



**US Army Corps
of Engineers®**
Engineer Research and
Development Center

Geochemical Models of Water-Quality Changes During Aquifer Storage Recovery (ASR) Cycle Tests, Phase I: Geochemical Models Using Existing Data

June E. Mirecki

September 2006



Geochemical Models of Water-Quality Changes During Aquifer Storage Recovery (ASR) Cycle Tests, Phase I: Geochemical Models Using Existing Data

June E. Mirecki

*Environmental Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199*

Final report

Approved for public release; distribution is unlimited.

Prepared for U.S. Army Corps of Engineers
Jacksonville, FL

Abstract: Geochemical models were developed using existing water-quality data sets from three permitted, potable-water Aquifer Storage Recovery (ASR) systems in south Florida. All three systems store and recover water in different permeable zones of the upper Floridan Aquifer System (FAS). At the Olga ASR system, water is stored in the Suwannee Limestone; at the North Reservoir ASR system, water is stored in the Arcadia Formation of the lower Hawthorn Group. Both sites are located in Lee County, along the southwest Gulf Coast of Florida. At the Eastern Hillsboro ASR system, water is stored in the basal Hawthorn unit; this system is located in Palm Beach County near the southeastern Atlantic Coast of Florida. The objectives of this study are to use geochemical modeling methods to simulate 1) mixing between native water of the upper FAS and recharge water during cycle testing; 2) geochemical reactions that occur during the storage phase of cycle tests in different lithologies; and 3) controls on arsenic transport and fate during ASR cycle testing. Existing cycle test data sets were developed for permitting purposes, not research; therefore, concentrations of some major dissolved constituents are estimated. Quantitative uncertainty that resulted from the use of incomplete water-quality datasets is defined for these geochemical models.

Mixing of recharge and native groundwater end members during cycle testing is simulated using chloride as a conservative tracer. Mixing models show that low-chloride groundwater mixes to different extents during recharge in the Arcadia Formation and Suwannee Limestone. At the North Reservoir ASR system (Arcadia Formation), recharge water is transported as plug flow, as shown by sigmoid-shaped breakthrough curves in monitor wells, and chloride trends that resemble conservative mixing lines. In contrast, at Olga ASR system, recharge water is affected by hydraulic factors because breakthrough curves at the monitor well are not sigmoidal, and chloride trends deviate from conservative mixing curves. Data were insufficient to simulate mixing at the Eastern Hillsboro ASR system.

Inverse geochemical models quantified phase mole-transfer between water and rock, which controls water quality during the storage phase of a cycle test. The greatest phase mole-transfer values resulted from reactions of iron and sulfur at the Olga and North Reservoir ASR systems. Specifically, these reactions included pyrite oxidation with subsequent iron oxyhydroxide precipitation, and sulfate reduction with hydrogen sulfide production. These reactions should proceed in a sequence, not simultaneously, and suggest that the redox evolution of the storage zone exerts a significant influence on stored water quality.

Arsenic mobility is a major challenge to ASR feasibility, so inverse geochemical models were developed to simulate redox conditions that facilitate arsenic mobility during ASR cycle testing. Trends in arsenic concentrations measured at ASR and monitor wells, along with additional water-quality data, arsenic speciation analyses, and bulk chemistry and major mineralogy in core samples from the Arcadia Formation and Suwannee Limestone constrain these models. The stability of iron oxyhydroxide phases changes as the storage zones evolve from oxic (during recharge) to sulfate-reducing (during storage and recovery). Because iron oxyhydroxide is an effective sorption surface for arsenic, the stability of this mineral is an important control. The onset of sulfate-reducing conditions causes reductive dissolution of iron oxyhydroxide, with subsequent release of sorbed arsenic. The instability of iron oxyhydroxide during recovery is supported by inverse geochemical models at Olga and North Reservoir ASR systems. However, phase mole-transfer values are small (micromoles/kilogram water), and it is unclear if this mass of iron is sufficient for effective arsenic sequestration.

DISCLAIMER: The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

DESTROY THIS REPORT WHEN NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

Contents

Figures and Tables.....	v
Preface	vii
Unit Conversion Factors.....	ix
1 Introduction.....	1
Objectives	1
Data-quality criteria and evaluation of South Florida ASR data sets	2
Geochemical modeling codes and conceptual model development	4
Sources of uncertainty in geochemical models	5
2 Hydrogeologic Setting	7
Regional hydrogeologic framework	7
Olga ASR System	7
North Reservoir ASR system.....	9
Eastern Hillsboro ASR system.....	11
3 Geochemical Models of Mixing During Recharge and Recovery	13
Conceptual model	13
Olga and North Reservoir ASR systems	14
4 Inverse Geochemical Models of Water-Quality Changes During Storage	19
Conceptual model	19
Olga ASR system	20
North Reservoir ASR system.....	23
Eastern Hillsboro ASR system.....	24
5 Geochemical Model of Changing Redox Conditions During Recovery	25
Conceptual model of arsenic transport and fate	25
Arsenic concentration trends during ASR cycle testing	27
Inverse geochemical model defining redox condition during recovery	30
6 Conclusions.....	33
References.....	37
Appendix A: Mineralogy and Chemical Data from Cores CCBRY-1 and EXBRY-1.....	41
Appendix B: PHREEQC Input Files	49
Mixing models	49
Inverse geochemical model of water-quality changes during storage	51
Inverse geochemical model: Reductive dissolution of iron oxyhydroxides during recovery	53

Appendix C: Selected Water-Quality Data from Cycle Tests.....	55
--	-----------

Report Documentation Page

Figures and Tables

Figures

Figure 1. Current framework for interpretation of lithostratigraphic and hydrostratigraphic units in South Florida (from Reese and Richardson, in review).....	8
Figure 2. Selected geophysical logs from Olga, North Reservoir, and East Hillsboro (PBCWUD) ASR systems. Stratigraphic picks at Olga and North Reservoir from Water Resource Solutions (2002a, 2002b); East Hillsboro from Reese and Mernberg (2000). Geophysical logs from DBHydro database (SFWMD, 2004). Gamma log for North Reservoir is a composite from two boreholes 250 ft apart. Hachured interval is the storage zone at each ASR system.	10
Figure 3. Breakthrough curves and mixing curves during recharge at Olga and North Reservoir ASR systems. Breakthrough curves (A, C, E) are plotted using chloride concentrations measured in monitor wells at Olga (A, 350 ft from ASR well; C, 400 ft from ASR well) and North Reservoir (E, 250 ft from ASR well) during recharge. Chloride concentrations measured in monitor well samples during recharge (B, D, F) are compared to model-generated conservative mixing lines at Olga and North Reservoir ASR systems.	16
Figure 4. Mixing models during recovery at Olga and North Reservoir ASR systems. Measured chloride concentrations from the Olga ASR well (A) and monitor wells (C, E) are compared to conservative mixing lines for Cycle Tests 1 through 3. Measured chloride concentrations from the North Reservoir ASR (B) and monitor (D) well are compared to conservative mixing lines for Cycle Tests 2 and 3. No data were available for Cycle 1 recovery at the North Reservoir ASR system.....	17
Figure 5. Bar graphs showing phase mole- transfer values calculated by PHREEQC inverse models (Table B1). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga, North Reservoir, and Eastern Hillsboro ASR systems.....	22
Figure 6. Linear regression plots that compare measured versus calculated concentrations of calcium and magnesium in Cycle 4 recovered water samples (ASR and monitor wells) at the Olga ASR system.....	23
Figure 7. Trends in total dissolved arsenic concentrations measured in ASR and monitor wells at the Olga and North Reservoir ASR systems during Cycle Tests 1 through 3. Concentrations plotted here as 3 µg/L actually were below the detection limit for the ICP-MS method. Data are tabulated in Appendix C.....	28
Figure 8. Trends in total dissolved arsenic and arsenite (AsIII) concentrations in ASR well samples from the recovery phase of Cycle Test 3 at Olga and North Reservoir ASR systems. Data are tabulated in Tables C8 and C9.....	30
Figure 9. Bar graphs showing phase mole-transfer values calculated by PHREEQC inverse models (Table B2). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga and North Reservoir ASR systems.	31

Tables

Table 1. Storage zone characteristics, chloride concentrations in native upper FAS and recharge waters, and pumping rates at representative ASR systems.	14
---	----

Table A1. Mineralogy of selected samples from the Arcadia Formation and Suwannee Limestone in core CCBRY-1.....	41
Table A2. Bulk chemistry of selected samples from the Arcadia Formation and Suwannee Limestone in core CCBRY-1 ¹	43
Table A3. Bulk chemistry of selected samples from the Arcadia Formation and Suwannee Limestone in core EXBRY-1 ¹	44
Table A4. Selected major and trace element concentrations in Arcadia Formation and Suwannee Limestone samples from core CCBRY-1 ¹	44
Table A5. Selected major and trace element concentrations in Arcadia Formation and Suwannee Limestone samples from core EXBRY-1 ¹	45
Table A6. X-ray diffractograms of Arcadia Formation and Suwannee Limestone samples from core CCBRY-1.....	46
Table B1. Inverse geochemical models showing water quality changes during storage.	52
Table B2. Inverse geochemical models simulating iron oxyhydroxide dissolution during recovery.	54
Table C1. Arsenic and chloride concentrations from Cycle Test 1 at Olga ASR system. Data from WRS (2002a).....	56
Table C2. Arsenic and chloride concentrations from Cycle Test 2 at Olga ASR system. Data from WRS (2003a).....	57
Table C3. Arsenic and chloride concentrations from Cycle Test 3 at Olga ASR system. Data from Monthly Operating Reports.	59
Table C4. Arsenic and chloride concentrations from Cycle Test 1 at the North Reservoir ASR system. Data from WRS (2002b).	60
Table C5. Arsenic and chloride concentrations from Cycle test 2 at the North Reservoir ASR system. Data from WRS (2003b).	61
Table C6. Arsenic and chloride concentrations from Cycle Test 3 at the North Reservoir ASR system. Data from WRS (2004).....	62
Table C7. Arsenic and chloride concentrations from Cycle Test 1 at the Eastern Hillsboro ASR system. Data from PBCWUD (2005).	63
Table C8. Dissolved arsenic species concentrations from Cycle Test 3 recovery at the Olga ASR system (ERDC data). All concentrations reported in µg/L.....	64
Table C9. Dissolved arsenic species concentrations from Cycle Test 3 recovery at the North Reservoir ASR system (ERDC data). All concentrations reported in µg/L.....	64

Preface

This report was prepared by the U. S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS, for the Jacksonville, FL, District of the U.S. Army Corps of Engineers. This report is a product of the Regional Aquifer Storage Recovery Project, within the Comprehensive Everglades Restoration Plan (CERP), administered by the U.S. Army Corps of Engineers, Jacksonville District, and the South Florida Water Management District. The principal investigator was Dr. June Mirecki, Research Physical Scientist (Geochemist), Environmental Processes and Engineering Division (EPED), ERDC-EL.

