3
BP	10-20	5-15	20-35	15-25	5-10	<2	5-10
BNP+F	<10	<5	20-30	<5	<2	<1	0.3-3

^aAS = activated sludge; F = granular-medium filtration; CA = carbon adsorption; N = nitrification; D = denitrification; MS = metal salt addition; BP = biological phosphorus removal; and BNP = biological nitrogen and phosphorus removal.

^bSS = suspended solids; BOD₅ = biochemical oxygen demand over 5 days; COD = chemical oxygen demand; N = nitrogen; NH₃ = ammonia; PO₄ = phosphate; P = phosphorus; and NTU = Nephelometric Turbidity Units

Disinfection is the most important process in removing microbiology and pathogens in the water, especially essential if the water is required to meet the drinking water standard. The type and concentration of microbiological species in combined wastewater could not be easily predicted and vary a lot depending on a number of factors, such as the composition of the wastewater, the flow path of the water, the ability of a species to survive in the environmental conditions of the wastewater.

Currently, the most popular processes used at wastewater treatment plants include chlorine, ozone, and ultraviolet (UV) radiation. Other options such as hydrogen peroxide, ultrafine membrane processes are also considered and shown to be effective in removing some microorganisms, but extensive research is still underway to enhance the economical, technological, and operational aspects of these relatively new technologies.

When water treated with disinfection is used as source water for injection, special attention is needed to monitor the possibility of disinfection-byproducts (DBPs) formation. Both chlorine and ozone are known to react with organic compounds in water to form DBPs, such as trihalomethane (THM) and halo-acetic acids (HAAs), which are classified carcinogenic by US EPA.

2) Storm water runoff

Characteristics

Storm water is an attractive source water recharge because of the substantial amount of volume available. However, the reasons that storm water is not yet widely used for recharge are poor water quality and reliability in terms of timing and quantity (Committee on Ground Water Recharge, National Research Council, 1994). In 1983, EPA conducted the largest and best-known study to characterize storm water runoff quality in the Nationwide Urban Runoff Program (NURP) (Table 6). Results showed that BOD concentration is close to treated municipal water, but significant treatment is needed to reduce the concentrations of nutrients and metal complexes. Furthermore, many parameters which are of key interests in groundwater injection control are not included in NURP. As shown in

Table 3, medium to high concern is associated with trace organics, metal compounds and microorganisms. *E. Coli* is the most common microbiological indicator used to quantify the microbiological characteristics of storm water. Olivieri *et al.* (1977) found that *Pseudomonas aeruginosa* is the most abundant pathogenic bacteria in urban runoff and surface waters, with a typical concentration of 1000 to 10000 organisms per 100 ml (Pitt and McLean, 1986).

Table 6 Concentration of pollutants in median strength storm water for different land use (U.S. EPA, 1983)

	Residential		Mixed Land Use		Commercial		Open/Nonurban	
	Median	COV	Median	COV	Median	COV	Median	COV
Biochemical Oxygen Demand (mg/l)	10	0.41	7.8	0.52	9.3	0.31	-	-
Chemical Oxygen Demand (mg/l)	73	0.55	65	0.58	57	0.39	40	0.78
Total Suspended Solids (mg/l)	101	0.96	67	1.14	69	0.85	70	2.92
Total Kjeldahl Nitrogen (µg/l)	1900	0.73	1288	0.50	1179	0.43	965	1.00
Nitrite Nitrogen Plus Nitrate Nitrogen (µg/l)	736	0.83	558	0.67	572	0.48	543	0.91
Total Phosphorus (µg/l)	383	0.69	263	0.75	201	0.67	121	1.66
Soluble Phosphorus	143	0.46	56	0.75	80	0.71	26	2.11
Total Lead (µg/l)	144	0.75	144	1.35	104	0.68	30	1.52
Total Copper (µg/l)	33	0.99	27	1.32	29	0.81		
Total Zinc (µg/l)	135	0.84	154	0.78	226	1.07	195	0.66

Note: COV= coefficient of variation – standard deviation/mean

Treatment Methods

Reuse of treated storm water runoff has been successfully implemented in many places in the U.S. Sedimentation is the most common process to reduce the particulate constituents in the runoff. In addition, coagulation and filtration are employed to remove the soluble pollutants such as salt, metal complexes, and trace organic pollutants. Selection of appropriate disinfection processes to eliminate bacteria and pathogenic species is also required to produce water meeting the regulation.

3) Surface water and ambient groundwater

Characteristics

Usually, quality of surface water and groundwater impose relatively low to medium concern when used as recharge water, especially if the water comes from a well-protected source and there are no known discharging sources of contaminants. As shown in Table 3, the most significant concerns are microorganism contents and dissolved organics. Compared with groundwater, surface water from rivers, streams and lakes could display greater seasonal variations in water quality, due to flow contributions from precipitation, snow-melt and irrigation return flows. Uncontaminated Groundwater is frequently of high quality with respect to synthetic organic pollutants, but can still have high salinity and elevated mineral contents including potentially toxic metals such as arsenic, depending on the geological matrix of the aquifer. Beside water quality considerations, availability of groundwater, given the widespread groundwater depletion status, is the major reason for not using groundwater as recharge source water.

Treatment

Treatment required for surface water may vary depending on the flow condition and water quality associated with it. Conventional water treatment plants are designed to remove total and dissolved suspended solids as well as to eliminate the pathogen-causing microorganisms. Coagulants and polymers are added to enhance formation of large flocs to facilitate removal by sedimentation later on. The last stage is usually disinfection control.

Typically only minimal treatment is deemed as necessary for groundwater. Common strategies used to pre-treat groundwater include softening by adding chemicals and eliminating toxic metals, if the mineral contents exceed the regulations.

Geochemical Compatibility

Depending on the type of source water for injection and the subsurface geologic matrix, recharge water that meets EPA Primary Drinking Water Standards may need additional degree of treatments to enhance the geochemical compatibility of the two waters. Common treatment adopted can be broadly categorized into two groups, pre-injection treatment and in-situ treatments.

1) Pre-injection treatment

- If surface water, which is typically saturated with oxygen, is used for injection, removal of oxygen may be needed to reduce the redox potential of the water. Redox reactions are one of the most important reactions between injected water and ambient groundwater.
- If chlorination is used in the disinfection process in treating the injection water, removal of the residual chlorine and chlorinated disinfection byproducts such as THMs is recommended to avoid contaminating the groundwater environment and to prevent potential harmful reactions between the residual chlorine with the organic matters in the aquifer. Besides, introduction of residual chlorine and chlorinated compounds could adversely affect the natural microbiota of the aquifer which may have an essential role in maintain the balance of the subsurface ecosystem.
- Other treatments maybe deemed necessary to match the water characteristics of recharge water to that of the receiving aquifer to reduce reactivity.

2) In-situ treatment

- Determine the extent of buffer zone by setting up monitoring wells in the vicinity of the wells. Once the boundary of the buffer zone is identified, avoid recover water from the buffer zone and allow contaminants to remain in the zone

- Discharge initial cycles of recharge water if certain element in the recovered water exceeds the regulatory limits until the recovered water meets the specified standard.

2.4 Mixing geochemistry

Mixing reactions

Beside hydrodynamics of injection and recovery, understanding the mixing reaction between two types of water that could have chemically and microbiologically very distinctive characteristics is essential to the feasibility of the ASR system. Potential reactions could ultimately improve in-situ water quality due to solid-aquifer treatment (SAT) (Asano and Cotruvo, 2004) or adversely impact the local water quality and recovery operations due to well clogging or dissolution from the aquifer matrix (Committee on Sustainable Underground Storage of Recoverable Water, Nation Research Council, 2008). Change in water quality is a very dynamic process and can occur with both space and time. Reactions could occur from mixing between groundwater and the recharge water, interaction between the recharged water and the aquifer matrix, and the changing environmental conditions of the recharged water (i.e. storing surface water which was previously in contact with the atmosphere in a confined subsurface environment). Disturbing the geochemical equilibrium of the aquifer by introducing water of very different origins is the main driving force for geochemical reactions that aim to establish a new equilibrium between recharged water, the native groundwater, and the aquifer matrix in the recharge zone. Extensive studies have been conducted to investigate the geochemical processes. Important chemical reactions that are found to influence the concentration of chemicals during recharge and storage include redox reactions, ion-exchange reactions, diffusion-dispersion or mechanical dispersion acid-base reactions, and precipitation-dissolution reactions (Drever, 1997; Langmuir, 1997; Stumm and Morgan, 1996), of which redox reactions are found to affect water quality and aquifer integrity most significantly.

Generally if injection water that meets drinking water quality is used for recharge only, minor changes in water quality are observed in the long run (Pyne *et al.*, 2003). However, studies have shown that a treatment zone with a radius of a few tens of feet develops close to the ASR well. Accelerated microbial activities, geochemical changes, and water-quality changes are reported to occur in this region (de Ruiter and Stuyfzand, 1998; Pyne, 1995).

Redox Reaction

A redox reaction is a coupled oxidation-reduction reaction. The redox condition of the system is determined by the dominant forms of redox elements in the system and expressed as the Eh or p_e of the system. A lower Eh indicate a more reduced condition. Most surface water, being exposed to the atmosphere, has a high Eh whereas many groundwaters are anoxic and have relatively higher concentrations of species in their reduced species, such as reduced iron (Fe^{2+}) or reduced sulfur (S^{2-}). When oxic water is introduced into an aquifer containing concentrations of reduced minerals some of the minerals will oxidize. For example, reduced forms of arsenic minerals may oxidize, leading to release of arsenic into the stored water (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008).

Changes in redox potential could also have an impact on the dissolution-precipitation reactions, resulting in reactions that dissolve the geological matrix or plug the aquifer or the wells.

Additionally, oxidation of the organic matters produces acidic products such as transformed organic acids. An acidifying aquifer can consume the aquifer media by reacting with the minerals and further increases the dissolved salts and hardness of the stored water.

Precipitation-Dissolution Reactions

A more specific redox reaction is precipitation-dissolution reactions, driven by an imbalanced equilibrium between the ions in the dissolved phase and the solid phase. Dissolution is driven when water containing low ionic contents is injected into the ground. An undersaturated mixed zone would drive the equilibrium to allow more

minerals to dissolve in the aquifer water. Although the extent of degradation of the total aquifer solids is small, dissolution of the aquifer could have significant local impact on integrity of the matrix. When the value of Eh is low, dissolved sulfide and iron tend to precipitate as reduced iron sulfide minerals (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008). Another well-studied iron reaction is precipitation of ferrous iron hydroxides when the aquifer water experiences an increase in Eh, which could happen during recharge or extraction. Precipitation reactions pose a greater concern in operational aspects as they could potentially clog the aquifer and the wells.

Ion Exchange Reactions

Ion exchange usually occurs as a water-rock interaction process. Typical species involved in the exchange reactions are between Ca^{2+} or Mg^{2+} with Na^+ or K^+ (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008). The number of available surface sites for reaction usually limits the rate and extent of the reactions. Total amount of charged species dissolved in the water is conserved, although the relative abundance of the constituent ions changes over time. Ion exchange is also an important reaction which accounts for significant changes in dissolved concentrations of trace metal cations (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008).

Although there are other significant reactions such as sorption of organic compounds, particle and microorganism transport, microbial inactivation and biotransformation, the scope of this paper focuses on discussing the reactions described above as they are of greater relevance to the context of the Sparta aquifer in Arkansas.

2.5 Key contaminants of Concern

In all ASR systems, water quality in the storage zone is frequently monitored during recharge, storage and extraction to ensure no breaching of the pertinent regulations and to minimize the potential of any operational failures. The occurrence and significance of the key contaminants of concern are briefly discussed below.

Metals and Metalloids

Changing geochemical conditions can cause changing speciation of metals and affect the mobility and toxicity of the species. Leaching of certain toxic metals such as arsenic, cobalt, iron, manganese, molybdenum, nickel, vanadium and uranium from the aquifer solids to the storage zone has been reported in several ASR systems in Florida (Arthur *et al.*, 2005).

Of particular concern is dissolution of arsenic due to its high toxicity and extensive presence underground. Welch (2000) reports that arsenic in groundwater is usually present as inorganic arsenite As (III) and arsenate As (V), with higher toxicity associated with As (III). Occurrence of As (V) dominates when the conditions is more oxidizing and As(V) tends to bind strongly with iron oxides and sediments (Meng *et al.*, 2002; Lin and Puls, 2003) whereas As(III) is more prevalent in anaerobic environment and only adsorbed to iron minerals around pH 7. Hence, mobilization of arsenic is observed under iron-reducing conditions as iron oxides dissolve and free the sorped arsenic (Smedly and Kinniburgh, 2002). Generally, in systems where sulfate and ferric oxides are absent with low pH, arsenic is expected to dissolve into the aquifer water. Conversely, if sulfate reduction occurs, production of H₂S can serve arsenic-binding compound to reduce the mobility of arsenic in the aquifer.