This report was reviewed by Dr. Christopher J. Brown, Jacksonville District, USACE, and Mr. Joseph Dunbar, Geotechnical and Structures Laboratory (GSL), ERDC. This report benefited from input by the independent technical review team (ITR) for CERP projects. The ITR team consisted of Dr. Sam B. Upchurch, SDII Global Corp., Tampa, FL; Dr. Robert G. Maliva, Camp Dresser McKee, Ft. Myers, FL; and Dr. Thomas Missimer, Groundwater Geosciences, Inc., Ft. Myers, FL. The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED, EL, and Dr. Elizabeth Fleming, Director, ERDC-EL. At the time of publication of this report, Director of ERDC was Dr. James R. Houston. The Commander was COL Richard B. Jenkins.

The author gratefully acknowledges the following colleagues for their time, fruitful discussions, and willingness to provide data for the ASR systems described in this report: Luis Molina, Lee County Utilities, Fort Myers, FL; Dan Acquaviva and Dr. Mark Pearce, Water Resource Solutions, Inc., Cape Coral, FL; Joe May, Len Fishkin, and Robyn James of the Florida Department of Environmental Protection, West Palm Beach, FL; and Nick Panayides and Tom Uram from the Palm Beach County Water Utilities District, Boca Raton, FL. Mark McNeal, CH2MHill, Tampa, FL, provided insight and data from other ASR systems that store water in the Suwannee Limestone for comparison. Dr. Jonathan Arthur and Cindy Fischler at the Florida Geological Survey, Tallahassee, FL, provided access and bulk chemical data from cores CCBRY-1 and EXBRY-1. Larry Campanelli and Brad Balogh, Lee County Utilities, FL, collected groundwater samples during Olga Cycle 3 for arsenic species analysis. Dr. Anthony J. Bednar,

ERDC-EL, analyzed the Olga samples for arsenic species. Dr. Charles Weiss, Jr., ERDC-GSL, performed x-ray diffraction analyses of samples from the CCBRY-1 core.

Unit Conversion Factors

Multiply	By	To Obtain
feet	0.3048	meters
miles (U.S. statute)	1,609.347	meters

1 Introduction

Objectives

Geochemical models quantify reactions, reaction rates, and phase mole-transfer between water and aquifer material in diverse hydrogeological settings. In the context of aquifer storage recovery (ASR) cycle tests, geochemical models were developed to quantify reactions that affect water quality, and the rates at which they occur (Castro 1995, Mirecki et al. 1998, Vanderzalm et al. 2002, Herczeg et al. 2004, Petkewich et al. 2004, Prommer and Stuyfzand 2005). Most of these models were developed at ASR systems that had a significant research component marked by an intensive data collection effort. In this report, geochemical models were developed using existing water-quality data obtained during routine cycle testing at potable water ASR systems in south Florida (Mirecki 2004). Some additional geochemical and lithological data were obtained to further define and constrain these models.

The primary focus is to present geochemical models that describe water quality during cycle testing at selected existing potable water ASR systems of south Florida. These models simulate geochemical reactions among recharge water, native water of the upper Floridan Aquifer System (FAS), and the predominantly carbonate lithologies of the lower Hawthorn Group, and Suwannee Limestone of southwest Florida, and equivalent strata of southeastern Florida.

Geochemical models are developed using existing data from three ASR systems located near planned pilot ASR systems for the Comprehensive Everglades Restoration Plan (CERP). Two ASR systems are located near the southwest Gulf Coast, in Lee County near Fort Myers. At the Olga ASR system, water is stored in the Suwannee Limestone; at the North Reservoir ASR system, water is stored in the Arcadia Formation of the lower Hawthorn Group. Hydrogeologic conditions encountered at these sites should be similar to those encountered at the proposed Caloosahatchee River pilot ASR system at Berry Groves. A third ASR system is located at East Hillsboro, in southeastern Palm Beach County. Water is stored at depths ranging between 1,005 and 1,225 ft below land surface (bls), in the basal Hawthorn unit at this site. Hydrogeologic conditions encountered here

should be similar to those at the West Hillsboro pilot ASR system that is under construction.

The objective of this report is to present geochemical models using existing ASR cycle test data. Geochemical models presented will simulate: 1) mixing between native water of the upper FAS and recharge water during cycle testing; 2) geochemical reactions that occur during the storage phase of cycle tests in different lithologies; 3) controls on arsenic transport and fate during ASR cycle testing, and 4) assessment of uncertainty due to the use of incomplete water-quality data sets.

Data-quality criteria and evaluation of South Florida ASR data sets

Several data-quality criteria must be fulfilled in order to develop a representative (accurate and/or valid) geochemical model. First, a “complete analysis” means that 90 percent of the dissolved solids load (or, species that occur at concentrations greater than 1 mg/L; Zhu and Anderson 2002) is measured in a groundwater sample. Analysis of all major anions and cations plus pH and carbonate alkalinity minimally satisfies this criterion (Davis 1988). Analysis of trace dissolved species concentrations (that is, anions and cations that occur at the parts per billion level) is necessary because these solutes often are very reactive in water-rock systems. Assessment of redox condition of the aquifer requires measurement of those redox-sensitive ions that occur in the greatest mass. Typically, these redox-sensitive ions include total dissolved and ferrous (Fe^{2+}) iron, and sulfate and total dissolved sulfide concentrations. Second, charge-balance errors should be within ± 2 percent in samples where all ion concentrations have been measured (Fritz 1994). Samples with small charge-balance errors suggest accurate analyses. Third, samples must be obtained with adequate frequency (throughout a cycle test) and spatial distribution (ASR and monitor wells) to describe hydrological and geochemical processes. The third criterion is evaluated site by site.

Water-quality data from south Florida ASR systems are collected primarily to fulfill Class V Underground Injection Control (UIC) well permit requirements (Florida Administrative Code 2005a), and drinking water quality standards (Florida Administrative Code 2005b). All analyses are performed at laboratories that comply with the National Environmental Laboratory Certification program to ensure precision and accuracy. However, these data are collected primarily for regulatory compliance, not geochemical reaction modeling. Therefore some analyses are incomplete, in

that major species concentrations were not measured. Some species concentrations are estimated (and identified as such in each model). Estimating concentrations in a sample increases uncertainty in the resultant geochemical model. Complete water-quality analyses should be required as part of the UIC permit so that geochemical reactions that control water quality during ASR cycle testing can be quantified.

Water-quality data collected during cycle tests at 12 operational, potable-water ASR systems throughout south Florida were compiled previously (Table 1 in Mirecki (2004)). The ASR systems in this report were among those surveyed. No data set fulfills all three data-quality criteria defined above. Data gaps in cycle test data sets are defined as follows:

- **Complete analyses.** Of the ASR systems considered, nearly all samples lack measurement of at least one major ion. Sodium was rarely measured, and sulfate was measured mostly in recovered water samples. In addition, calcium and magnesium concentrations were not measured directly. Instead, calcium and magnesium were back-calculated from “total hardness” and “calcium hardness” measurements resulting in significant error. Redox potential (Eh or pE, reported as Oxidation Reduction Potential [ORP] in millivolts) is rarely reported as a field parameter. Redox potential can be estimated only at a few systems for the following reasons. Species that quantify redox state in oxic aquifer environments (dissolved oxygen (DO)) sometimes are measured inaccurately in the field, most likely the result of a non-equilibrated DO probe or exposure to air in the well bore. Species that quantify redox state in anoxic aquifer environments (sulfide/sulfate, ferrous/ferric iron) are not measured during routine cycle testing at most ASR systems. Total dissolved (ferrous plus ferric) iron concentrations typically are very low (less than 100 µg/L, and frequently below detection, approximately 40 µg/L) in recharge and native upper FAS samples, thus increasing model uncertainty. Incomplete analyses are the greatest source of uncertainty in most ASR cycle test data sets. Complete analytical data sets should be required for regulatory compliance.
- **Charge-balance errors.** If major ion concentrations are not measured, then accurate charge-balance errors cannot be calculated, thus limiting an assessment of data quality. Selected major element concentrations (for example, sodium) were estimated so that charge balance errors were less than ±5 percent. Estimated major element concentra-

tions are a source of uncertainty in geochemical models presented here.

- ***Sampling frequency and spatial distribution of samples.*** In existing data sets, samples are collected most frequently at the ASR well during recharge and recovery stages of a cycle test. Fewer samples were collected at monitor wells. This sample collection strategy satisfies permit requirements. Evolving Florida regulatory guidance for UIC Class V wells at ASR systems will lead to increased sampling frequency at monitor wells, and this will benefit geochemical investigations.

Geochemical modeling codes and conceptual model development

Several codes are available for building and testing aqueous geochemical models in groundwater systems. In the public domain, the most widely used geochemical model code is PHREEQC (Parkhurst and Appelo 1999). This code has the following capabilities: 1) solute speciation and mineral saturation index calculations; 2) batch-reaction and one-dimensional transport calculations involving a variety of reaction types (solubility, surface complexation, ion exchange, mixing); and 3) inverse modeling (Parkhurst and Appelo 1999). PHREEQC can be downloaded freely (version 2.12; US Geological Survey 2005). Geochemist's Workbench (release 6.0; Bethke 2005) has similar capabilities, better graphics, and can also perform reactive transport calculations in the "Professional" version. Use of Geochemist's Workbench requires a license. Models presented here were developed using PHREEQC version 2.12. As additional data are obtained, data sets will be incorporated into Geochemist's Workbench for further evaluation. Readers are referred to the geochemical model code manuals, and also Bethke (1996) and Zhu and Anderson (2002) for a more complete discussion of geochemical model development.

A conceptual geochemical model for ASR cycle testing first requires definition of a flowpath. The recharge flowpath is defined by transport of oxygenated treated water away from the recharge/recovery (or ASR) well. During recharge, water travels away from the ASR well. Water quality evolves due to interactions between water and aquifer material and advective mixing between recharge and native groundwater. Changes include increasingly reducing redox condition as dissolved oxygen is consumed, and increased salinity (ionic strength) due to mixing. During storage, increasingly reducing conditions prevail, along with diffusive mixing. During recovery, the flowpath is defined by transport of stored water, from distal

monitor wells back to the ASR well. Water-quality changes are not identical along the recharge versus recovery flowpaths. Redox conditions in the upper FAS evolve from oxic to sulfate-reducing conditions during cycle tests that last several hundred days. Increasingly reducing redox environments will affect the stability of major iron and sulfur phases, particularly the stability of iron sulfide and iron oxyhydroxide mineral phases. Iron and sulfur mineral phases control trace element mobility by sorption or coprecipitation. Therefore, an understanding of mineral stability in an evolving redox environment is critical for trace element transport.

The evolving geochemical environment that occurs in the upper FAS during an ASR cycle test is not easily simulated in a single geochemical model. Therefore, the approach here will be to develop geochemical models for discrete portions of the flowpath; that is, specific geochemical processes during recharge, storage, and recovery.

Sources of uncertainty in geochemical models

Several factors introduce uncertainty into geochemical models and subsequent interpretations. Uncertainty can be readily defined in an inverse model as the percent variation in concentration of any solute that can be tolerated yet still produce a valid mass-balance model. Ten percent variation or less is a generally accepted error level for analytical and sampling error. All inverse models developed in this work were run with the minimum percent variation that would result in the production of a valid model. Uncertainties (as percent variation in solute concentrations) are tabulated in Tables B1 and B2, and range generally between 7 and 13 percent. These result in sum of residuals values between 2 and 10, where smaller values indicate less variation.