Disinfection Byproducts (DBPs)

Most common DBPs are formed between chlorine-based disinfectants and the natural organic matters in the water. DBP encompass a spectrum of chlorinated chemicals, of which most prominently are trihalomethanes (THMs) and haloacetic acids (HAAs). Most of DBPs are small and soluble, so attenuation due to adsorption is low, especially in low carbon content aquifers. Results from both laboratory and field studies agreed that transformation is the primary process that reduces DBP concentration during aquifer storage. THM, one of the most important DBPs, is more persistent in aerobic conditions than in anaerobic conditions with an attenuation rate greater by two orders of magnitude (Pavelic *et al.*, 2006). HAAs are not as persistent as THMs. Thomas *et al.* (2000) monitored the aerobic ASR system in Las Vegas and found that the

concentration of HAAs decreased below detection limits after an initial spike in concentration. A small amount of excess residual disinfectant is purposefully left in drinking water supply to control microbiological activity in the distribution system (Fox *et al.*, 1998). If residual disinfectant is injected into aquifer, new DBPs could be formed if precursor natural organic matters (NOM) are present in the aquifer (Pavelic *et al.*, 2006; Thomas *et al.*, 2000), degrading water quality in the aquifer.

Pharmaceuticals, Personal Care Products (PPCPs) and Other Emerging Compounds

The presence of micro pollutants such as PPCPs, EDCs and trace organic compounds in surface waters is attracting extensive scientific research on controlling these anthropogenic chemicals. After sampling 139 streams in the U.S. and analyzing the samples for 93 organic waste contaminants, Kolpin *et al.* (2002) concluded that widespread occurrence of organic waste contaminants is threatening the safety of using surface water as drinking water supply. Due to the extremely low concentration and poor characterization of the environmental impacts of these emerging compounds, regulations on controlling these contaminants are not fully developed. However, in a joint study between European and American researchers to study subsurface persistence and mobility of PPCPs, results have shown that attenuation is achieved for majority of the compounds through biological transformation and sorption (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008). However, the extent of these processes varied depending on the compound of interest, matrix structure, microorganisms present and the flow conditions.

Radionuclide

Leaching and dissolution of uranium is of great geochemical interest. When treated surface water containing oxygen and carbon come to chemical equilibrium with groundwater, there is the possibility of uranium leaching or re-precipitating in the aquifer. Furthermore, uranium is not currently regulated in the federal primary drinking water standard but can pose a significant concern to public health.

Microorganisms

Presence of microorganisms in the ASR recharge water that might contaminate the aquifer and endanger groundwater supplies is always of great public concern. Case studies investigating the survival rate of resistant protozoan *Cryptosporidium parvum* in representative aquifer and reservoir waters of Florida have been conducted. Inactivation rates were found to have a wide range from $0.0088 \log_{10}d^{-1}$ at $5^{\circ}C$ to $-0.20 \log_{10}d^{-1}$ at $30^{\circ}C$. Temperature, water type and availability of nutrients were found to have statistically significant effects on microbiological activity (Committee on Sustainable Underground Storage of Recoverable Water, National Research Council, 2008).

2.6 Recovery of stored water

The ultimate success of ASR wells depends on how much stored water meeting the water-quality standards can be recovered for beneficial uses. Recovery efficiency is defined as the volume of water that can be recovered during one individual cycle as a percentage of the volume stored in that cycle. It is important in evaluating the economic feasibility of ASR projects. Stored water usually meets water-quality standards and thus has considerable economic value.

Well clogging is identified as the major reason causing low recovery efficiency. Multiple factors contribute to well clogging, including (Cole, 2009):

- Suspended solids in source water
- Iron/Manganese precipitation
- Biofilm production on well screens
- Carbonate precipitation
- Remobilization of drilling mud or fines
- Air entrainment/gas binding

Appropriate pre-treatment of injection water and geochemical monitoring in the aquifer are effective strategies to control the aforementioned issues. If low recovery efficiency due to clogging is observed during recovery operation, periodic purging or back flushing should be scheduled to combat the problem. Previous ASR projects and

studies have shown that the frequency of back flushing is on the order of a few times per month (Cole, 2009).

Recovery efficiency of 100 percent is hard to achieve. Usually, an efficiency goal is designed with reference to the local surface water-storage capacity. Due to high evaporation, transpiration, seepage, and conveyance losses typically associated with surface-water bodies, any recovery efficiency that is higher than existing surface-water storage is considered beneficial to the regional water balance.

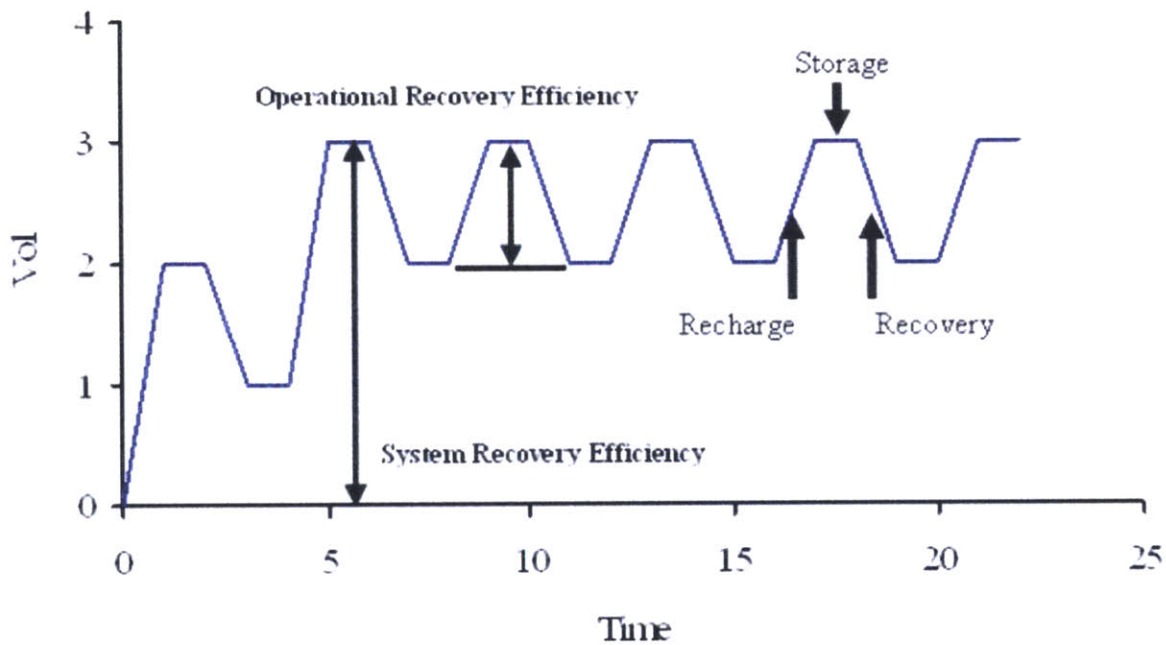


Figure 12 Recovery efficiency of ASR well (Sheng *et al.*, 2007)

Design of the ASR cycle essentially depends on the availability of source water for injection and the demand for stored water. Typical ASR storage times are in the magnitude of several months. In some places such as the Southwestern states, ASR storage can last for several years to meet the demand between wet and dry years. In other extreme cases, there are ASR wells designed to be diurnal, water stored at night is recovered for use during the day. Great flexibility exists in designing ASR systems to meet multiple purposes, such as diurnal, seasonal or long-term and emergency storage.

2.7 Geochemical Modeling

Due to the complexity of the reactions involved , a comprehensive feasibility study of the temporal changes in water quality when it is initially mixed with groundwater as well as when it is transported and stored in the aquifer is critical. Results from appropriate modeling tools for analyzing water quality changes offer important guidance in selecting the source water and level of treatment needed, designing the injection and recovery cycle and determining the end use of the stored water. Key questions that geochemical simulation modeling can help address include 1) interaction of the induced flow with the ambient water in the aquifer with respect to time and distance 2) the important geochemical reactions; 4) the transport and flow of the solute of concerns and 5) other unanswered specific hypothesis regarding the system.

Common types of geochemical modeling that are adopted include speciation modeling, 1-D, 2-D or 3-D modeling of reactive-transport of solutes, mole-balance modeling and batch-reaction modeling. Depending on the level of modeling complexity, requirements on data input varies depending on the types of computer program used for analysis. If a computer programs have built-in database of the thermodynamic and kinetic constants for the reactions, additional data that need to be specified include time, composition of the injection water and water in the aquifer, geological formation of the subsurface environment, especially the mineral phases of the aquifer.

3. Methodology

3.1 Water quality of injection water and the Sparta aquifer water

3.1.1 Injection water

As discussed in section 2, treated surface water has the best potential to be used as recharge water with minimal adverse impacts on the groundwater quality compared to other surface water alternative sources. In Union County, the existing Ouachita River Alternative Water Supply Facility with a treatment capacity of 65 MGD from and potential for expansion in the future provides a very cost-effective source of recharge water for ASR projects in Union County. The main treatment stages are illustrated in Figure 13. For a true scaled sketch of the plant layout and treatment train, please see Appendix F. Three points of potential water withdrawal are found along the treatment train, 1) intake water; 2) raw water after disinfection; 3) product water. Appendix E provides detailed water analysis of water from the three points of withdrawal. The set of data was collected and sampled on Sep 20, 2012. However, as the water quality of Ouachita River and the performance of the treatment devices are usually very consistent, the data set offers a good representation of the general water quality of the raw water and treated water from the clarification plant. Comparing water quality of the treated water at the three points of withdrawal and EPA Primary National Drinking Water Standard, it is determined that raw water (Table 7) after disinfection satisfies requirements except for Arsenic. The current detection limit of arsenic is 0.1 ppm while EPA requires concentration of arsenic in drinking water to be below 0.01mg/L¹. If water from the treatment facility is to be used for recharge, equipment with a lower detection limit is needed to quantify the arsenic concentration.

¹ For low concentration aqueous solution and assuming the density of the solution is 1kg/l, ppm \cong mg/l.

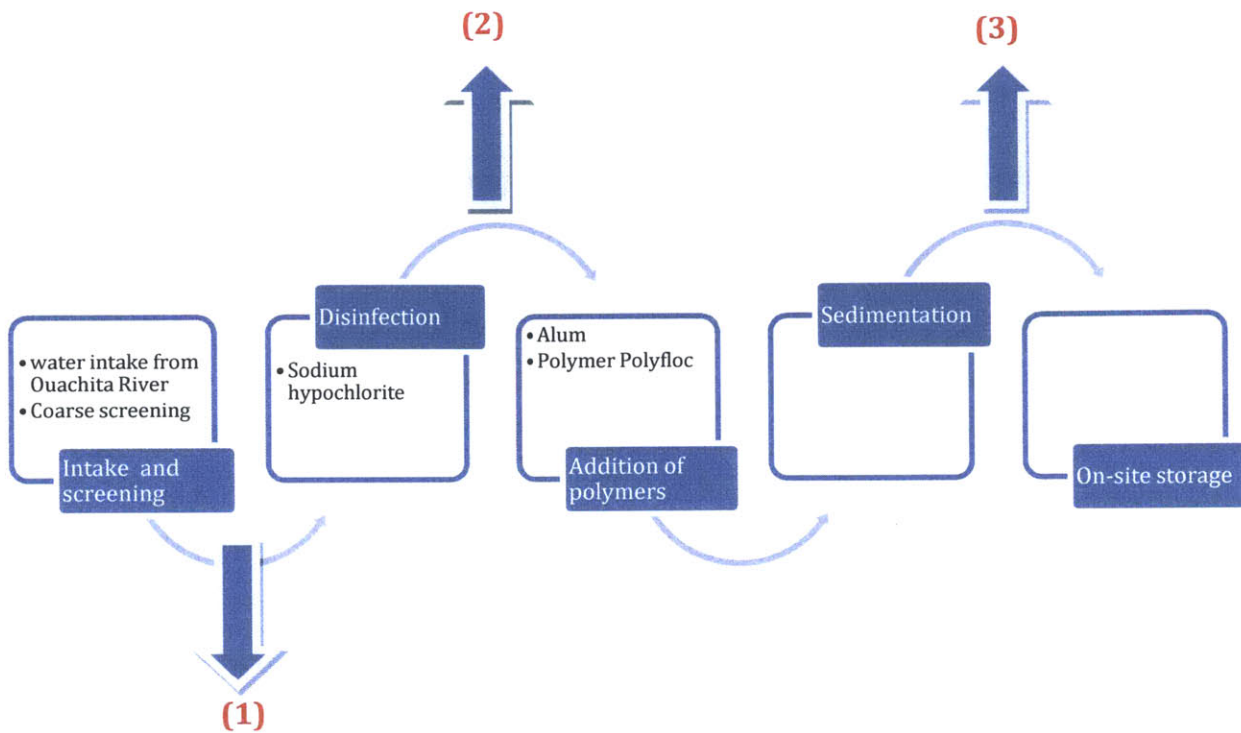


Figure 13 Treatment train of Ouachita River Water Clarification Facility and potential points of water withdrawal for recharge

Table 7 Key water quality parameters of partially treated water from Ouachita Water Clarification Facility (Sept 20, 2012)

	Parameter	Units	Raw Water ²
Physical	pH		7.1
	Hardness, total	as CaCO ₃ , ppm	25
	Color	FAU	356
	Turbidity	NTU	39
	Specific conductance	umhos at 25°C	122
	Temperature	Deg. C	12.2
	Alkalinity	as CaCO ₃ , ppm	14.5
Inorganic, nonmetal	Chlorine as Cl ₂	ppm	1
	Sulfur, Total	as SO ₄ , ppm	9.2
	Phosphate, total	as PO ₄ , ppm	<0.4
	Chloride	as Cl, ppm	22
Inorganic, metal	Aluminum	ppm	0.6
	Arsenic	ppm	<0.1
	Barium	ppm	0.05
	Beryllium	ppm	<0.01
	Calcium, as CaCO ₃	ppm	16.4
	Cadmium	ppm	<0.01
	Chromium	ppm	<0.02
	Copper	ppm ³	<0.05
	Iron	ppm	0.77
	Lead	ppm	<0.05

² Water quality data is sampled and analyzed by the Union Power Plant, a major client of the treated water from Ouachita Water Clarification Facility.

Manganese	ppm	0.1
Selenium	ppm	<0.1
Thallium	ppm	<0.1
Sodium	ppm	14.7

3.1.2 Water quality of the Sparta aquifer

Water quality data that are of particular interest for an aquifer storage and recovery system include the general physical characteristics , such as pH, temperature, and specific conductance, major ionic compositions of ground water, the carbonate and oxyhydroxide contents whose presence may lead to potential dissolution and precipitation reactions, salinity concentration and the redox potential of the water. The main source to retrieve data on ground water quality is <http://nwis.waterdata.usgs.gov/ar/nwis/qwdata> . The online database contains a comprehensive list of contaminants and their concentrations detected at the specific Hydrological Unit Code (HUC). Selected water quality parameters of interest at our study area for one sampling event are shown in Table 8. Other sampling events for wells in the study area available online did not include nearly as many parameters as shown.



Figure 14 Lower Ouachita - Smackover Watershed -- HUC 080400201

Table 8 Characteristics of Sparta water quality at El Dorado

# agency_cd	- Agency Code	USGS
# site_no	- Station number	33211309242
		1001
# sample_dt	- Begin date	10/17/2012
# sample_tm	- Begin time	11:00
# medium_cd	- Medium code	WG
# P00010	- Temperature, water, degrees Celsius	21.8
# P00095	- Specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius	457
# P00300	- Dissolved oxygen, water, unfiltered, milligrams per liter	0.3
# P00405	- Carbon dioxide, water, unfiltered, milligrams per liter	0.8
# P00440	- Bicarbonate, water, unfiltered, fixed endpoint (pH 4.5) titration, field, milligrams per liter	7
# P00445	- Carbonate, water, unfiltered, fixed endpoint (pH 8.3) titration, field, milligrams per liter	238
# P00400	- pH, water, unfiltered, field, standard units	8.7
# P00915	- Calcium, water, filtered, milligrams per liter	0.576
# P00940	- Chloride, water, filtered, milligrams per liter	21.3
# P01000	- Arsenic, water, filtered, micrograms per liter	0.07
# P01005	- Barium, water, filtered, micrograms per liter	7.93
# P01010	- Beryllium, water, filtered, micrograms per liter	< 0.006
# P01025	- Cadmium, water, filtered, micrograms per liter	< 0.016
# P01030	- Chromium, water, filtered, micrograms per liter	0.07
# P01040	- Copper, water, filtered, micrograms per liter	1.8
# P01049	- Lead, water, filtered, micrograms per liter	0.598
# P01057	- Thallium, water, filtered, micrograms per liter	< 0.010
# P01046	- Iron, water, filtered, micrograms per liter	19.6
# P01056	- Manganese, water, filtered, micrograms per liter	3.53
# P00930	- Sodium, water, filtered, micrograms per liter	128

3.2 Geochemical modeling - PHREEQC

PHREEQC is an open source modeling program written in C and C++ programming languages. It is designed to perform solution-based geochemical calculations to simulate chemical reactions and transport processes in a user-defined system that simulates a water body. Three widely applied capabilities of PHREEQC include 1) speciation calculations; 2) batch-reaction and 1-dimensional transport process for both reversible and irreversible reactions; 3) inverse modeling which is useful in accounting for intermediate reactions between sets of initial and final water states. The major advantage of PHREEQC is the wide range of reactions between multiple phases it can model, such as aqueous, mineral, gas, solid-solution, surface complexation, ion exchange, kinetics-dependent reactions, temperature and pressure-dependent reactions and mixing of solutions with reactions (Parkhurst, 2003).

4 Results and Analysis

4.1 Initial Mixing Model

Defining Key Data Input

Movement of recharge water in the aquifer is controlled by both the natural flow conditions in the aquifer and the flow pattern created by the injection activity. Hence, by controlling the injection rate, flow of the injected water in the aquifer can be managed and a mixing ratio of the recharge water to groundwater can be designed (Harpaz and Bear, 1963). Although recharge water and groundwater could have very different composition and are subjected to very different environmental conditions, they can be treated as two fully miscible solutions. As surface water is injected through wells, a transition zone is developed as two waters are mixed initially (Bear and Jacobs, 1965). In this study, the scenario of injecting water to the cone of depression is modeled as a complete mixing batch-reaction within a defined zone of immediate influence. As illustrated in Figure 15 (Pyne, 2008), a proximal zone of immediate mixing is developed around the injection well where injected water can be assumed to be completely mixed with the local water. Estimation of the proximal zone depends on several factors such as transmissivity of the aquifer, the local gravity gradient, and pressure gradient (Pyne, 2007). A radial zone extending 50 feet away from the injection well is appropriate in this study to set up the boundary conditions of the initial complete mixing reaction in our case. Three representative mixing ratios of injection water to groundwater, 1:9, 1:1 and 9:1, are specified and analyzed to evaluate potential impacts in the proximal zone.

Due to detection limit, arsenic concentration in the injected water is determined as less than 100ug/l. To simulate the worst-case scenario, arsenic concentration is assumed to be 100ug/l in the modeling simulation.

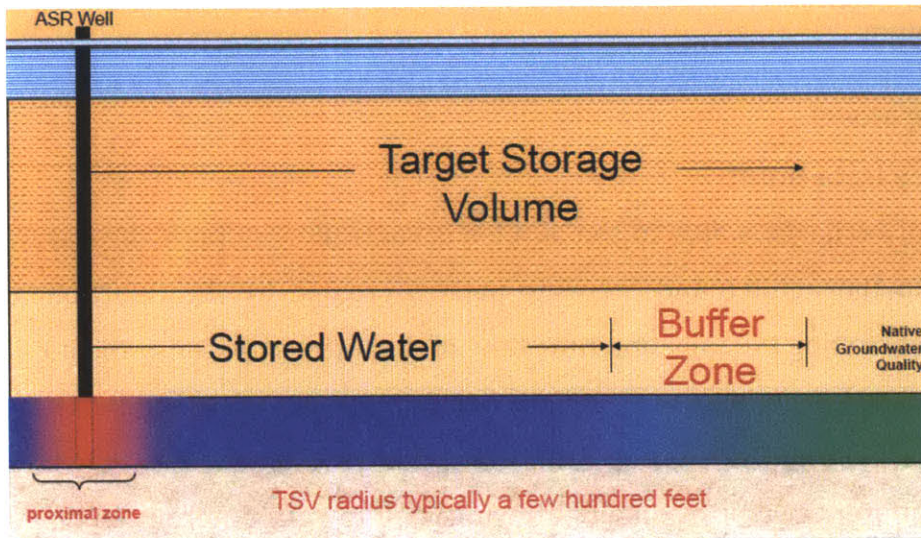


Figure 15 A cross-sectional view of the ASR system (Pyne, 2007)

Modeling

Simulation of the mixing reaction is performed primarily with the keyword data block MIX and EQUILIBRIUM_PHASES in PHREEQC. Modeling of injecting treated water into the Sparta aquifer is performed in four stages.

- A. The physical and chemical characteristics of injection water as indicated in Table 7 is defined in SOLUTION 1
- B. Composition of aquifer water is defined as SOLUTION 2 as indicated in Table 5.
- C. The two solutions are mixed at the pre-determined ratio in the proximal zone
- D. The final mixture is equilibrated with quartz (the main constituent of Sparta sand), goethite and a subsurface environment of a carbon dioxide partial pressure of $10^{-2.0}$ atm.

Application of keyword data block, MIX, performs a batch-reaction calculation reaching an equilibrium aqueous state. It can be used to mix together two or more aqueous solutions. The composition of each solution is first defined with a solution number to specify the amount of individual elements in the solution. The moles of the all elements in the solution are then multiplied by the mixing fraction input. The composition of the final mixed solution is found by adding up the fractional

solutions from the individual solutions. Similar methodology is applied to calculate the charge imbalance and temperature of the mixture.

Use of the keyword data block EQUILIBRIUM_PHASES defines the assemblage of pure phases in the aquifer system and performs calculations between with the specified aqueous phase. Based on the geological analysis of the Sparta layer, the relevant solid phases are determined as quartz, which is the main constituent of aquifer sand and goethite (FeO(OH)), an iron oxyhydroxide to represent the iron minerals in the aquifer matrix (Arthur, 2005) and a carbon dioxide partial pressure of $10^{-2.0}$ atm is assumed for ground water environment based on a similar ASR geochemical modeling study conducted by Parkhurst and Appelo in Central Oklahoma aquifer (1996). By specifying the phases, the program extracts the chemical compositions, reaction mechanisms and thermodynamic data that are built in the database phreeqc.dat.

```
Quartz SiO2 + 2 H2O = H4SiO4
      -log_k      -3.98
      -delta_h    5.990 kcal
      -Vm 22.67
```

```
Goethite FeOOH + 3 H+ = Fe+3 + 2 H2O
      -log_k      -1.0
      -delta_h    -14.48 kcal
```

Results

Compositions of recharge water, local groundwater, and the three types of mixture water are summarized in Table 9. Water quality data of the injection water and groundwater are adapted from Table 7 and Table 8. Radar representations are used to illustrate the distribution of the five major ionic groups of the highest concentrations, Ca, Cu, Fe, Mn and Na (Figure 16 - 18). It is clear from the graphical representations that ionic contents in the aquifer water is insignificant compared to

that in the injection water. Na and Ca are two ions of the highest concentration in injection water. As the ratio of injection water increases, the total amount of ionic contents in the final mixture is increased. The resulting completely mixed solutions are used as the base solution subsequently to evaluate the potential of other geochemical reactions, such as ion-exchange, sorption/adsorption and the oxidizing potential of the mixed solutions.

Iron equilibrium

In all three mixing scenarios, concentration of dissolved iron in the mixed solution is significantly reduced to an insignificant amount (Table 9). Speciation of iron in different forms can be found in PHREEQC output sheet in Appendix B. Direct data on the chemical forms and the amount of iron complexation formed is not displayed in the output data sheet. A simple mole-balance on iron by taking the difference between the dissolved iron concentration in the mixture and the original iron concentration in the aquifer reveals that almost all the dissolved iron in the proximal zone is precipitated out. The issue of iron precipitation when aquifer water is mixed with oxygenated surface water is highlighted frequently in research on ASR geochemistry as a primary cause for ASR well clogging. Modeling result for the Sparta aquifer in Union county confirms that an ASR well is likely to be subjected to cloggings due to the rapid precipitation of dissolved iron in the proximal zone.