Analytical factors also introduce uncertainty into the geochemical models, although the magnitude is difficult to quantify. Analytical factors that contribute to uncertainty are 1) back-calculation of calcium and magnesium concentrations from total and calcium hardness values; 2) estimation of most sodium concentrations; 3) estimation of most total dissolved sulfide values; 4) lack of ORP measurements throughout the cycle test; and 5) variation in end-member chloride concentrations for use in mixing models. Uncertainty (or error) that results from factor 1 is random, and is discussed in the section that describes the inverse geochemical model for the Olga ASR system. Uncertainty that results from factor 4 is more conceptual, because ORP is an indicator of overall redox state. It is not possi-

ble to assign quantitative uncertainties to factors 2 and 3 because concentrations were selected so that resultant charge balance errors were less than 5 percent. Uncertainty in factor 5 cannot be evaluated because most end-members are characterized by a single sample. Therefore, variations in these solute concentrations may or may not overlap the 7 to 13 percent uncertainty already assigned to the models.

Inverse models developed here are meant to serve as guides for model development using more complete geochemical data sets. Subsequent modeling efforts will focus on 1) acquisition of more detailed mineralogic data to better understand reactive solid phases; and 2) incorporation of advective transport modules to better simulate mixing behavior and subsequent geochemical changes from chloride and sulfate; and 3) obtaining more complete water quality analyses to reduce model uncertainty.

2 Hydrogeologic Setting

Regional hydrogeologic framework

A revised hydrogeologic framework is nearing completion by the Regional ASR Study team in CERP (Reese and Richardson, in review). Figure 1 shows the lithostratigraphic setting for Eocene through Miocene strata, and the occurrence of hydrostratigraphic units of the upper FAS. All ASR systems discussed in this report store water in the upper FAS, as it occurs in either the Arcadia Formation, basal Hawthorn unit or the Suwannee Limestone. West of Lake Okeechobee, the Arcadia Formation and Suwannee Limestone are well-defined using geophysical log data from exploratory wells. East of Lake Okeechobee, it is more difficult to distinguish the units of the lower Hawthorn Group, the Suwannee Limestone and the Ocala Formation because a contrast in geophysical log data is not as pronounced (Reese and Mernberg 2000). Some practitioners recognize the “basal Hawthorn unit” instead of the Arcadia Formation and parts of the Suwannee Limestone along the southeastern Atlantic Coast (Reese and Mernberg 2000).

Olga ASR System

The Olga ASR system is located south of the Caloosahatchee River on Route 80 east of Fort Myers in Lee County, FL. At present, this ASR system consists of one recharge/recovery (or ASR) well (LM-6086) and two monitor wells located approximately 350 ft (LM-6209) and 400 ft (LM-6615) away from the ASR well (Water Resource Solutions [WRS], Inc. 2002a, 2003a). Treated surface water from the Caloosahatchee River is stored in the upper FAS at depths between 859 and 920 ft bls. At this depth range, the upper FAS occurs in the upper permeable zones of the Suwannee Limestone. The Olga ASR system is located approximately 5 miles west of the proposed Comprehensive Everglades Restoration Plan (CERP) Caloosahatchee River pilot ASR system at Berry Groves in Hendry County. The hydrogeologic setting is similar at both sites, so that Olga ASR system data are useful predictors for the pilot site. Lithologic data (core logs, mineralogy, bulk chemistry, and selected trace elements) were measured in samples from the Arcadia Formation and Suwannee Limestone in two cores collected at the Berry Groves site (Appendix A). Core CCBRY-1 (Florida Geological Survey [FGS] core W-18594) was sampled

between 545 ft and 1,000 ft bls. Core EXBRY-1 (FGS W-18464), located approximately 1,000 ft east of CCBRY-1, was sampled between 550 ft and 1,100 ft bls.

Series		Geologic Unit		Lithology	Hydrogeologic unit		Approximate thickness (feet)	
HOLOCENE TO PLEISTOCENE		UNDIFFERENTIATED		Quartz sand, silt, clay, and shell	SURFICIAL AQUIFER SYSTEM	WATER-TABLE / BISCAYNE AQUIFER		20-300
		TAMIAMI FORMATION		Silt, sandy clay, micritic limestone, sandy, shelly limestone, calcareous sandstone, and quartz sand				
				CONFINING BEDS				
				LOWER TAMIAMI AQUIFER				
MIOCENE AND LATE OLIGOCENE		HAWTHORN GROUP	PEACE RIVER FORMATION	Interbedded sand, silt, gravel, clay, carbonate, and phosphatic sand	INTERMEDIATE AQUIFER SYSTEM OR CONFINING UNIT	CONFINING UNIT		250-750
			ARCADIA FORMATION	Sandy micritic limestone, marlstone, shell beds, dolomite, phosphatic sand and carbonate, sand, silt, and clay		SANDSTONE AQUIFER		
						CONFINING UNIT		
						MID-HAWTHORN AQUIFER		
				CONFINING UNIT				
EARLY OLIGOCENE		SUWANNEE LIMESTONE		Fossiliferous, calcarenitic limestone	SYSTEM AQUIFER	LOWER HAWTHORN PRODUCING ZONE		0-300
		OCALA LIMESTONE		Chalky to fossiliferous, calcarenitic limestone		UPPER FLORIDAN AQUIFER (UF)		100-700
EOCENE	LATE	AVON PARK FORMATION		Fine-grained, micritic to fossiliferous limestone, dolomitic limestone, dolostone, and anhydrite/ gypsum	FLORIDAN AQUIFER	MIDDLE CONFINING UNIT		500-1,300
	MIDDLE					MF		0-400
	EARLY							
				LOWER FLORIDAN AQUIFER		LF1	1,400-1,800	
							200-700	
PALEOCENE		CEDAR KEYS FORMATION		Dolomite and dolomitic limestone				
				Massive anhydrite beds			SUB-FLORIDAN CONFINING UNIT	1,200?

Figure 1. Current framework for interpretation of lithostratigraphic and hydrostratigraphic units in South Florida (from Reese and Richardson, in review).

Suwannee Limestone lithologies consist of white to pale-orange to light-brown packstone and wackestone with minor sandstone (Wedderburn et al. 1982, Brewster-Wingard et al. 1997, Reese 2000, Missimer 2002, South Florida Water Management District [SFWMD] & WRS 2005). Major mineralogy was determined by x-ray diffractometry in selected bulk samples from core CCBRY-1 (Tables A1 and A6). Quartz, calcite, and hydroxylapatite are the major minerals in Suwannee Limestone samples. Bulk chemical oxide data are consistent with major mineralogy, in that calcium and magnesium oxides, and silicates account for 53 to 75 weight percent of Suwannee Limestone in CCBRY-1 (Table A2), and 55 to 69 weight percent in EXBRY-1 (Table A3). Iron oxide content is low, ranging between 0.03 and 0.33 weight percent in CCBRY-1 (Table A2) and between 0.04 and 0.59 weight percent in EXBRY-1 (Table A3). Selected trace element data

in Suwannee Limestone bulk samples show low arsenic content in cores CCBRY-1 (<1 to 8 mg/kg; Table A4) and EXBRY-1 (<1 to 4 mg/kg; Table A5). Suwannee Limestone samples also show low organic carbon content (<0.05 to 0.13 weight percent); and sulfur occurring as sulfide rather than sulfate (Tables A4 and A5).

Gamma ray, caliper, and borehole flowmeter log data were obtained from monitor well LM-6615 at the Olga ASR system (Figure 2). Natural gamma-ray intensity is greater in the Arcadia Formation than the Suwannee Limestone, most likely due to greater phosphate content. A pronounced decrease in natural gamma-log intensity often defines the contact between the Arcadia Formation and Suwannee Limestone in this area (Wedderburn et al. 1982, Scott 1988, Brewster-Wingard et al. 1997). This decrease appears between 500 and 600 ft bls in the LM-6615 log (Figure 2), at 560 ft bls in CCBRY-1, and at 630 ft in EXBRY-1 (SFWMD & WRS 2005). The borehole flowmeter log (well LM-6615) suggests several superposed flow zones within the interval of 600 to 950 ft bls within the Arcadia Formation and Suwannee Limestone. Previous investigations suggest hydraulic connection among these flow zones in Lee County (Missimer and Martin 2001).

North Reservoir ASR system

The North Reservoir ASR system is located north of the Caloosahatchee River approximately 1.5 miles west of Interstate-75 in Lee County, FL. This ASR system consists of one ASR well (LM-6210) and one monitor well (LM-6208) located approximately 250 ft from the ASR well (WRS 2002b, 2003b). Treated surface water from the Olga ASR system is transferred and stored at North Reservoir in the Lower Hawthorn Aquifer (local name of the upper FAS) at depths between 540 and 640 ft bls (WRS 2002b, 2003b, 2004). At this depth range, the Lower Hawthorn Aquifer occurs in permeable zones of the Arcadia Formation of the Hawthorn Group.

Arcadia Formation lithologies consist predominantly of carbonates with siliciclastics in southwest Florida (Scott 1988, Brewster-Wingard et al. 1997). Arcadia Formation samples in cores CCBRY-1 and EXBRY-1 consist of marl, mudstone, wackestone, and packstone with minor dolomite and clastics (SFWMD & WRS 2005; Table A1). An unconformable contact exists between the Suwannee Limestone and the Arcadia Formation, and this