Table 9 Compositions of injection water, aquifer and mixed water in equilibrium with aquifer phases for the specified injection ratio

Concentration (*10 ⁻⁴ mol/L)	Injection	Aquifer	Mixture 1	Mixture 2	Mixture 3
Ca	4.092E+00	1.437E-01	5.386E-01	2.118E+00	3.697E+00
Cu	7.869E-03	2.833E-04	1.042E-03	4.076E-03	7.110E-03
Fe	1.379E-01	3.510E-03	9.970E-07	2.644E-09	1.534E-09
Mn	1.820E-02	6.426E-04	2.399E-03	9.423E-03	1.645E-02
Na	6.395E+00	5.569E-02	6.896E-01	3.225E+00	5.761E+00
pH	7.10	8.70	5.34	5.90	6.12

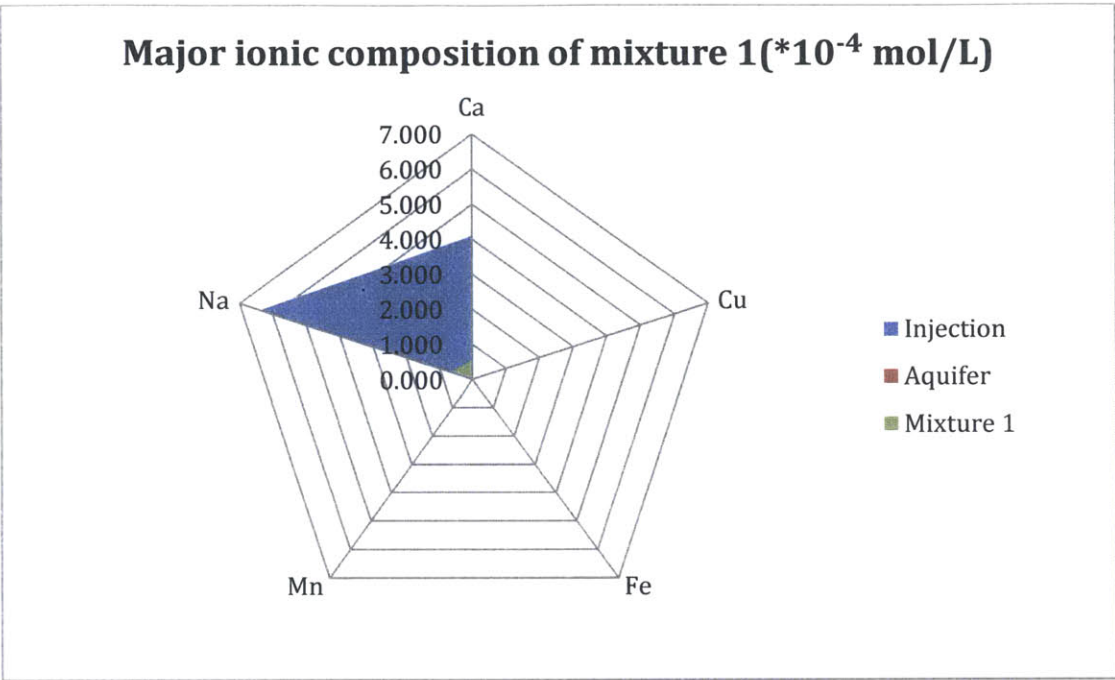


Figure 16 Radar chart representation of the major ionic compositions in the recharge water, groundwater and mixture with 10% of injection water

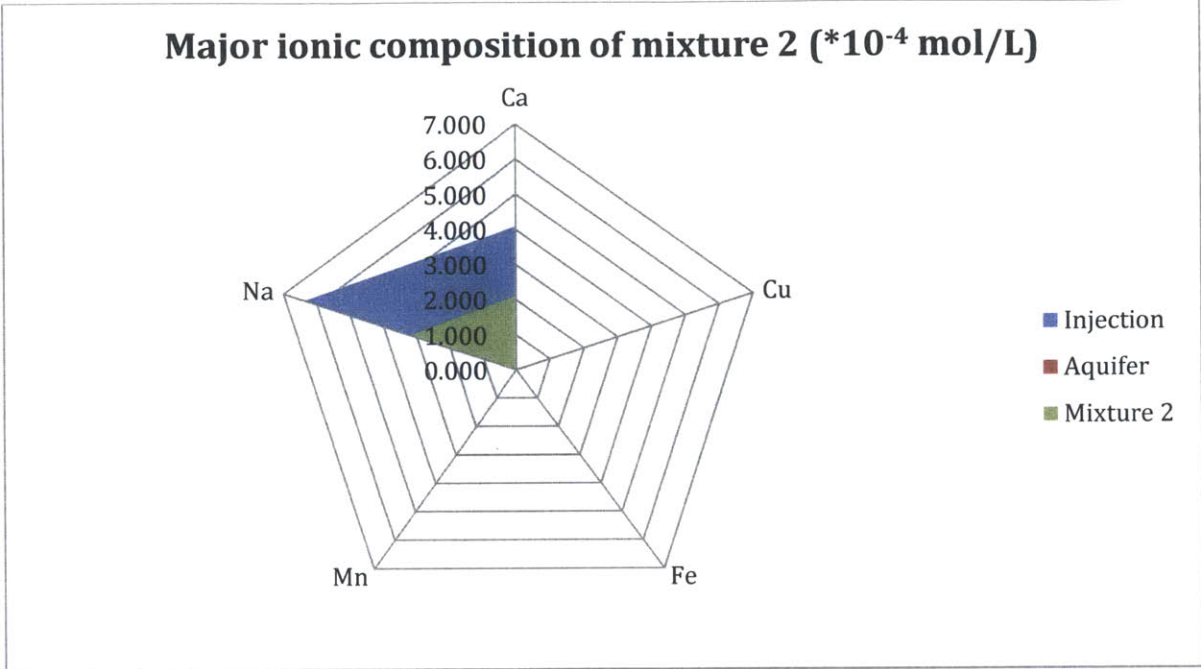


Figure 17 Radar chart representation of the major ionic compositions in the recharge water, groundwater and mixture with 50% of injection water

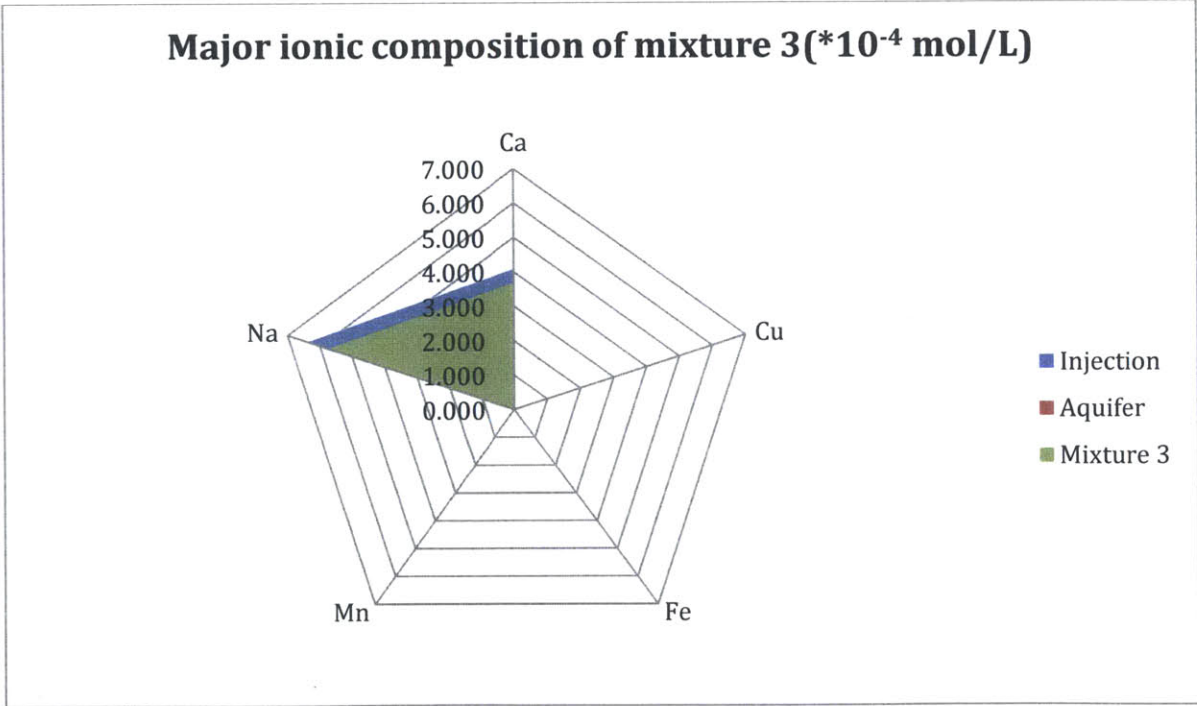


Figure 18 Radar chart representation of the major ionic compositions in the recharge water, groundwater and mixture with 90% of injection water

4.2 Transport of major cations with equilibrium-phases, exchange and surface reaction.

Modeling

A very important geochemical reaction to investigate in ASR is the interaction of trace elements between the aquifer surfaces and the stored water, in particular arsenic (Maliva and Missimer, 2008). Arsenic is a naturally occurring element in a ground water environment. USGS data shows that concentration of arsenic at Location 1 is 0.07ug/L, which is in compliance with the National Primary Drinking Water Regulations standard of 10 ug/L set by EPA. However, as literature shows that arsenic mobilization is typically observed when oxic recharge water reacts with anoxic Sparta aquifer water.

Another group of species that are modeled is sodium and calcium as they are two major species with highest concentrations in the mixture. The extent and time scale of cation exchange are determined by the concentration of sodium and calcium cations in the aqueous solution.

The conceptual model of the calculations uses the final mixed solution from the first simulation and equilibrates it with the two phases, goethite and quartz, in the proximal zone. The second stage of the simulation models the movement of the mixed water through the zone of targeted storage volume. The water enters the storage zone, where it reacts with the aquifer in the presence of the cation exchangers and the hydrous ferric-oxide goethite surfaces. Movement of the mixture follows a 1-dimensional advective-transport pathway, using the keyword data block ADVECTION. Duration of 200 days is estimated to provide a sufficient time frame to reach reaction equilibrium.

The database *waterq4f.dat* (Parkhurst and Appelo, 1999) contains the thermodynamic data for arsenic aqueous speciation and arsenic surface complexation as defined by Dzombak and Morel (1990). The amount of arsenic on the surface is derived from extraction data on core samples. (Mosier *et al*, 1991) Data used for the number of cation-exchange sites in the aquifer per liter of water is

provided by Parkhurst *et al* (1996). Consistent pure-phases assemblage consisting of goethite and quartz are defined as EQUILIBRIUM_PHASES 1. The number of cation exchange sites is specified by EXCHANGE 1 and the number of surface sites is specified by SURFACE 1. Charge balance for each solution is made on chlorine as the chloride ions are the predominant anions in the aquifer system. Simulations performed for charge balance on redox potential (pe) and alkalinity generate the same results. Agreement in results when different charge balance criteria are used confirms the validity of charge balance assumptions.

Results

A complete profile of the compositions of the equilibrated solution after an advection time step of 200 days and the surface complexation is attached as Appendix C. Figure 19-21 plot the changes in the ionic concentrations in the aqueous system in 200 days for the mixture solution 1, 2 and 3.

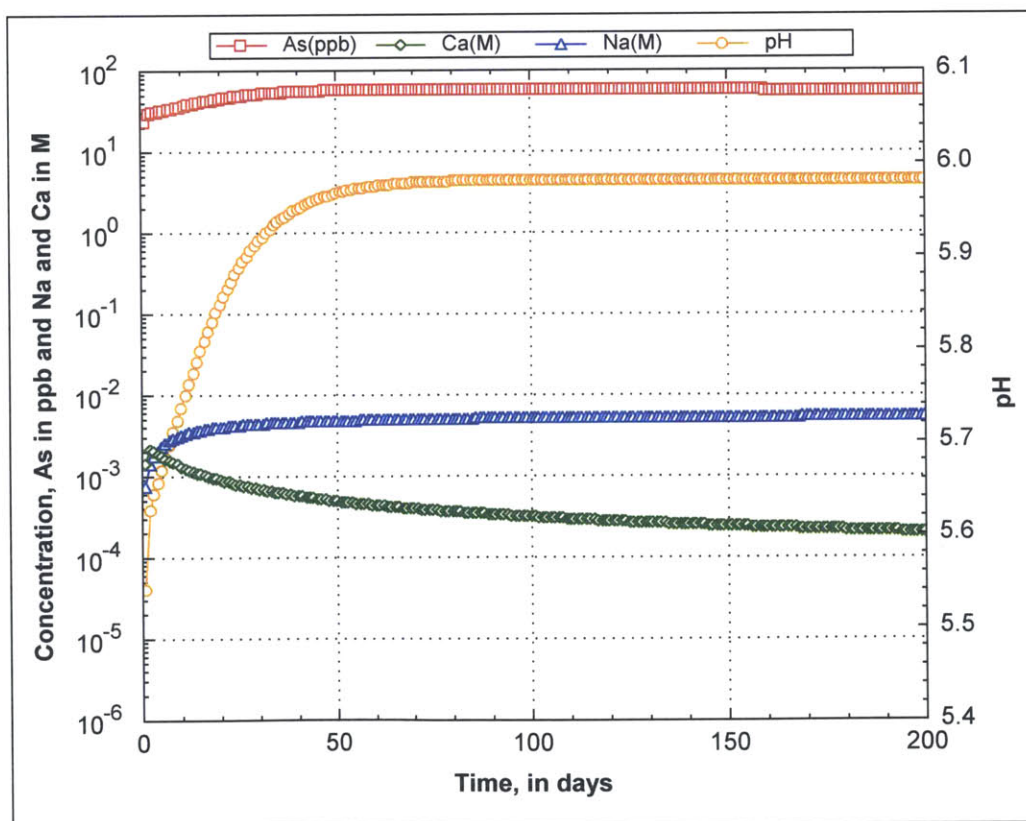


Figure 19 Transport and speciation of major cations Ca, Na and As in the aquifer with 10% injection water

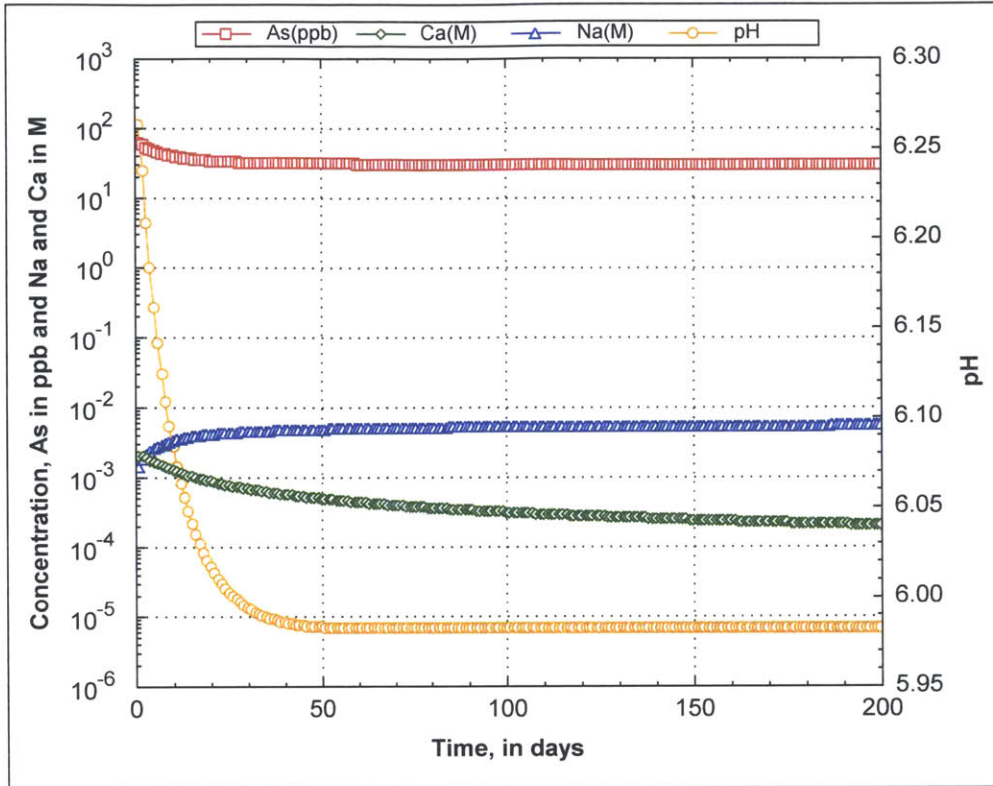


Figure 20 Transport and speciation of major cations Ca, Na and As in the aquifer with 50% injection water

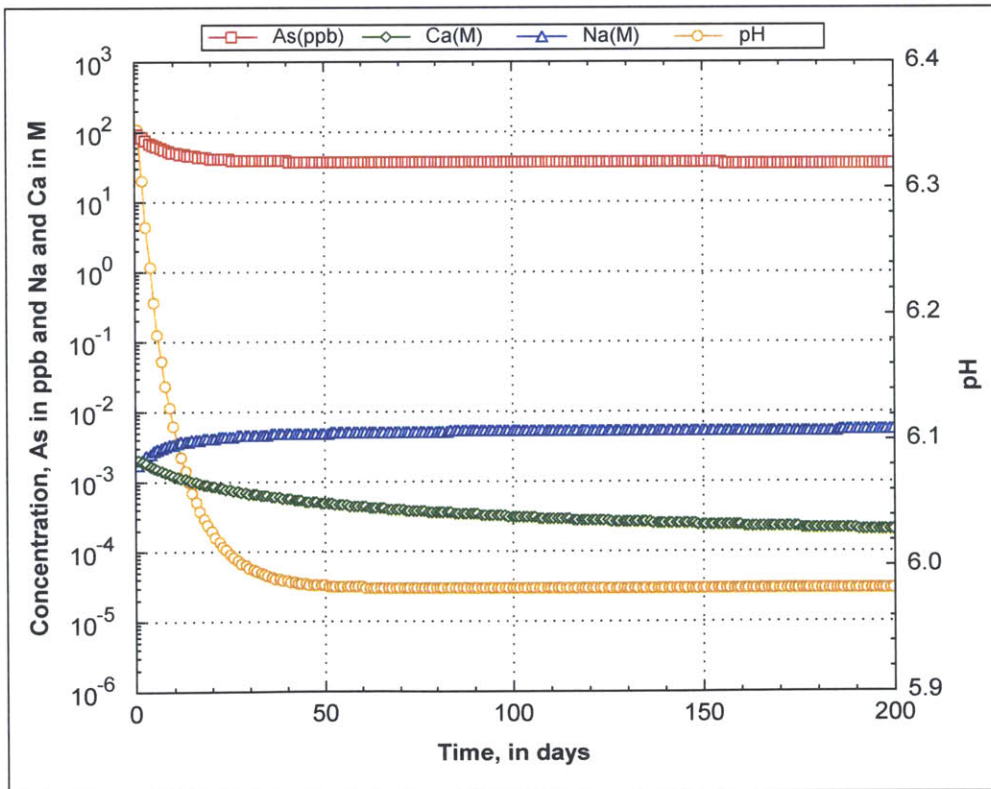


Figure 21 Transport and speciation of major cations Ca, Na and As in the aquifer with 90% injection water

1) Arsenic

In the three evaluated mixing ratios, arsenic attenuation is observed with mixing ratio of injection water to aquifer water 1:1 and 9:1. As the mixed water moves through the aquifer, the concentration of arsenic declined from an initial of $6.670\text{E}10^{-7}$ mol/L (50.03 ug/L) to an equilibrium of $3.874\text{E}10^{-7}$ mol/L (29.06 ug/L) for mixing ratio of 1:1 (Figure 20). For mixing ratio of 9:1, the concentration of arsenic declined from an initial of $1.201\text{E}10^{-6}$ mol/L (90.08ug/L) to an equilibrium of $4.631\text{E}10^{-7}$ mol/L (34.7 ug/L) (Figure 21). The time taken to reach equilibrium for both scenarios is approximately within 50 days. Research on arsenic water chemistry in ASR wells conducted in the Netherlands also showed that arsenic attenuation during recharge of oxic water into anoxic, in particular, a sandy aquifer, has been observed in field experiments (Pyne, 2003). Results from several new ASR wells in Florida have also shown that arsenic concentration declined from an initial concentration of 88 ug/L to 58 ug/l and to 34 ug/L on subsequent testing cycles (Pyne, 2003). Arsenic concentrations generally declined with time, with distance from points of injection and also with repeated cycle of recovery.

In contrast, an increase in dissolved arsenic concentration from an initial of $1.342\text{E}10^{-7}$ mol/L (10.06 ug/L) to an equilibrium of $7.255\text{E}10^{-7}$ mol/L (54.4 ug/L) (Figure 19) is observed when 10% injection water is mixed with the aquifer water. Arsenic is often associated with the presence of oxides of iron and manganese in groundwater in the iron-rich Sparta environment. Mobilization of arsenic during recharge is predominantly affected by oxidation-reduction reaction, with possible contribution from actions by the natural bacterial activity (Pyne, 2003). Water with low redox potential and neutral pH is less likely to result in dissolution of arsenic from the aquifer minerals. If injection wells are used for recovery of stored water, concentration of arsenic is expected to be higher in the proximity of the wells due to higher availability of oxygen-saturated injection water.

If arsenic is presented at levels higher than the regulation, there are broadly three types of treatment available to reduce the concentration of arsenic, 1) pretreatment of injection water to lower the redox potential; 2) in-situ treatment of the contaminated water; 3) post-treatment of recovered water before it is used as a

water supply. Conclusion from an ASR Expert Meeting conducted by US EPA Underground Injection Control Program (2009) proposed a set of successful operational guidelines to establish the Best Management Practices of an ASR system. A summary of the key findings are,

1) Pretreatment of injection water

- Increase the pH of recharge water to reduce the potential for arsenic dissolution
- Remove and reduce oxygen by bank filtration or addition of chemicals
- Eliminate microbiota which could cause arsenic mobilization

2) In-situ treatment

- Inject chemical to induce re-precipitation of arsenic in the aquifer
- Size a buffer zone to ensure leaching of arsenic occurs out of the storage zone
- Improved well design to avoid recovering water from places with known high-concentration of arsenic-bearing minerals

3) Post-treatment of recovered water

- Discharge the initial cycles of recovered water until the concentration of arsenic drops to below drinking water standards
- Treat to remove arsenic in recovered water

2) Calcium and sodium exchange

Calculations from PHREEQC show that the exchange reaction, which removes calcium from solution to the exchange sites on the mineral surfaces and removes sodium from exchanger to the solution, is observed to the same extent in all three scenarios. Equilibrium is approximately established after 150 days. Concentration of calcium decreases from 78.3 mmol/L to 0.2016 mmol/L and concentration of sodium increases from 0.441 mmol/L to 5.352 mmol/L. Calculation of the exchange of calcium ions for sodium ions on the mineral surface indicates that the extent of cations exchange was relatively small. Literature has shown that clays are the most important minerals providing exchange sites for cation exchange (McNeal and Coleman, 1996; Brown and Silvey, 1977). Since clays only accounts for a small

percentage of the geological matrix in our study area, the Sparta aquifer is considered as a zone with very little capacity for cation exchange due to limited availability of exchange sites on the mineral surfaces. Hence, although ion exchange reaction of calcium ions with sodium ions is observed, the extent of exchange does not account for a significant change in the ionic concentration.

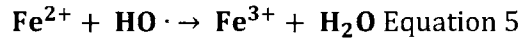
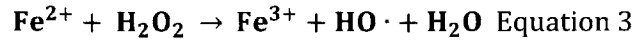
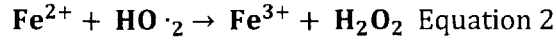
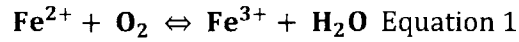
4.3 Speciation of ferrous/ferric oxide

Modeling

In addition to the ionic chemistry when aquifer water is mixed with oxygenated recharge surface water, another important type of issue that affects the viability of ASR system is the oxidation of the dissolved or particulate organic matters when the oxidizing potential of the aqueous system is increased by the injection of oxygen-rich surface water. Carbon in organic compounds is usually in the zero C (0) or C (-IV) valence state, which is not in stable equilibrium with the high concentration of dissolved oxygen in the system. The preferred oxidation state of C in the presence of O₂ is C (IV). Disequilibrium between O₂ and organic carbon, if it is present at a significant amount in the proximal zone, drives the oxidation reaction until equilibrium condition is reached by consuming the organic carbon and dissolved oxygen in the system. In this project, direct analysis of oxidization reaction of the organic matters could not be performed with the PHREEQC. However, other redox-sensitive minerals in their reduced forms such as Fe²⁺ and Mn²⁺, if present at a measureable amount in the aqueous system, could be used to assess the oxidizing capacity of the system.

Iron is one of the most important redox-sensitive elements in the groundwater environment and could be used to illustrate the oxidation/reduction processes (Deutsch, 1997). Iron occurs predominantly in two ionic forms in natural waters, as ferrous iron, Fe²⁺ or as ferric iron, Fe³⁺. While Fe²⁺ is quite soluble, Fe³⁺ dissolves less readily. The extent to which iron dissolves in water depends on the oxidizing potential of the water and the pH of the system. Weiss (1935) described

the oxygenation of ferrous iron in an oxidizing environment in the following sequences:



Kinetics of the oxidation reaction of ferrous irons in aqueous solution is described by Singer and Stumm (1970) as below,

$$\frac{dm_{\text{Fe}^{3+}}}{dt} = -(2.91e^{-9} + 1.33e^{12}a_{\text{OH}}^2p_{\text{O}_2})m_{\text{Fe}^{2+}} \text{ Equation 1}$$

Where a_{OH}^2 is the activity of the hydroxyl ion

m_{Fe} is the molarity of iron in solution

p_{O_2} is the oxygen partial pressure (atm)

The reaction typically occurs very fast in an alkaline solution. However, as pH drops below 7, ferric ions react with hydroxide ions and form solute complexes (Parkhurst and Appelo, 2003), resulting in a decrease in pH. Since the rate of reaction is related to square of the activity of hydroxyl ions, the rate of oxidation diminishes rapidly as pH drops. An embedded 3rd-order Runge-Kutta-Fehlberg algorithm is used in PHREEQC to calculate the concentration of the species when the keyword data block KINETICS is invoked. Time steps over which the kinetic reactions are integrated are specified in by identifier – step in the KINETICS data block for an accumulated time of 10 days.