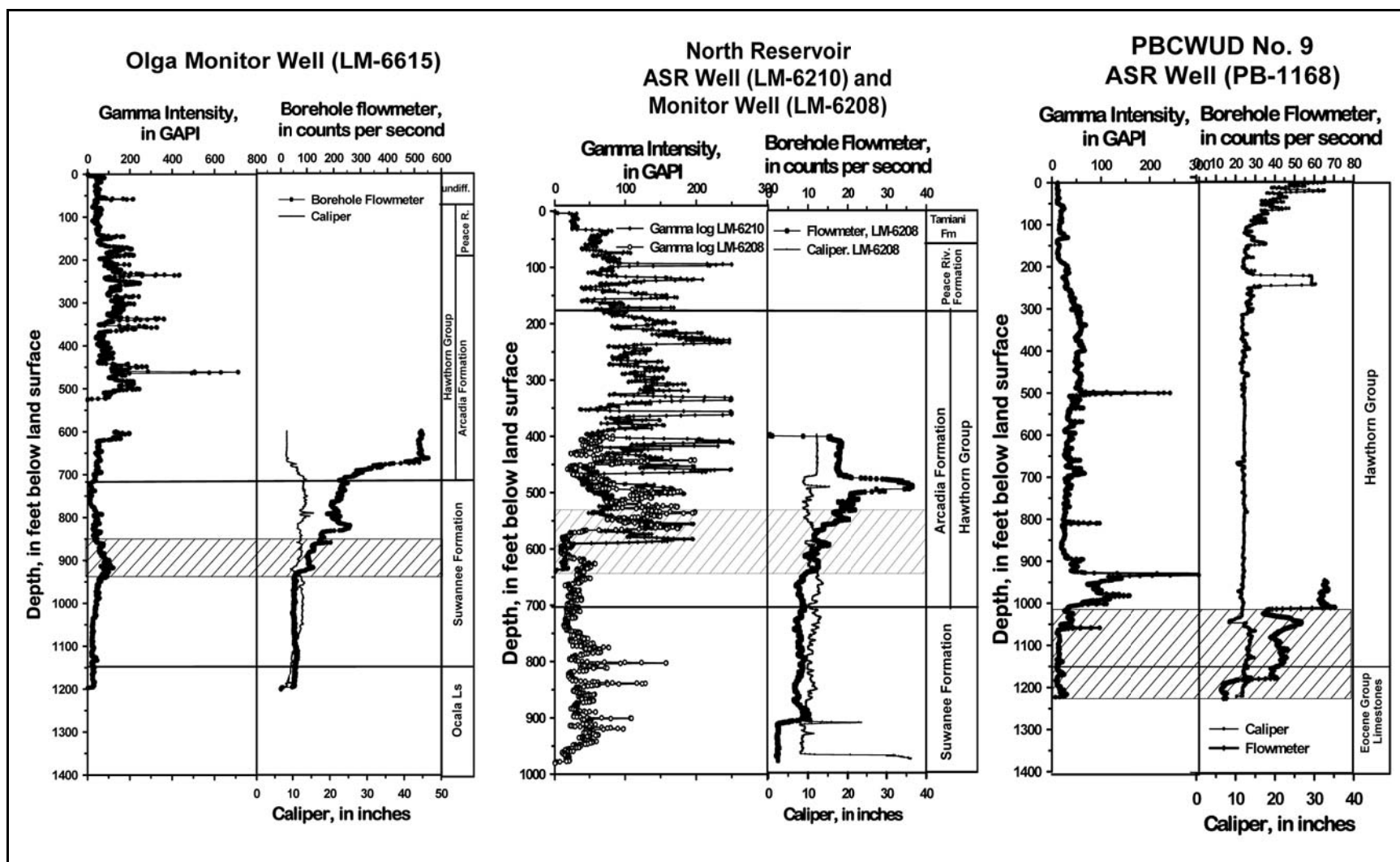


Figure 2. Selected geophysical logs from Olga, North Reservoir, and East Hillsboro (PBCWUD) ASR systems. Stratigraphic picks at Olga and North Reservoir from Water Resource Solutions (2002a,,2002b); East Hillsboro from Reese and Memberg (2000). Geophysical logs from DBHydro database (SFWMD 2004). Gamma log for North Reservoir is a composite from two boreholes 250 ft apart. Hachured interval is the storage zone at each ASR system.

contact often is coincident with a change in gamma-ray intensity (Scott 1988, Reese 2000). Major mineralogy in Arcadia Formation samples from CCBRY-1 differs somewhat from those of the Suwannee Limestone, with the presence of conspicuous phosphate as carbonate-hydroxylapatite, and ferroan dolomite (Tables A1 and A6). Bulk chemical oxide data from Arcadia Formation samples in CCBRY-1 and EXBRY-1 are consistent with lithological and mineralogical data, showing higher percentages of P_2O_5 and Fe_2O_3 in solids that consist primarily of calcium and magnesium oxides and silicates (Tables A2 and A3). Selected trace elemental data from Arcadia Formation bulk samples show low arsenic content in CCBRY-1 (2 and 6 mg/kg; Table A4), and EXBRY-1 (<1 to 2 mg/kg; Table A5). Arcadia Formation samples show low organic carbon content (<0.05 weight percent); and sulfur occurring as a sulfide rather than sulfate (Tables A4 and A5).

Gamma ray, caliper, and borehole flowmeter log data were compiled from the ASR (LM-6210) and monitor (LM-6208) wells at the North Reservoir ASR system (Figure 2). Natural gamma-ray intensity is significantly greater in the Arcadia Formation compared to the Suwannee Limestone, reflecting greater phosphate content. The borehole flowmeter log suggests that the greatest flows are coincident with the storage zone (540 to 640 ft bls) at this ASR system.

Eastern Hillsboro ASR system

The Eastern Hillsboro ASR system is located north of the Hillsboro Canal, west of US 441 at the Palm Beach County Water Utilities Department (PBCWUD) Water Treatment Plant No. 9, in Palm Beach County, FL. This ASR system consists of one ASR well, one Floridan Aquifer monitor well (FAMW) located approximately 300 ft from the ASR well, and several wells screened in the Biscayne Aquifer. Raw (untreated) groundwater from the Biscayne Aquifer is stored in the upper FAS at depths between approximately 1,010 and 1,225 ft bls (PBCWUD 2003, Figure 2). At this depth range, the upper FAS occurs in the permeable zones of the basal Hawthorn unit (Reese and Memberg 2000) or the Arcadia Formation (Bennett et al. 2001). Reese (2000) refers to the lower part of the Arcadia Formation as the basal Hawthorn unit, because the Arcadia Formation is not present east of western Palm Beach County. Below approximately 1,150 ft bls (PB-1168, Reese and Memberg 2000, Plate 2) the basal Hawthorn unit lies unconformably on lithologies informally called "Eocene limestones," which consist of Suwannee Limestone, Ocala Limestone,

Avon Park Formation, and Oldsmar Formation (Reese and Memberg 2000, Bennett et al. 2001).

3 Geochemical Models of Mixing During Recharge and Recovery

Conceptual model

Mixing behavior of recharge and native waters during ASR cycle testing in the upper FAS has been the focus of recent attention, because mixing can affect recovery efficiency (Missimer et al. 2002, Reese 2002, Vacher et al. 2006). The extent of mixing between native upper FAS and recharge water depends on transmissivity of the aquifer (and the distribution among conduit, fracture, and matrix permeability), density stratification of buoyant recharge water and more saline native water, anisotropy in the aquifer, aquifer heterogeneity, and pumping rates during recharge and recovery. Site-specific flow model simulations can identify dominant hydraulic controls on the flow of recharge water during ASR cycle testing.

Geochemical models can provide some insight into mixing behavior during successive cycle tests. Site-specific conservative mixing models are compared with measured solute concentrations during recharge at monitor wells, and recovery at both ASR and monitor wells. Chloride is a conservative tracer, defined as a solute whose concentration is diminished only by dilution, not chemical reactions. Chloride concentrations differ significantly between recharge and native FAS end members (Table 1), resulting in a characteristic slope of the conservative mixing line at each ASR system. Conservative mixing lines are calculated using PHREEQC by mixing different percentages (80:20, 60:40, etc.) of recharge and native upper FAS end members, and plotting the resultant chloride concentration versus percent of recharge or upper native FAS water. Unfortunately, native upper FAS water analyses at Olga show chloride concentrations that vary by 20 percent, which is a source of error in these mixing models. Superimposed on these plots are measured chloride concentrations collected from ASR and monitor wells throughout a cycle test.

Table 1. Storage zone characteristics, chloride concentrations in native upper FAS and recharge waters, and pumping rates at representative ASR systems.

ASR System	Storage Zone		Chloride, mg/L		Chloride, mMol/kg		Typical Recharge Pumping Rate, iMGD
	Lithology	Depth, ft bls	Native Upper FAS	Recharge	Native Upper FAS	Recharge	
Olga	Suwannee Ls	859-920	1110	78.1	31.4	2.2	0.5
North Reservoir	Arcadia Fm	537-614	670	70	18.9	2.2	0.5-0.8
East Hillsboro	Basal Hawthorn unit	1,010-1,225	2150	51	60.6	1.4	4.8-5.1

During recharge, breakthrough curves show the passage of low chloride water (less than 100 mg/L) through the monitor well. Recharge water displaces, mixes with, and likely is buoyed by more saline native upper FAS water. Breakthrough curves are plotted using the ratio of chloride concentrations (C/C_0 , chloride at time t /chloride at time 0, in mMol/kg water) in monitor well samples (Figure 2). The ratio will decline as the low-chloride recharge water front passes through the monitor well. Theoretical breakthrough curves are sigmoid-shaped as a result of advective transport (Fetter 2001). Characteristic breakthrough curves are observed only on Cycle 1. During typical ASR recovery, some low-chloride recharge water remains in the aquifer as a “buffer zone.” During subsequent cycles, there is increasingly less contrast between recharge water and aquifer water composition.

During recovery, native water-recharge water mixtures travel back toward the ASR well. Curve shapes and chloride trends are compared with model-generated conservative mixing curves for the Olga and North Reservoir ASR systems. Mixing behavior is plotted as chloride concentration versus percent volume recharged (Figure 2) or recovered (Figure 3). Percent volume was calculated from totalizer readings at the Olga and North Reservoir ASR wells, and represents the progress of the recharge or recovery portions of the ASR cycle.

Olga and North Reservoir ASR systems

Recharge water is stored in permeable zones within different lithostratigraphic units at Olga and North Reservoir ASR systems. However, both ASR systems are operated similarly. Both sites recharge using treated water from the Olga water treatment plant. Water is recharged through a single ASR well at pumping rates of 0.5 to 0.8 MGD. Both ASR systems

were operated so that potable water (60 to 130 million gallons per cycle) was recharged, stored for more than 100 days, and recovered with efficiencies ranging between 10 and 30 percent (chloride concentration 200 to 272 mg/L), except for Olga Cycle 3. This management strategy resulted in the development of a buffer between fresh recharge water and native upper FAS water. Olga Cycle 3 showed 74 percent recovery efficiency, enabling more complete geochemical characterization of the stored water volume and buffer zone. Storage zone thickness is 61 ft at the Olga ASR system, and 102 ft at the North Reservoir ASR system.

Breakthrough curves during Cycle 1 recharge at Olga ASR system monitor wells are not sigmoid-shaped, suggesting that transport of recharge water was affected by hydraulic factors (Figures 3A and 3C). Factors include the effects of aquifer heterogeneity, dual porosity, density stratification, and mixing in the aquifer and the open-hole portion of the well bore. Chloride measured in monitor well samples during recharge shows trends that approximate a conservative mixing line, but only during Cycle 1 (Figures 3B and 3D). Successive cycles show flatter chloride trends during recharge. This is expected because significant volumes of recharge water remain in the aquifer during successive cycle tests, thus freshening the storage zone.

Interpreting chloride trends in recovered water from cycle tests 1 and 2 at the Olga ASR system is difficult because recovery is relatively short (<120 days, 10 to 30 percent total volume recovered; Figures 4A, 4C, 4E). Cycle Test 3 at the Olga ASR system was significantly long to observe chloride trends during recovery (180 days, 74 percent total volume recovered, final chloride concentration 204 mg/L). Chloride concentrations increase slightly through Cycle 3 recovery, as measured in ASR and monitor well samples. Chloride concentration in the ASR well increases from 77 to 204 mg/L (2 to 6 mMol/kgw; Figure 4A). Chloride concentrations in monitor well samples increase from 350 to 600 mg/L (10 to 17 mMol/kgw; Figures 4C, 4E). These trends confirm that conservative tracer concentration does not increase linearly along a radius extending away from the ASR well in Cycle Test 3.