Results

Figure 22 **Error! Reference source not found.**-24 illustrate the calculation output results from PHREEQC, depicting the variation of concentrations of ferrous ions, ferric ions and pH with time for each mixing ratio. Generally, a very rapid initial rate of reaction is observed in the first two days of reaction for all three injection

scenarios. Charette and Sholkovitz (2002) noted that time scale for complete oxidation of dissolved Fe^{2+} to form ferric precipitate when fresh air is stirred into a groundwater sample is over 2-3 hours., which corresponds well with the simulation results. Results from PHREEQC shows that as surface water is introduced, change in redox potential drives mobilization of iron in the solid phases to dissolve more as Fe^{2+} . Ferrous irons are generally more soluble than ferric compounds. Respective solubilities of ferrous and ferric ions are documented by Stumm and Lee (1961) as shown in Table 10. The major anions participating in the precipitation reactions are CO_3^{2-} and OH^- . In our simulation, OH^- is dominating as the Sparta aquifer is not a carbonate-rich system. From the solubility equations of ferrous and ferric ions listed in Table 10, it is clear that the ferrous iron has a much higher solubility than ferric iron. Solubility of the two species is highly dependently on the concentration of hydroxyl ions. As the pH drops, the solubility of both ferrous and ferric iron increases. Since ferrous iron has a much higher solubility than ferric iron, concentration of ferrous iron increases as the pH drops. To maintain charge balance of the system, increase in the ferrous iron is compensated by a decrease in the ferric iron concentration as illustrated by PHREEQC output.

Table 10 Solubilities of ferrous and ferric irons in solutions (Stumm and Lee, 1961)

Reaction	Equilibrium Constant at 25°C
Fe²⁺ Solubility	
$\text{Fe}(\text{OH})_2(\text{s}) = \text{Fe}^{2+} + 2 \text{OH}^-$	8×10^{-16}
$\text{Fe}(\text{OH})_2(\text{s}) = \text{Fe}(\text{OH})^+ + \text{OH}^-$	4×10^{-10}
$\text{Fe}(\text{CO}_3)(\text{s}) = \text{Fe}^{2+} + \text{CO}_3^{2-}$	2.1×10^{-11}
$\text{Fe}(\text{CO}_3)(\text{s}) + \text{OH}^- = \text{Fe}(\text{OH})^+ + \text{CO}_3^{2-}$	1×10^{-5}
Fe³⁺ Solubility	
$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}^{3+} + 3\text{OH}^-$	$\sim 10^{-36}$
$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}(\text{OH})_2^+ + \text{OH}^-$	1.7×10^{-16}
$\text{Fe}(\text{OH})_3(\text{s}) = \text{Fe}(\text{OH})^{2+} + 2\text{OH}^-$	6.8×10^{-25}
$2\text{Fe}(\text{OH})^{2+} = \text{Fe}_2(\text{OH})_2^{4+}$	30

Extreme low solubility of ferric complexes results in formation of ferric precipitate in the proximal zone, raising the concern of well clogging and even porous aquifer media clogging. As pH approaches 5, the reaction slows down as new equilibrium is reached between the interacting iron species and the hydroxyl ions.

Comparing the results of the three mixing ratios, increasing the percentage of the injection water enhances the oxidizing potential of the mixed water, creating longer times needed to reach equilibrium in the aquifer. Dissolution of Fe^{2+} into the aquifer water is highly pH-dependent. As the pH continues to decrease, concentration of dissolved Fe^{2+} increases correspondingly. Concentration of Fe^{3+} stabilizes after 50 days in all injection scenarios. The greatest reduction in the amount of Fe^{3+} occurs with 90% of injection water, from 10.901 $\mu\text{mol/l}$ to 7.187 $\mu\text{mol/l}$, indicating a potential of iron precipitation clogging the porous medium or the ASR wells.

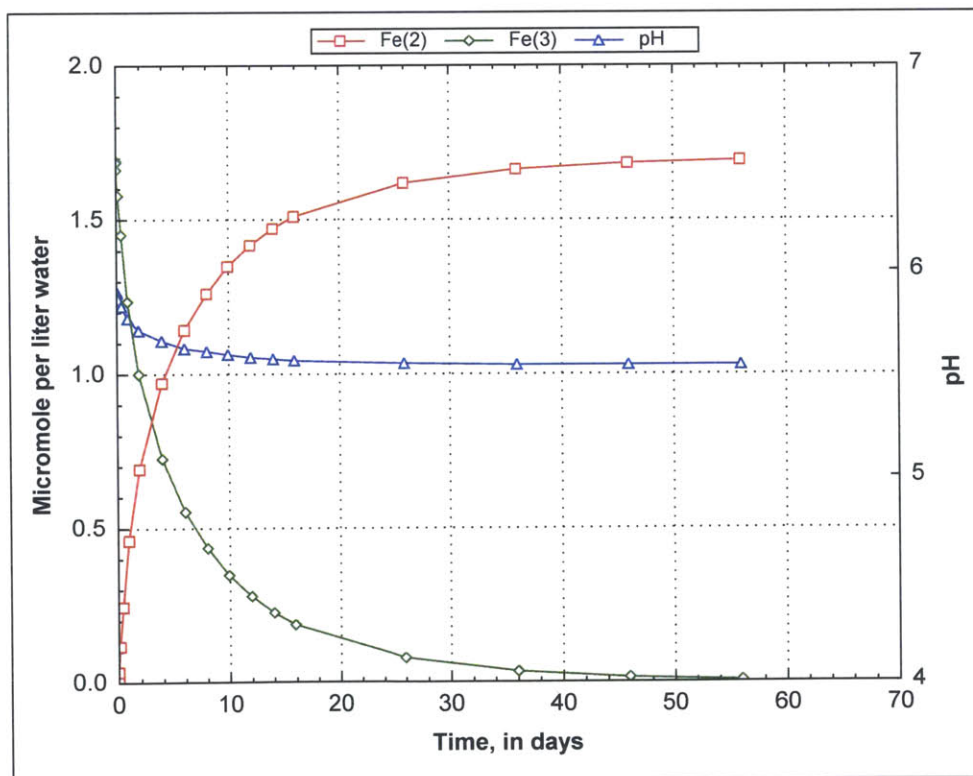


Figure 22 Speciation of ferrous/ferric cations in the aquifer with 10% injection water

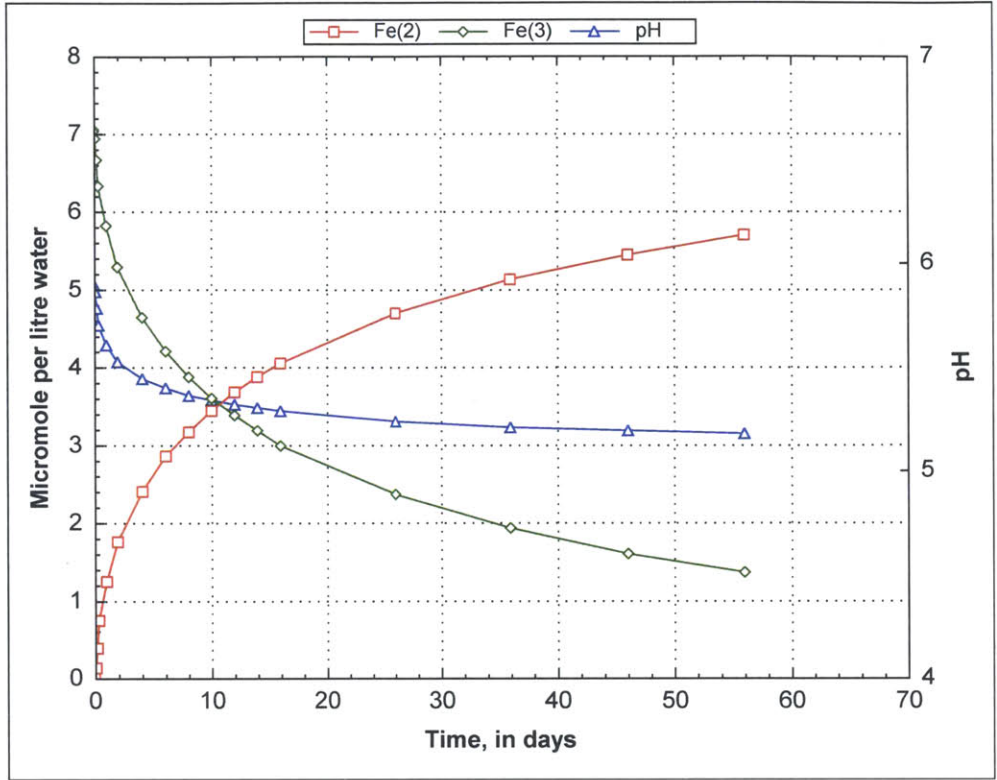


Figure 23 Speciation of ferrous/ferric cations in the aquifer with 50% injection water

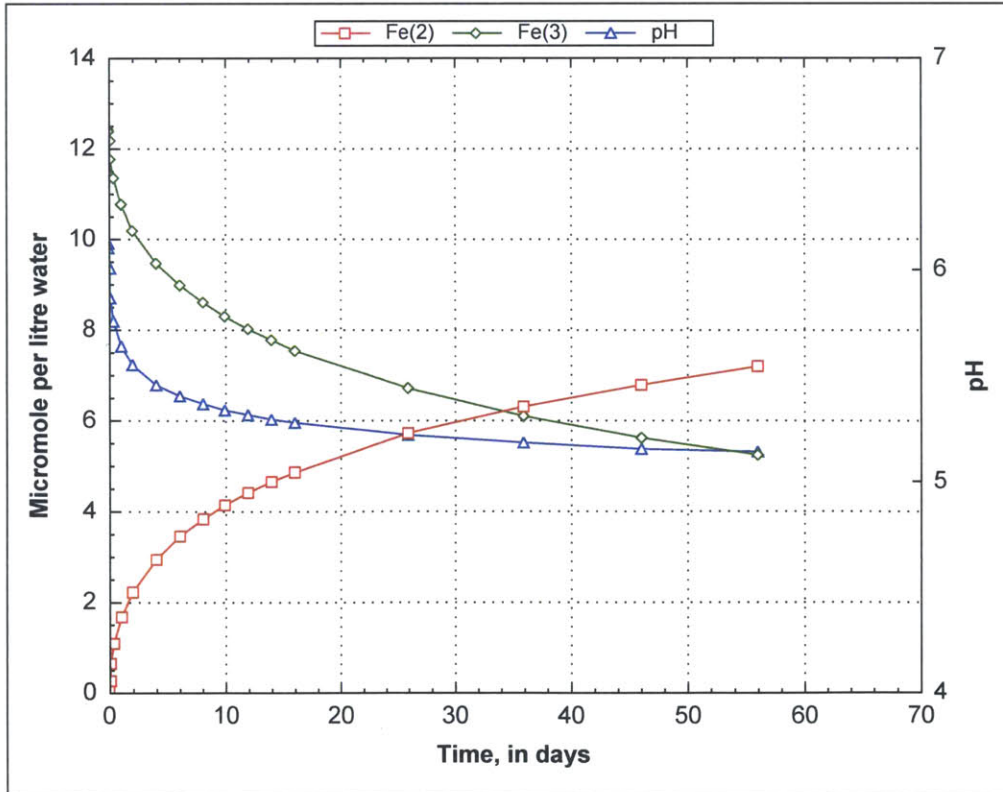


Figure 24 Speciation of ferrous/ferric cations in the aquifer with 90% injection water

5. Conclusion

One key aspect in the preliminary study to evaluate the potential feasibility of an ASR system is to fully understand the complex geochemical reactions that could occur when surface water is injected into the ground. Modeling results using the geochemical software PHREEQC reveals some issues which will need to be addressed if partially treated water from the local Ouachita Water Clarification Facility could be used for recharge.

- Better characterization of the ionic concentration in the injected water, in particular arsenic, to ensure injection activity is in compliance with the federal regulations
- Oxidizing potential of injection water is significantly higher than water in the Sparta aquifer. To control the potential of redox reactions, which could lead to iron precipitations, pre-treating the injected water to reduce the oxygen content is recommended.
- Both arsenic attenuation and dissolution were observed in the modeling simulations. Results showed that with a mixture of 10% of injected water, arsenic tends to desorb from the mineral surfaces into the aquifer water, resulting in potential breaching of the National Primary Drinking Water Standard. A better detection and monitoring scheme would need to be proposed if a low mixing ratio of injection water to groundwater were to be adopted.

The work of this paper includes 1) characterizing water quality in the Sparta aquifer and the geological matrix at the cone of depression; 2) exploring potential sources of water for injection and treatment method if required; 3) analyzing geochemical reactions among the major cations in the immediate proximal zones. However, many questions have yet to be addressed in a comprehensive geochemical modeling study, such as occurrence and reactions of organics, fate of DBPs and PPCPs and investigations on microbiological activity. In a complete ASR operation, flow and transport of the mixed water and the solute would also be of key interest in designing ASR cycles and the end-use of the stored water.