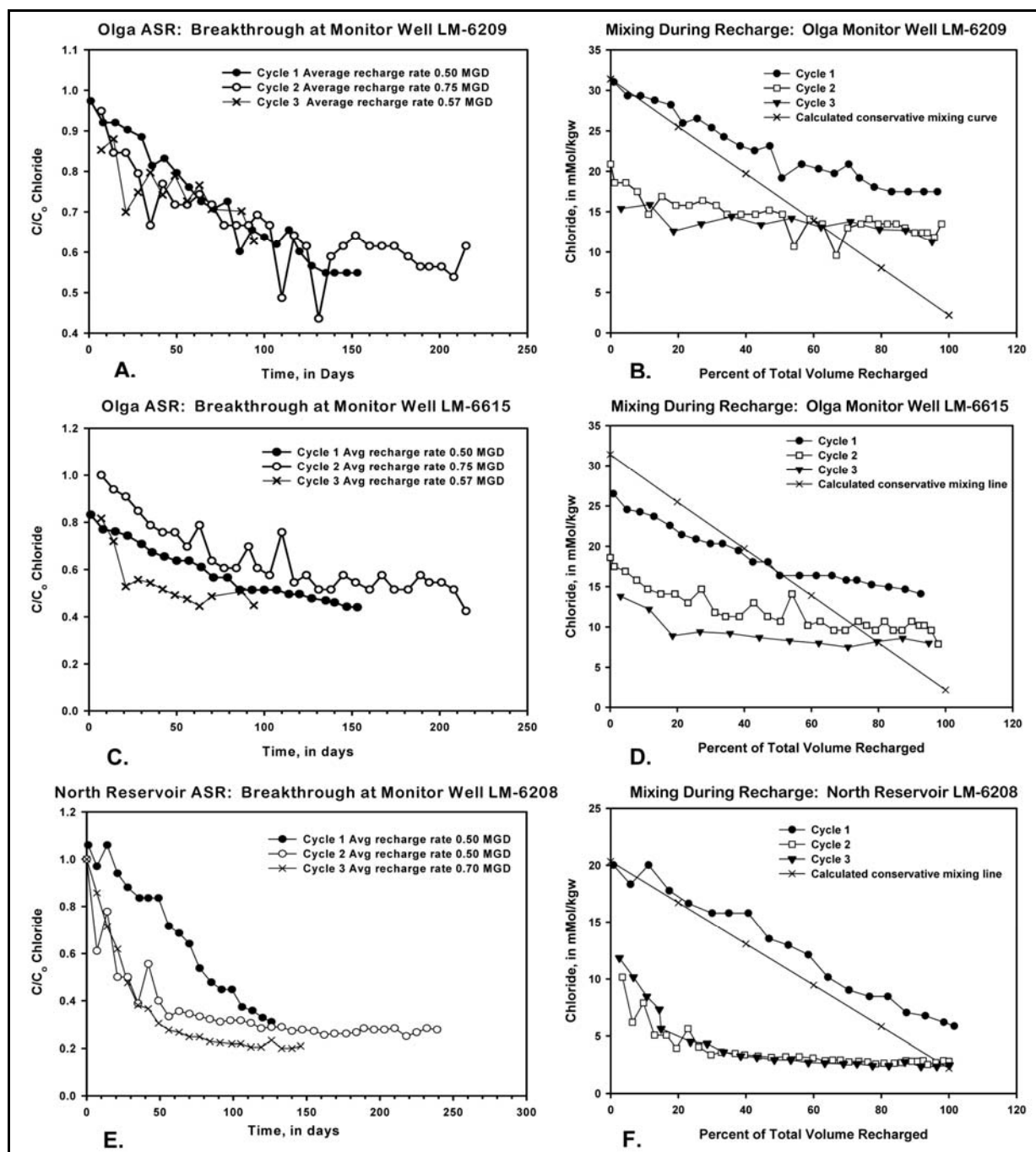


Figure 3. Breakthrough curves and mixing curves during recharge at Olga and North Reservoir ASR systems. Breakthrough curves (A, C, E) are plotted using chloride concentrations measured in monitor wells at Olga (A, 350 ft from ASR well; C, 400 ft from ASR well) and North Reservoir (E, 250 ft from ASR well) during recharge. Chloride concentrations measured in monitor well samples during recharge (B, D, F) are compared to model-generated conservative mixing lines at Olga and North Reservoir ASR systems.

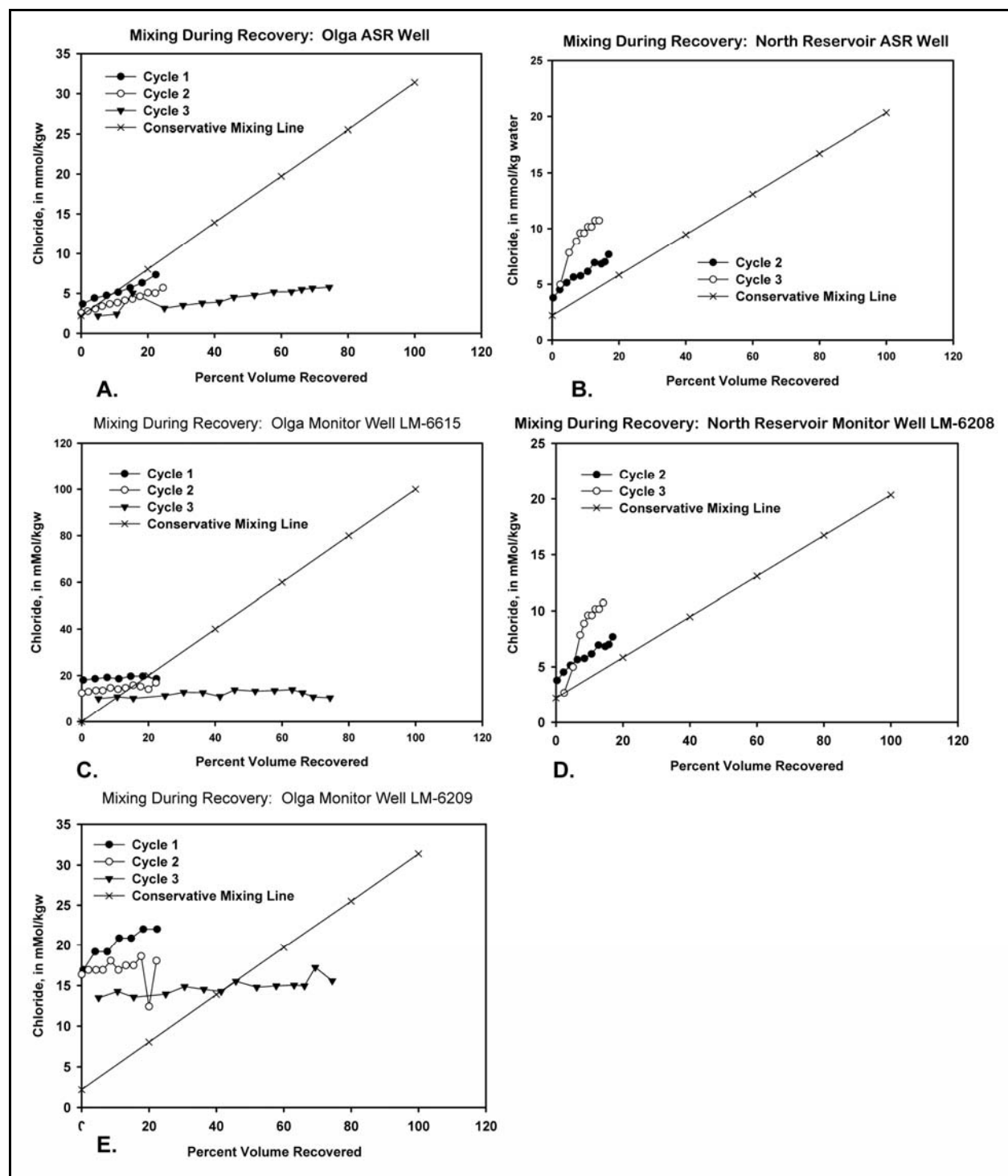


Figure 4. Mixing models during recovery at Olga and North Reservoir ASR systems. Measured chloride concentrations from the Olga ASR well (A) and monitor wells (C, E) are compared to conservative mixing lines for Cycle Tests 1 through 3. Measured chloride concentrations from the North Reservoir ASR (B) and monitor (D) well are compared to conservative mixing lines for Cycle Tests 2 and 3. No data were available for Cycle 1 recovery at the North Reservoir ASR system.

Breakthrough curves during recharge at the North Reservoir ASR system monitor wells are sigmoid-shaped, suggesting that water flows through the permeable zone as plug flow (Figure 3E). The trend in chloride concentration mimics that of the conservative mixing line during the first cycle, when the contrast between native and recharge water is greatest (Figure 3F). Chloride trends during recovery are similar to those observed at the Olga ASR site (Figures 4B and 4D). Recovery is short for Cycles 2 and 3 (50 and 133 days, 19 and 17 percent total volume recovered, final chloride 272 and 254 mg/L, respectively) so it is difficult to define characteristics of the recharge volume from these data. Comparing chloride trends and breakthrough curves for the Olga and North Reservoir ASR system suggests different permeability characteristics and aquifer heterogeneity in the Suwannee Limestone and Arcadia Formations.

4 Inverse Geochemical Models of Water-Quality Changes During Storage

Conceptual model

Inverse geochemical models quantify net solute flux from water-rock interactions. Geochemical reactions (precipitation/dissolution, redox, and surface complexation) between stored water and aquifer material will change the mass of dissolved species, typically in millimolal concentrations. Assumptions of inverse models are 1) initial and final conditions occur along a single flowpath; that is, are hydraulically connected; 2) dispersion and diffusion do not affect dissolved concentrations; 3) reactions are at steady state; 4) major reactive mineral phases have been identified in aquifer material (Zhu and Anderson 2002). Quantification of water-quality changes during storage is suited for inverse modeling, because groundwater transport is not a major factor. Finally, inverse geochemical models serve as appropriate precursors to define the data collection effort for more complex reactive transport simulations.

Inverse geochemical modeling is used here to calculate water-quality changes during storage at three representative ASR systems. The model inputs are measured initial and final water-quality conditions. The initial condition is represented by recharge water, and a final condition is recovered water. Both samples were collected at the ASR well, just prior to, or after completion of, the storage phase of an ASR cycle test. Major geochemical reactions are considered here; a more complex model involving redox changes and arsenic mobility is presented later.

Conceptually, the following geochemical reactions should proceed during storage, and these are simulated with inverse geochemical models:

- Precipitation or dissolution of calcite, dolomite, and gypsum
- Reduction of dissolved oxygen in recharge water
- Oxidation of pyrite with precipitation of amorphous iron oxyhydroxide
- Sulfate reduction with the evolution of hydrogen sulfide (H_2S)
- “Freshening” of the aquifer water as recharge water mixes with native upper FAS water

- Closed-system behavior with respect to CO₂ (no ingassing or degassing)

These reactions are simulated for three cycle tests at the Olga and North Reservoir ASR systems, and one cycle test at the East Hillsboro ASR system. Thus, water-quality changes in three storage zone lithologies (Suwannee Limestone, Arcadia Formation, and the basal Hawthorn unit, respectively) are considered. Representative model input, summary output, and model evaluation criteria are tabulated in Appendix B.

Olga ASR system

The geochemical reactions that cause the greatest phase mole-transfer in simulations of storage in the Suwannee Limestone are pyrite oxidation and subsequent iron oxyhydroxide precipitation, and the evolution of hydrogen sulfide from sulfate reduction. Minor mass changes result from apparent dissolution of calcite, dolomite, halite, and gypsum (Figure 5; Table B1), reactions that have been inferred elsewhere in the upper FAS of western Florida (Wicks et al. 1995). Considerable uncertainty is associated with calcium and magnesium values used in these simulations, because calcium and magnesium concentrations were back-calculated from total and calcium hardness values using stoichiometry defined in Hem (1992). Calculated calcium and magnesium values vary unsystematically from measured concentrations, and this problem is discussed in detail later in this section. Consequently, there is significant uncertainty associated with calcite, dolomite, and gypsum solubilities, and phase mole-transfer values.

Calcite dissolution is indicated by positive phase-mole transfer values (Figure 5, Table B1). Calcite dissolution is plausible because recharge water is undersaturated with respect to calcite (saturation index for typical recharge water is -0.5). However, calcite precipitates commonly near the well bore as CO₂ degasses. In this simulation, dissolved CO₂ was not permitted to degas in the confined aquifer. Calcite dissolution in these simulations results from the following factors: 1) erroneous calculated calcium and magnesium values in groundwater samples; and 2) varying calcite solubility as recharge water equilibrates with the Suwannee Limestone aquifer material during a cycle test. Minor dolomite dissolution also was shown by positive phase mole transfer values, although dolomite was not identified by x-ray diffractometry in samples from core CCBRY-1 (Table A1). Dolomite has been identified elsewhere in the Suwannee Lime-

stone of southwest Florida (e.g., Maliva et al. 2002). The validity of minor dolomite dissolution also is questionable due to erroneous calculated magnesium values.

Halite dissolution also was inferred in these models, as shown by positive phase-mole transfer values (Figure 5; Table B1). Halite was not identified by x-ray diffractometry in Suwannee Limestone samples (Table A1), and is not expected because the Suwannee Limestone is not an evaporite lithology. In the model, halite is a “theoretical” sink for sodium and chloride because concentrations of these solutes increase during storage. An alternative simulation (and more likely) is that solutes are contributed by mixing with native upper FAS water during recharge and storage. Development of a 1-D model that included advective mixing with geochemical reactions was not successful with the Olga ASR system dataset.

Model simulations indicate that iron released during pyrite oxidation is precipitated quantitatively as iron oxyhydroxide. Dissolved iron concentrations in recharge water are low, typically ranging between 40 and 140 µg/L. Dissolved iron concentrations in ASR and monitor well samples usually are less than 60 µg/L throughout all three cycle tests, and frequently are below detection (40 µg/L; data from WRS 2002a, 2003a; and monthly operating reports). Precipitation of iron oxyhydroxide grain coatings is likely in the presence of dissolved oxygen during recharge. However, it is not clear whether the precipitated mass of iron oxyhydroxide results in a sufficient surface for ion exchange and complexation in this aquifer system. Naturally occurring iron oxyhydroxides are rare in the Suwannee Limestone (Price and Pichler 2006).

Sulfate reduction is indicated from negative phase-mole transfer values (degassing of hydrogen sulfide gas), and by the strong hydrogen sulfide odor emanating from Cycle 3 samples, even those collected early during recovery. Storage durations of 98 to 181 days apparently are sufficient for the redox condition of the aquifer to evolve from oxic (dissolved oxygen greater than 0.2 mg/L) to sulfate-reducing (dissolved sulfide greater than 0.1 mg/L). Sulfate, contributed from native upper FAS water and gypsum dissolution, serves as a source of hydrogen sulfide (Rye et al. 1981). Microbe-mediated sulfate reduction is coupled with oxidation of dissolved organic carbon from recharge water, after dissolved oxygen is consumed.

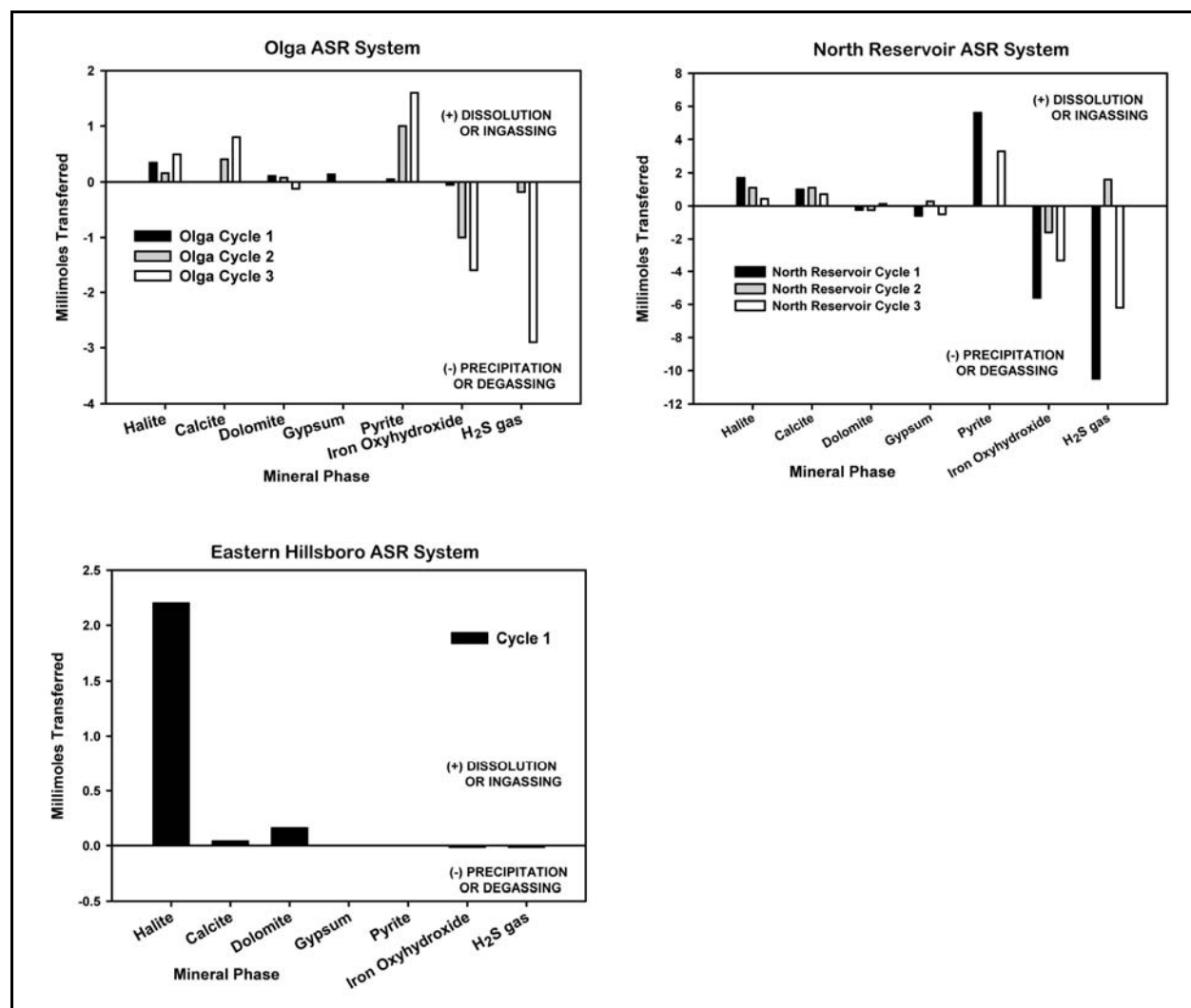


Figure 5. Bar graphs showing phase mole-transfer values calculated by PHREEQC inverse models (Table B1). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga, North Reservoir, and Eastern Hillsboro ASR systems.

Uncertainty estimates were included in each model run (Table B1). Inverse models for the Olga ASR cycle tests were solved given an uncertainty of 7 percent for any given dissolved constituent. This error would comprise measurement error plus error that results from variations in concentration that result from hydraulic factors in the aquifer or well bore.

Significant errors appear when “apparent” calcium and magnesium concentrations are obtained by back-calculation from total and calcium hardness values. Calcium and magnesium concentrations are calculated from total and calcium hardness measurements using the relationship specified by Hem (1992). New data from ASR and monitor wells were analyzed for calcium and magnesium concentrations during Cycle 4 recovery at the

Olga ASR system. Total and calcium hardness values were also determined in the same samples. These data allow direct comparison of measured concentrations with calculated values for calcium and magnesium (Figure 6). Linear regression of measured versus calculated calcium ($n = 20$) and magnesium ($n = 19$) shows poor correlation ($r^2 = 0.49$ for both). Error appears to be random for calcium in that there is no statistically significant difference between measured and calculated data populations (Mann-Whitney rank sum test $P = 0.292$). Error appears to be systematic for magnesium ($P = 0.041$), although this likely is a calculation artifact. Error probably results from the variable non-carbonate hardness component in recharge and native aquifer waters. Errors from the use of calculated calcium and magnesium values are propagated through solubility indices for calcite, dolomite, and gypsum in the geochemical models.

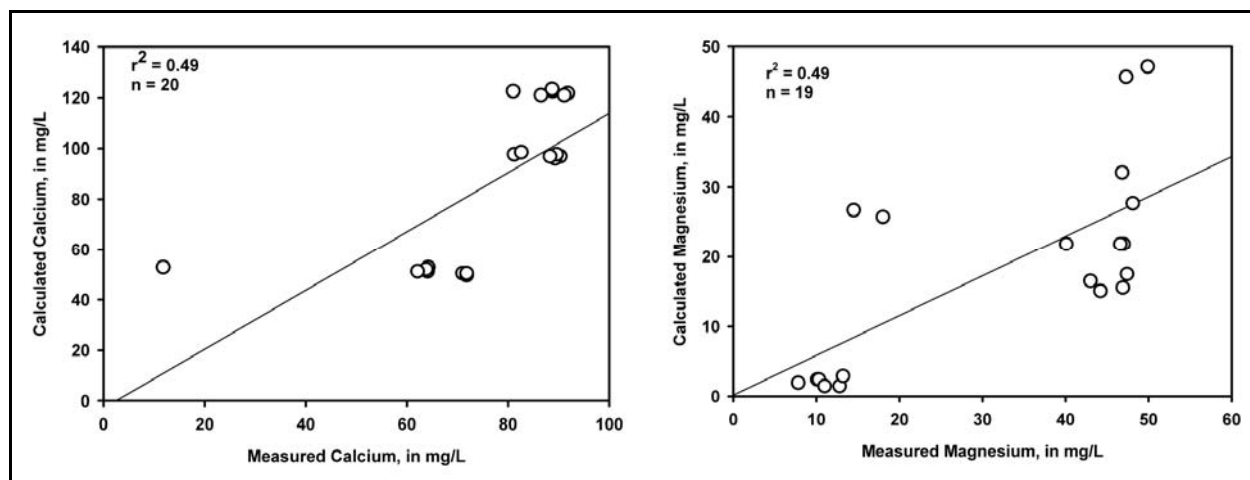


Figure 6. Linear regression plots that compare measured versus calculated concentrations of calcium and magnesium in Cycle 4 recovered water samples (ASR and monitor wells) at the Olga ASR system.