REFERENCES

- Albin, D. R. (1964). *Geology and ground-water resources of Bradley, Calhoun, and Ouachita counties, Arkansas*. (U.S. Geological Survey Water Supply Paper No. 1779-G).U.S. Geological Survey.
- Alley, W. M., Reily, T. E., & Franke, O. L. (1999). *Sustainability of ground-water resources*. (U.S. Geological Survey Circular No. 1186).U.S. Geological Survey.
- Arkansas Department of Environmental Quality. (2004). *Fact sheet for the underground injection control program in Arkansas*.
- Arkansas underground injection control code, Regulation 17 (2005).
- Arthur, J. D., Dabous, A. A., & Cowart, J. B. (2005). Water-rock geochemical considerations for aquifer storage and recovery: Florida case studies. In C. F. Tsang, & J. A. Apps (Eds.), *Underground injection science and technology, developments in water science, Amsterdam* (pp. 327-339) Elsevier.
- Asano, T., & Cotruvo, J. A. (2004). Groundwater recharge with reclaimed municipal wastewater: Health and regulatory considerations. *Water Res.*, 38(8), 1941-1951.
- Bear, J., & Jacobs, M. (1965). On the movement of water bodies injected into aquifers. *Journal of Hydrology*, 3, 35-57.
- Bloetscher, F., Muniz, A., & Witt, G. M. (2005). *Groundwater injection: Modeling, risks, and regulations*. New York: McGraw-Hill.
- Brahana, J. V., & Broshears, R. E. (2001). *Hydrogeology and ground-water flow in the Memphis and fort pillow aquifers in the Memphis area, Tennessee*. Nashville, Tenn.; Denver, Colo.: U.S. Dept. of the Interior, U.S. Geological Survey.
- Broom, M. E., Kraemer, T. F., & Bush, W. V. (1984). *A reconnaissance study of saltwater contamination in the El Dorado aquifer, union county, Arkansas*. (U.S. Geological Survey Water-Resources Investigation Report No. 84-4012).U.S. Geological Survey.
- Brown, D. L., & Silvey, W. D. (1977). *Artificial recharge to a freshwater-sensitive brackish-water sand aquifer*. (U.S. Geological Survey Professional Paper No. 939).U.S. Geological Survey.
- Burns & McDonnell. (2010, Sparta aquifer is making a comeback. *Benchmark*, 2010 No. 2, 15-16.
- Carlson, R. R., Lindstedt, K. D., Bennett, E. R., & Hartman, R. B. (1982). Rapid infiltration treatment of primary and secondary effluent. *J. Water Pollut. Contr. Fed.*, 54(3), 270-280.
- Charette, M. A., & Sholkovitz, E. R. (2002). Oxidative precipitation of groundwater-derived ferrous iron in subterranean estuary of a coastal bay. *Geophysical Research Letters*, 29(10)

- Clark, B. R., & Hart, R. M. (2009). *The Mississippi embayment regional aquifer study (MERAS): Documentation of a groundwater-flow model constructed to assess water availability in the Mississippi embayment*. Reston, Va.: U.S. Dept. of the Interior; U.S. Geological Survey.
- Clifton, C., Evans, R., Hayes, S., Hirji, R., Puz, G., & Pizarro, C. (2010). *Water and climate change: Impacts on groundwater resources and adaptation options*. (Water Working Notes No. 55027). The Water Sector Board of the Sustainable Development Network of the World Bank Group.
- Cole, E. (2009). Current practices in aquifer storage and recovery. *ASR Meeting*, Chicago.
- Committee on Ground Water Recharge, National Research Council. (1994). Source waters and their treatment. *Ground water recharge using waters of impaired quality* (). The National Academics Press.
- Committee on Sustainable Underground Storage of Recoverable Water, National Research Council. (2008). Water quality considerations. *Prospects for managed underground storage of recoverable water* (). Washington, DC: The National Academics Press.
- Crook, J. (1992). Water reclamation. *Encyclopedia Physical Science and Technology*, 17, 559-589.
- David L. Parkhurst, & C.A.J. Appelo. (2013). Description of input and examples for PHREEQC version 3--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Groundwater book 6, modeling techniques* (). Denver, Colorado: Unites States Geological Survey.
- David L., P., & Matthew D., P. (2002). *Geochemical modeling of an aquifer storage recovery experiment, Charleston, South Carolina*. (Open-File Report No. 02-89). Sacramento, California: U.S. Geological Survey.
- David, R., Pyne, G., & President, P. E. (2003). Water quality in aquifer storage recovery (ASR) wells. *American Water Works Association (Florida Section) Annual Meeting*, Orlando, Florida. doi:November 18, 2003
- De Ruiter, H., & Stuyfzand, P. S. (1998). An experiment on well recharge of oxic water into an anoxic aquifer. *Artificial Recharge of Groundwater, Proceedings of the Third International Symposium on Artificial Recharge*, Amsterdam.
- Deutsch., W. J. (1997). Solution, redox and gas exchange processes. *Groundwater geochemistry: Fundamentals and applications to contamination* (pp. 30-31). United States: Lewis.
- Drever, J. I. (1997). *The geochemistry of natural waters*. New York: Prentice-Hall.
- Dzombak, D. A., & Morel, F. M. M. (1990). *Surface complexation modeling- hydrous ferric oxide*. New York: John Wiley.
- Ellinger, S. (2010). *Sparta aquifer vulnerability assessment at the former Shumaker naval ammunition depot, east Camden, Arkansas*. (Hydrogeologic investigation report). United States EPA.

- Foreman, T. L., & Wuttig, M. (1998). *Las pases basin groundwater model simulations of ASR wellfield operations and development of design criteria for wellfield no.2.* (technical memorandum).CH2MHILL.
- Freeze, R. A., & Cherry, J. A., (1979). *Groundwater* (pp. 604 p.). Englewood Cliffs, New Jersey: Prentice-Hall.
- Freiwald, D.A., and Johnson, S.F., 2007, Monitoring of Sparta aquifer recovery in Southern Arkansas and Northern Louisiana, 2003–07: U.S. Geological Survey Fact Sheet 2007–3102, 4 p.
- Galloway, D. L., Jones, D. R., & Ingebritsen, S. E. (2000). *Land subsidence in the united states.* (U.S. Geological Survey Fact Sheet 087-00).U.S. Geological Survey.
- Halberg, H. N., & Stephens, J. W. (1966). *Use of water in Arkansas, 1965.* (Arkansas Geological Commission Water Resources Summary 5, 12p).
- Harpz, H., & Bear, J. (1963). *Investigations on mixing of waters in underground storage operations.* (No. Publ. No. 64 of the IASH). Israel: Commission of Subterranean Waters.
- Hays, P. D. (2000). *Sustainable-yield estimation for the Sparta aquifer in union county, Arkansas.* (USGS Numbered Series No. 99-4274).U.S. Dept. of the Interior, U.S. Geological Survey ; Branch of Information Services [distributor],.
- Hays, P. D. (2001). *Simulated response of the Sparta aquifer to outcrop area recharge augmentation, southeastern Arkansas.* Little Rock, Ark.: U.S. Dept. of the Interior, U.S. Geological Survey.
- Hays, P. D., Lovelace, J. K., & Reed, T. B. (1998). *Simulated response to pumping stress in the Sparta aquifer of southeastern Arkansas and north-central Louisiana, 1998-2027.* Little Rock, Ark.; Denver, Colo.: U.S. Dept. of the Interior, U.S. Geological Survey.
- Herczeg, A. L., Rattray, K. J., Dillon, P. J., Pavelic, P., & Barry, K. E. (2004). Geochemical processes during five years of aquifer storage recharge. *Ground Water*, 42(3), 438-445.
- Hosman, R. L., Long, A. T., & Lambert, T. W. (1968). *Tertiary aquifers in the Mississippi embayment, with discussions of quality of the water.* (U.S. Geological Survey Professional Paper No. 448-D).U.S. Geological Survey.
- Hosman, R. L., & Weiss, J. S. (1991). *Geohydrologic units of the Mississippi embayment and Texas coastal uplands aquifer systems, south-central united states.* Washington: U.S. G.P.O.
- Johnson, S. (2006). *Ouachita river alternative water supply project.* ().Union County Water Conservation Board.
- Joseph, R. L. (2000). *Status of water levels and selected water-quality conditions in the Sparta and Memphis aquifers in eastern and south-central Arkansas.* (U.S. Geological Survey Water Resources Investigations Report No. 00-4009).U.S. Geological Survey.
- Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., & Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S.

streams. 1999-2000: A national reconnaissance. *Environmental Science & Technology*, 36, 1202-1211.

Kresic, N. (2009). *Groundwater resources: Sustainability, management, and restoration*. New York: McGraw-Hill.

Lance, J. C., Rice, R. C., & Gilbert, R. G. (1980). Renovation of sewage water by soil columns flooded with primary effluent. *J. Water Pollut. Contr. Fed.*, 52(2), 381-388.

Langmuir, D. *Aqueous environment geochemistry*. Prentice-Hall: Upper Saddle River, NJ.

Lin, Z., & Puls, R. W. (2003). Potential indicators for the assessment of arsenic natural attenuation in the subsurface. *Advances in Environmental Research*, 7, 825-834.

Louisiana Sparta ground water commission. Water quality changes with distance from outcrop area and with depth. Retrieved 04/23, 2013, from http://www.spartaaquifer.com/index.php?option=com_content&view=article&id=77&Itemid=95

Maliva, R. G., & Missimer, T. M. (2008). *Aquifer storage and recovery and the development of sustainable water supplies*. American Water Works Association.

McKee, P. W., & Clark, B. R. (2003). *Development and calibration of a ground-water flow model for the Sparta aquifer of southeastern Arkansas and north-central Louisiana and simulated response to withdrawals, 1998-2027*. Little Rock, Ark.; Denver, Colo.: U.S. Dept. of the Interior, U.S. Geological Survey.

McKee, P. W., Clark, B. R., & Czarnecki, J. B. (2004). *Conjunctive-use optimization model and sustainable-yield estimation for the Sparta aquifer of southeastern Arkansas and north-central Louisiana*. Little Rock, Ark.; Denver, Colo.: U.S. Dept. of the Interior, U.S. Geological Survey.

McKee, P. W., & Hays, P. D. (2004). *The Sparta aquifer: A sustainable water resource?*. Reston, Va.: U.S. Dept. of Interior, U.S. Geological Survey.

McNeal, B. L., & Coleman, N. T. (1966). Effect of solution composition on soil hydraulic conductivity and effect of solution composition on the swelling of extracted soil clays. *Soil Science Society of America Proceedings*, 30(3), 308-317.

Meng, X., Korfiatis, G. P., Bang, S., & Bang, K. W. (2002). Combined effects of anions and arsenic removal by iron hydroxides. *Toxicology Letters*, 133(1), 103-111.

Metcalf & Eddy, I. (1991). *Wastewater engineering: Treatment, disposal, and reuse*. New York: McGraw-Hill.

Mosier, E. L., Papp, C. S. E., Motooka, J. M., Kennedy, K. R., & Riddle, G. O., (1991). *Sequential extraction analyses of drill core samples, central Oklahoma aquifer*. (U.S. Geological Survey Open-File Report No. 91-347).U.S. Geological Survey.

- Narayan, K. A., Schleberger, C., Charlesworth, P. B., & Bristow, K. L. (2003). Effects of groundwater pumping on saltwater intrusion in the lower Burdekin delta, north Queensland. *International Congress on Modeling and Simulation- Integrative Modeling of Biophysical, Social and Economic Systems for Resource Management Solutions*.
- National primary drinking water regulations, (2009). doi:EPA 816-F-09-0004
- National Research Council. (1994). *Ground water recharge using waters of impaired quality USA: ()*. Washington, DC, USA: National Academy Press.
- Olivieri, V. P., Kruse, C. W., Kawata, K., & Smith, J. E. (1977). *Microorganisms in urban storm water*. (No. EPA-600/2-77-087). Washington, D.C.: U.S. Environmental Protection Agency.
- Parkhurst, D. L., & Appelo, C. A. J. (2003). User's guide to PHREEQC--A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. *U.S. geological survey techniques and methods ()* U.S. Geological Survey.
- Parkhurst, D. L., Christenson, , Scott, , & Breiv, G. N. (1996). *Ground-water-quality assessment of the central Oklahoma aquifer, Oklahoma--geochemical and geohydrologic investigations*. (U.S. Geological Survey Water-Supply Paper No. 2357-C).U.S. Geological Survey.
- Pavelic, P., Dillon, P. J., & Nicholson, B. C. (2006). Comparative evaluation of the fate of disinfection byproducts at eight aquifer storage and recovery sites. *Environmental Science & Technology*, 40(2), 501-508.
- Payne, J. N. (1968). *Hydrologic significance of the lithofacies of the Sparta sand in Arkansas, Louisiana, Mississippi, and Texas*. (U.S. Geological Survey Professional Paper No. 659-A).U.S. Geological Survey.
- Pitt, R., & McLean, J. (1986). *Toronto area watershed management strategy study*. (). Toronto, Ont: Ontario Ministry of the Environment.
- Pyne, G. (2009). Where is ASR? Retrieved April/17, 2013, from <http://asrforum.com/picturepages/usa.html>
- Pyne, R. D. G. (1995). *Groundwater recharge and wells: A guide to aquifer storage recovery*. U.S.: CRC Press LLC.
- Pyne, R. D. G. (2003). Water quality in aquifer storage recovery (ASR) wells. *American Water Works Associations Annual Meeting*, Orlando, Florida.
- Pyne, R. D. G. (2007). Overview of aquifer storage recovery in the USA and the world. *Presentation to Conference on Aquifer Storage Recovery and Artificial Recharge in Oregon, "Overcoming Technical , Regulatory and Social Challenges"*,
- Rice, R. C., & Bouwer, H. (1984). Soil-aquifer treatment using primary effluent. *J. Water Pollut. Contr. Fed.*, 56(1), 84-88.