North Reservoir ASR system

Similar geochemical reaction trends were interpreted from inverse geochemical models of water quality changes during storage at the North Reservoir ASR system (Figure 5, Table B1). Dissolution of halite and calcite and precipitation of dolomite and gypsum are inferred from phase mole-transfer values. Mineral solubilities are questionable because they are based on calculated calcium and magnesium values. The mineral ankerite was identified by x-ray diffractometry in some Arcadia Formation samples from core CCBRY-1 (Tables A1 and A6). The presence of ankerite is interpreted to represent ferroan dolomite having variable iron content, and this iron content causes variation of d-spacings between $d = 2.9140$ and $d = 2.9065$. This model suggests that ferroan dolomite is a stable solid in con-

tact with recharge water. Both North Reservoir and Olga ASR systems use the same recharge water, so differences in phase-mole transfer values probably result from interactions between water and different lithologies in the storage zone.

The greatest mass change during storage results from pyrite oxidation and subsequent iron oxyhydroxide precipitation, and the evolution of hydrogen sulfide gas during sulfate reduction. Comparison of model simulations between North Reservoir and Olga ASR systems shows that more than twice the iron mass is precipitated as iron oxyhydroxide during storage at the North Reservoir ASR system. Similarly, more than three times the mass of hydrogen sulfide is generated at North Reservoir ASR system compared to the Olga ASR system. It should be noted that in this equilibrium model, pyrite is forced to oxidize, and iron oxyhydroxide is forced to precipitate, all under sulfate-reducing conditions. It is unlikely that these three reactions co-exist in reality. A better (non-equilibrium) reactive transport conceptual model would simulate pyrite oxidation and iron oxyhydroxide under oxic conditions early in the ASR cycle test. As the redox environment shifts to sulfate-reducing conditions (approximately -200 mV) late in the cycle test, iron oxyhydroxide likely would become unstable, and re-dissolve.

Eastern Hillsboro ASR system

The most significant change during storage at the Eastern Hillsboro ASR system is apparent “halite dissolution.” In this equilibrium inverse model, the only way sodium and chloride can be contributed to the system is through dissolution of a mineral, rather than advective mixing. The contrast in chloride between native upper FAS and recharge water is significant at this ASR system (Table 1), suggesting that advective mixing does affect recharge water quality. Phase-mole transfer values for all other minerals are minor, amounting to tenths of millimoles dissolved or precipitated.

5 Geochemical Model of Changing Redox Conditions During Recovery

Factors that control the source, transport, and fate of arsenic are important at many south Florida ASR systems, because arsenic concentrations in recovered water can exceed the state and Federal Maximum Contaminant Level (MCL; 10 µg/L, Florida Administrative Code 2005b) for drinking water. Few ASR systems have measured arsenic concentrations over successive cycle tests, because measurement was not a UIC Class V permit requirement, and because elevated dissolved arsenic was not recognized as a problem until relatively recently (Arthur et al. 2002).

Conceptual model of arsenic transport and fate

The geochemical controls on dissolved arsenic are complex because solubility and speciation depend on pH, redox (Eh) environment, and the presence of iron. These controls are discussed extensively in the literature (for example, Dixit and Hering 2003). The geochemical environment of the native upper FAS can be characterized broadly as having mildly alkaline pH (7.5 to 8.3), negative Eh values (-100 to -250 millivolts), with stable total dissolved sulfide (greater than 0.2 mg/L), and low dissolved iron (less than 0.2 mg/L). Under these conditions, arsenic is stable as a trace element within iron sulfide minerals. As evidence, dissolved arsenic concentrations in native upper FAS samples in south Florida wells (n=21) are below the detection level for HPLC/ICP-MS (high performance liquid chromatography/inductively coupled plasma-mass spectrometry) methods (1 µg/L; Mirecki and Hendel, in preparation). Bulk arsenic concentrations in Suwannee Limestone and Arcadia Formation samples reported here range between <1 to 8 mg/kg (Tables A4 and A5). Bulk arsenic concentrations are variable throughout the Suwannee Limestone and Arcadia Formation (Price and Pichler 2006). Sulfide solids generally occur in trace quantities (less than 5 weight percent; Tables A4 and A5). A hypothetical sequence of geochemical reactions that control arsenic transport and fate during an ASR cycle test is described below. Data to support this hypothesis are provided in the subsequent section.

During recharge, the pH and redox environment of the upper FAS shifts to reflect the temporary presence of dissolved oxygen, lower carbonate alka-

linity, and slightly increased dissolved organic carbon and total dissolved iron in recharge water. Arsenic is released during oxidation of iron sulfide minerals by dissolved oxygen along a flowpath in the Suwannee Limestone, and perhaps in the Arcadia Formation. In this Eh-pH environment (pH between 6.5 and 8.3), dissolved arsenic occurs primarily as the arsenate anion (HAsO_4^{2-} ; arsenic as AsV; Vink 1996; Nordstrom and Archer 2003).

The pH and carbonate alkalinity do not change much (pH less than 1 unit, carbonate alkalinity declines from approximately 200 to 100 mg/L) in this well-buffered aquifer system. Recharge water is treated with a lime-softening step prior to introduction, which will elevate pH but minimize calcium and magnesium concentrations (as hardness). Introduction of lime-softened water to a carbonate aquifer can result in minor calcite dissolution due to undersaturation of recharge water with respect to calcium and magnesium. However, the carbonate buffer system adjusts quickly (within days) to equilibrate the mixture of recharge and native upper FAS waters with carbonate rock.

Dissolved iron concentrations in recharge water typically are greater than those measured in the aquifer (40 to 100 $\mu\text{g/L}$ in recharge water; less than 40 $\mu\text{g/L}$ measured in the aquifer at either ASR or monitor wells). Dissolved iron in recharge water (and also released by pyrite oxidation) precipitates as amorphous iron oxyhydroxide, as long as oxidizing conditions (greater than +50 to +100 mV) are maintained in the aquifer. Dissolved ferric iron can also oxidize pyrite, although this likely is a minor contributor to the total iron pool due to low (ppb) concentrations. Dissolved iron likely is precipitated locally as amorphous iron oxyhydroxide.

During storage, the aquifer redox environment evolves from oxidized to reduced condition as dissolved oxygen is consumed. Native sulfate-reducing microbes, if not inactivated by dissolved oxygen, will couple oxidation of dissolved organic carbon with sulfate reduction, to yield dissolved sulfide and carbonate species. Under these conditions, the arsenate anion will reduce to the neutrally charged ion pair (H_3AsO_3^0 , arsenic as AsIII), or at more alkaline pH (>8.5), the arsenite anion (H_2AsO_3^- , arsenic as AsIII; Vink 1996). When the arsenic species has a negative or neutral charge, sorption is minimal because mineral surfaces generally have a net negative charge. However, iron oxyhydroxide can adsorb or complex both arsenic species, although the strength of sorption is pH-dependent (Man-

ning et al. 1998, Goldberg and Johnson 2001). These reactions proceed during typical storage durations of a few months.

During recovery, anoxic to sulfide-rich waters having ORP values more negative than -200 mV pass back along the flowpath toward the ASR well. Under reducing conditions that increasingly resemble the native FAS, any iron oxyhydroxide precipitated previously would become unstable, and undergo reductive dissolution. Reductive dissolution of iron oxyhydroxide would release arsenic species sorbed previously. Dissolved arsenic, measured during recovery, occurs primarily as the neutral arsenite complex (H_3AsO_3^0) at pH less than 9.1 (Vink 1996).

Data required to test this hypothesis include 1) arsenic concentrations from ASR and monitor wells through a complete ASR cycle test; 2) solid phase mineralogy, which define the sources and sinks of arsenic; and 3) concentrations of major redox couples (ferrous and ferric iron, sulfate and hydrogen sulfide), to define the evolution from oxidizing through reducing conditions. Site-specific data supporting criteria 1 and 2 are presented in the appendices of this report.

Arsenic concentration trends during ASR cycle testing

A commonly observed phenomenon during cycle testing at the Olga ASR system is that arsenic concentrations remain constant (or increase slightly) during recharge at most monitor wells located 300 ft or more away from the ASR well, even though recharge water flowed beyond that point (as shown by declining chloride concentrations; Figures 3 and 7). However, arsenic concentration increases significantly, often exceeding the MCL, during recovery in ASR well samples. Arsenic concentrations increase fairly early during recovery, when less than 30 percent of the total volume has been recovered (Figure 7). It is not clear whether maximum arsenic concentrations were observed during the relatively short recovery phases of Cycle tests 1 and 2. During Cycle 3, a maximum arsenic concentration (68 $\mu\text{g/L}$) was measured at 69 percent recovery (Figure 7). The trends in arsenic concentration during recharge and recovery are consistent with the transport and fate hypothesis defined in the previous section.