- Scheiderer, R. M., & Freiwald, D. A. (2006). *Monitoring the recovery of the Sparta aquifer in southern Arkansas and northern Louisiana*. (U.S. Geological Survey Fact Sheet No. 2006-3090). U.S. Geological Survey.
- Schrader, T. P. (2004). *Status of water levels and selected water-quality conditions in the Sparta-Memphis aquifer in Arkansas and the Sparta aquifer in Louisiana, spring-summer 2001*. Reston, Va.: U.S. Geological Survey.
- Sheng, Z., Li, J., King, P. J., & Miller, W. (2011). Development of groundwater resources. In M. M. Aral, & S. W. Taylor (Eds.), *Groundwater quantity and quality management* (pp. 203-294). Reston, Va.: American Society of Civil Engineers, Environmental and Water Resources Institute, Groundwater Management Technical Committee.
- Singer, P. C., & Stumm, W. (1970). Acid mine drainage--the rate determining step. *Science*, *167*, 1121-1123.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry*, *17*, 517-568.
- Sowby, R. (2013). *Hydrologic and hydraulic assessment of artificial recharge in the Sparta aquifer of union county, Arkansas*. (Unpublished Master of Engineering). Massachusetts Institute of Technology,
- Stumm, W., & Lee, G.F., (1961). Oxygenation of ferrous iron. *Industrial and Engineering Chemistry*, Vol. 53. Page 143.
- Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry, chemical equilibrium and rates in natural waters* (Third Edition ed.). New York: John Wiley & Sons.
- Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2002). *Wastewater engineering* (4th edition ed.) Metcalf & Eddy.
- Thangarajan, M. (Ed.). (2007). *Groundwater: Resource evaluation, augmentation, contamination, restoration, modeling and management*. Dordrecht: Springer.
- Thomas, J. M., McKay, W. A., Cole, E., Landmeyer, J. E., & Bradley, P. M. (2000). The fate of haloacetic acids and trihalomethanes in an aquifer storage and recovery program. *Ground Water*, *38*(4), 605-614.
- Timmer, H., & Stuyfzand, P. S. (1998). Deep well recharge in a polder area near the river Rhine. *Artificial Recharge of Groundwater, Proceedings of the Fourth International Symposium on Artificial Recharge*, Amsterdam, Balkema Press.
- Tony, S. (2013). In Ni Z. (Ed.), *GW data request*
- Treweek, G. P. (1985). In Asano T. (Ed.), *Pretreatment processes for groundwater recharge in artificial recharge of groundwater*. Boston, Mass: Butterworth.

- U.S. Environmental Protection Agency (EPA). (2012). Aquifer recharge (AR) and aquifer storage & recovery (ASR). Retrieved 23 Nov. 2012, 2012, from <http://water.epa.gov/type/groundwater/uic/aquiferrecharge.cfm>
- U.S. Environmental Protection Agency(EPA). (1983). *Results of the nationwide urban runoff program*. (No. Urban Planning Division, PB 84-185552). Washington, D.C.: U.S. Environmental Protection Agency.
- U.S. Environmental Protection Agency. (2009). Aquifer storage & recovery: Policy considerations. *ASR Experts Meetings: Policy Considerations*,
- U.S. Geological Survey (USGS). (2013). Mississippi embayment regional aquifer study (MERAS). Retrieved 05/22, 2013, from <http://ar.water.usgs.gov/PROJECTS/MerasModel.html>
- Union County Water Conservation Board. (2007). Sparta aquifer recovery study: Reporting the documented impact of the Ouachita river alternative water supply project on the Sparta aquifer in south Arkansas and north Louisiana, 2002–2007.
- U.S. EPA Underground Injection Control Program. (2009). Summaries of technical expert discussions. *Aquifer Storage and Recovery (ASR) Expert Meeting*, Chicago, IL.
- Water Pollution Control Federation. (1989). *Water reuse-- manual of practice* (2nd Ed. ed.). Alexandria, VA: Water Pollution Control Federation.
- Weiss, J. (1935). *Naturwissenschaften*, 23(64)
- Welch, A. H., Westjohn, D. B., Helsel, D. R., & Wanty, R. B. (2000). Arsenic in ground water of the United States: Occurrence and geochemistry. *Ground Water*, 28(4), 589-604.
- Yeatts, D. S. (2004). *Monitoring water-level and water-quality response to conservation measures in the Sparta aquifer of the union county, Arkansas area*. Reston, Va.: U.S. Dept. of the Interior, U.S. Geological Survey.

APPENDIX A

The list of regulated contaminants under the National Primary Drinking Water Regulations can be found at U.S. Environmental Protection Agency website

<http://water.epa.gov/drink/contaminants/index.cfm#Primary>

APPENDIX B

Data output for simulation 1 – Initial mixing model

Program output is attached in the disk.

APPENDIX C

Data output for simulation 2 - Transport of major cations with equilibrium-phases, exchange and surface reaction

Program output is attached in the disk.

APPENDIX D

Data output for simulation 3 – Speciation of ferrous/ferric ions

Program output is attached in the disk.

APPENDIX E

WATER ANALYSIS REPORT

4000055259

UNION POWER PARTNERS LP

6434 CALION HIGHWAY

El Dorado, AR

UNITED STATES 71730-9462

Sampled: 20-SEP-2012

Reported: 04-OCT-2012

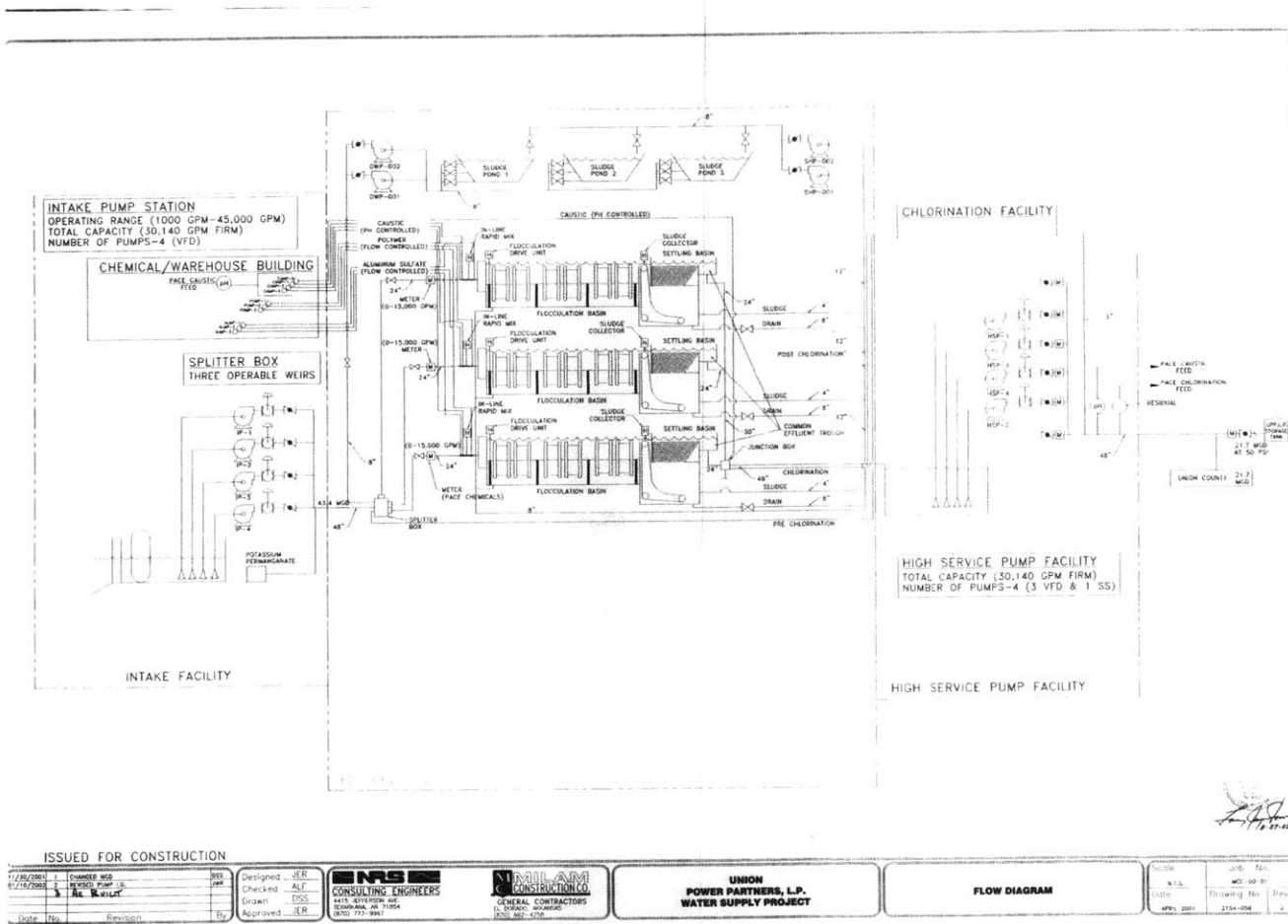
Field Rep: Horton, Eddie M.

	RIVER BOX <u>W0926153</u>	RAW <u>W0926154</u>	FINISHED <u>W0926155</u>
pH	7.0	7.1	7.4
Specific Conductance, at 25°C, µmhos	117	122	131
Alkalinity, "P" as CaCO ₃ , ppm	0	0	0
Alkalinity, "M" as CaCO ₃ , ppm	13.5	14.5	15.9
Sulfur, Total, as SO ₄ , ppm	9.1	9.2	8.3
Chloride, as Cl, ppm	17.5	22	23
Hardness, Total, as CaCO ₃ , ppm	24	25	24
Calcium Hardness, Total, as CaCO ₃ , ppm	16.1	16.4	15.7
Magnesium Hardness, Total as CaCO ₃ , ppm	8.1	8.3	8.0

Barium, Total, as Ba, ppm	0.05	0.05	0.04
Strontium, Total, as Sr, ppm	0.11	0.12	0.11
Copper, Total, as Cu, ppm	< 0.05	< 0.05	< 0.05
Iron, Total, as Fe, ppm	0.83	0.77	0.21
Sodium, as Na, ppm	10.5	14.7	16.3
Potassium, as K, ppm	1.7	1.7	1.6
Zinc, Total, as Zn, ppm	0.04	< 0.01	< 0.01
Aluminum, Total, as Al, ppm	0.7	0.6	0.6
Manganese, Total, as Mn, ppm	0.12	0.1	0.07
Molybdenum, as Mo, ppm	< 0.06	< 0.06	< 0.06
Phosphate, Total, as PO ₄ , ppm	< 0.4	< 0.4	< 0.4
Phosphate, Ortho-, as PO ₄ , ppm	< 0.2	< 0.2	< 0.2
Silica, Total, as SiO ₂ , ppm	6.8	6.7	5.4
Arsenic, Total, as As, ppm	< 0.1	< 0.1	< 0.1
Beryllium, as Be, ppm	< 0.01	< 0.01	< 0.01

Boron, as B, ppm	< 0.05	< 0.05	< 0.05
Cadmium, as Cd, ppm	< 0.01	< 0.01	< 0.01
Chromium, Total, as Cr, ppm	< 0.02	< 0.02	< 0.02
Cobalt, Total, as Co, ppm	< 0.01	< 0.01	< 0.01
Lead, Total, as Pb, ppm	< 0.05	< 0.05	< 0.05
Nickel, Total, as Ni, ppm	< 0.01	< 0.01	< 0.01
Selenium, Total, as Se, ppm	< 0.1	< 0.1	< 0.1
Tin, Total, as Sn, ppm	< 0.05	< 0.05	< 0.05
Titanium, Total, as Ti, ppm	< 0.01	< 0.01	< 0.01
Vanadium, Total, as V, ppm	< 0.01	< 0.01	< 0.01
Thallium, Total, as Tl, ppm	< 0.1	< 0.1	< 0.1

APPENDIX F



ISSUED FOR CONSTRUCTION						UNION POWER PARTNERS, L.P. WATER SUPPLY PROJECT	FLOW DIAGRAM	Date: APR 2011 Title:	Job No: 213-004 Rev: 2
1/26/2011 6/19/2011	CHANGES REVISIONS	DESIGNED DRAWN APPROVED	BY DATE						

⁴ Drawing is provided by Thomas C. Burger, the plant manager of the Union Power Station, on May 16 2013.