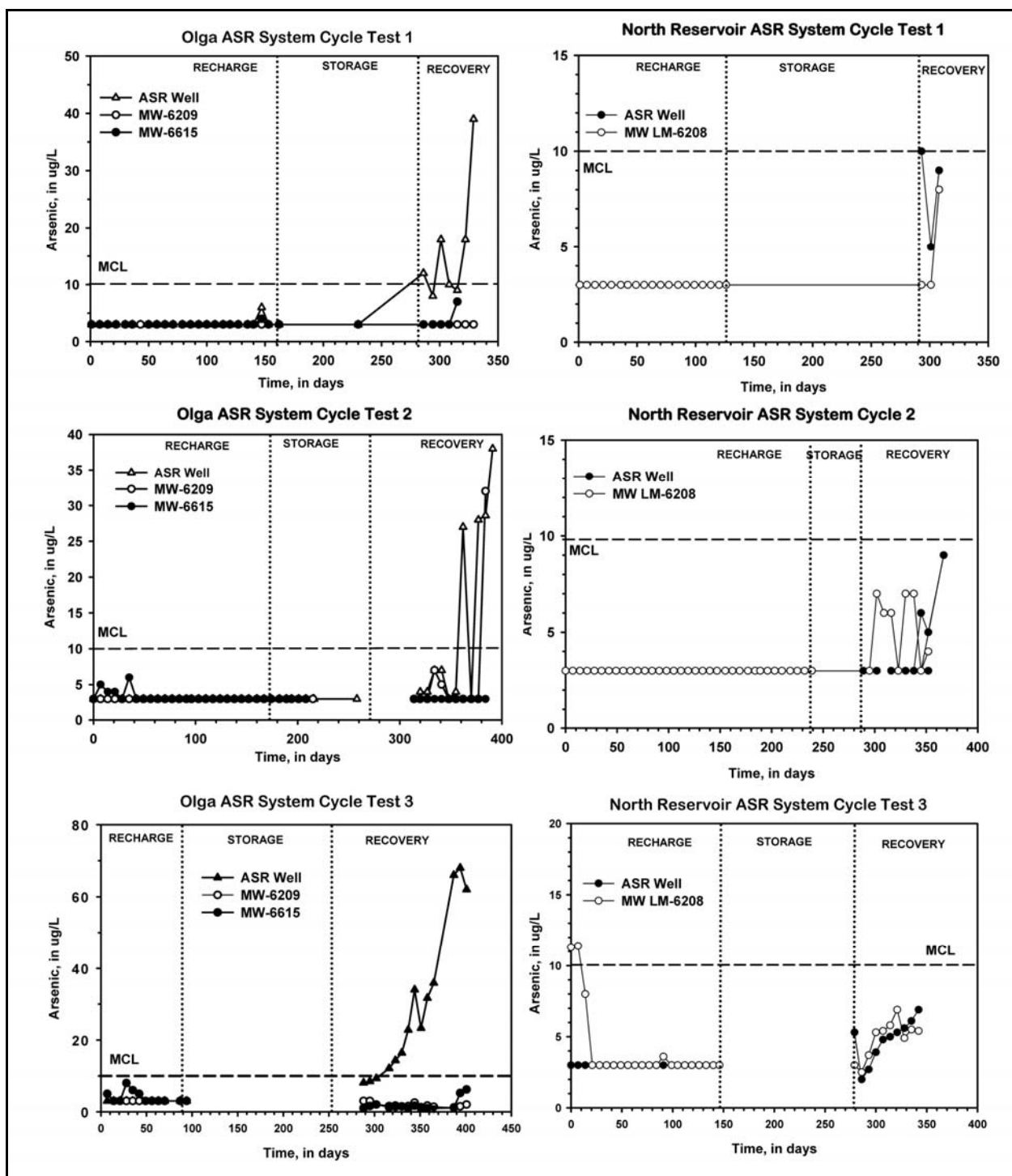


Figure 7. Trends in total dissolved arsenic concentrations measured in ASR and monitor wells at the Olga and North Reservoir ASR systems during Cycle Tests 1 through 3. Concentrations plotted here as 3 $\mu\text{g/L}$ actually were below the detection limit for the ICP-MS method. Data are tabulated in Appendix C.

At the North Reservoir ASR system, arsenic concentrations remain low (approximately 3 $\mu\text{g/L}$) during recharge at the monitor well located approximately 250 ft from the ASR well, even though recharge water flowed

beyond that point (Figures 3 and 7). During recovery, only one ASR well sample exceeded the MCL during three cycle tests. Recharge water sources are identical at both Olga and North Reservoir ASR systems, so lower arsenic concentrations at the latter must result either from less pyrite in the Arcadia Formation, or the presence of sorption surfaces in the Arcadia Formation that control arsenic transport. Bulk arsenic concentrations, iron oxide, and total sulfur values are similar in Arcadia Formation and Suwannee Limestone samples in cores CCBRY-1 and EXBRY-1 (Tables A4 and A5), although few Arcadia Formation samples were analyzed. The relative abundance of pyrite (as an arsenic source) in Arcadia Formation versus Suwannee Limestone samples has not been established. It is possible that the presence of ferroan dolomite (Table A1) in the Arcadia Formation serve as a sorption surface, thus attenuating arsenic transport during cycle testing at the North Reservoir ASR system.

Evaluation of changing aquifer redox environment during cycle testing is critical to define arsenic mobility. Overall condition can be assessed using ORP (oxidation-reduction potential) measurements throughout the cycle. Unfortunately, these data were not recorded for any ASR system considered here. However, ORP measurements during cycle tests at the City of Tampa-Rome Avenue ASR system (where water is stored in the Suwannee Limestone aquifer) show Eh values ranging between -150 and -250 mV in ASR wells during recovery (M. McNeal, personal communication, 2005). Similar values are expected at the Olga ASR system. The presence of hydrogen sulfide (and thus dissolved bisulfide) is obvious by odor in samples recovered from both systems during Cycle 3 recovery.

Redox environment will also determine arsenic speciation (arsenite and arsenate), which could control arsenic mobility during ASR cycle testing. Arsenic species concentrations were measured during Cycle 3 recovery at Olga and North Reservoir ASR systems (Figure 8). At the Olga ASR system, the proportion of the reduced species (arsenite, AsIII) in total dissolved arsenic increased as recovery proceeded. The trend of increasing AsIII/AsV values as recovery proceeds (Figure 8; Table C8) suggests that a redox gradient exists, with more reducing conditions extending away from the ASR well. If the redox potential declines to Eh values of approximately -200mV (pE -3.4), these conditions will favor arsenite (as a neutral ion pair or an anion) as the stable arsenic species. Because the primary dissolved arsenic species is neutral or negatively charged, sorption on clay

surfaces is less likely. Complexation by amorphous iron oxyhydroxides is the only surface that can effectively immobilize dissolved arsenite.

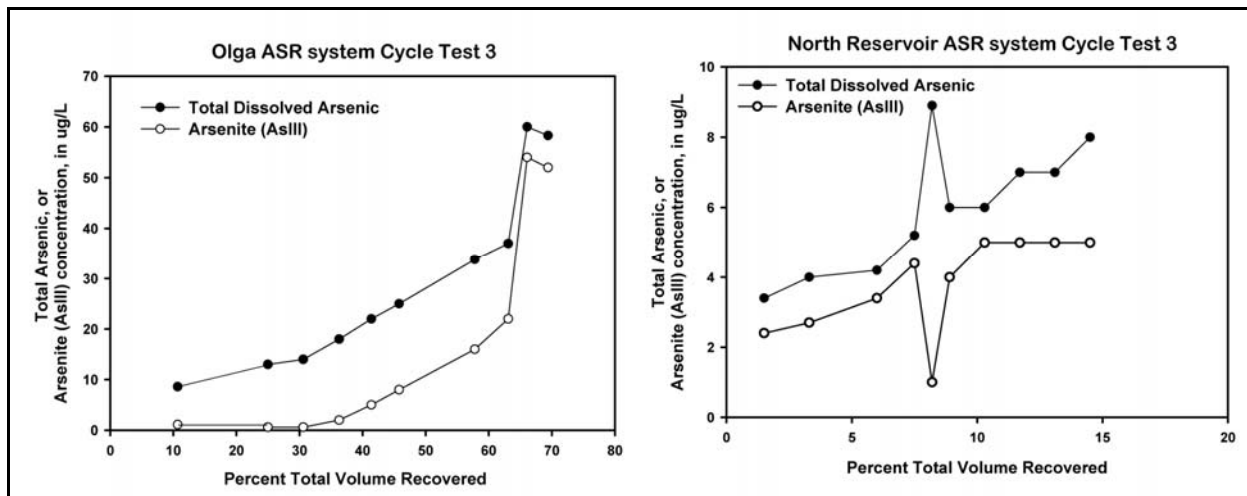


Figure 8. Trends in total dissolved arsenic and arsenite (AsIII) concentrations in ASR well samples from the recovery phase of Cycle Test 3 at Olga and North Reservoir ASR systems. Data are tabulated in Tables C8 and C9.

The trend in AsIII/AsV values during recovery at the North Reservoir ASR system is less evident. Arsenite comprises about half of total dissolved arsenic. However, total dissolved arsenic concentrations are consistently low (approximately 3-8 $\mu\text{g/L}$; Table C9), making it difficult to quantify separate species concentrations.

Inverse geochemical model defining redox condition during recovery

Water-quality data measured throughout cycle tests at the Olga ASR system can define the redox environment with respect to iron mineral stability, and ultimately arsenic mobility. Here, inverse geochemical models are developed to assess iron oxyhydroxide stability during recovery. If iron oxyhydroxide undergoes reductive dissolution as increasingly reducing water flows toward the ASR well, then that is a plausible mechanism to explain increasing arsenic concentrations in recovered water at the ASR well. Inverse models were developed to consider the following geochemical reactions: 1) reduction of Eh from 0.0 to -200 mV; sulfate reduction with H_2S production; 3) dissolved organic matter oxidation (forced); 4) precipitation or dissolution of carbonate minerals; and 5) precipitation or dissolution of iron oxyhydroxide.

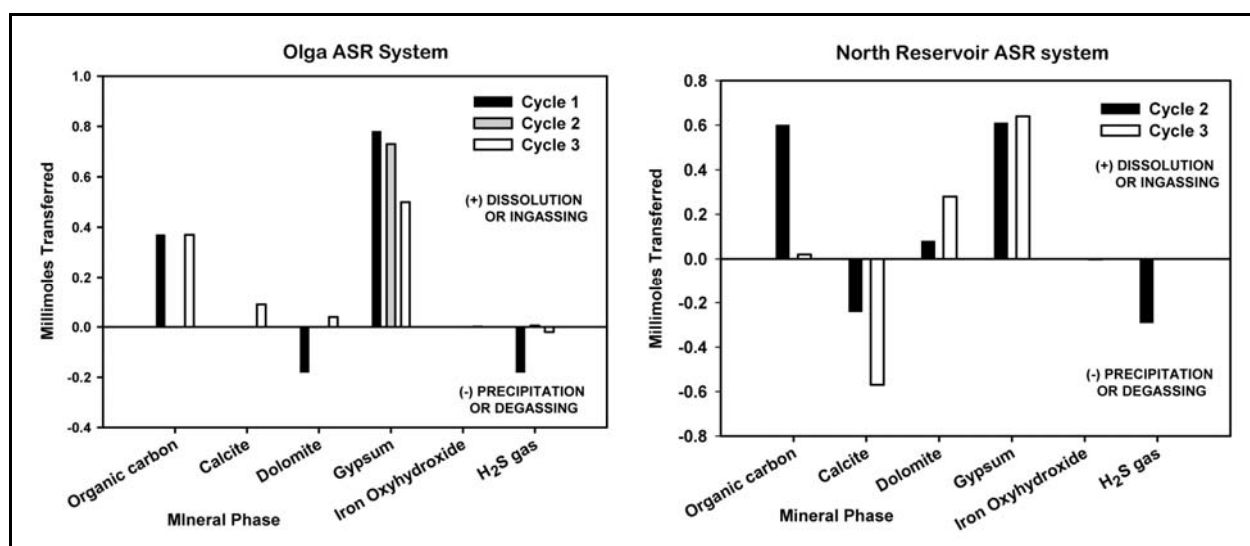


Figure 9. Bar graphs showing phase mole-transfer values calculated by PHREEQC inverse models (Table B2). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga and North Reservoir ASR systems.

The flowpath defined in these inverse geochemical models extends from the monitor well toward the ASR well. The samples used for these models are ASR well samples obtained at the beginning and end of recovery, for Cycles 1 through 3 at the Olga ASR system, and Cycles 2 and 3 at the North Reservoir ASR system (Appendix B). Model output includes phase mole-transfer values that result from water-rock interactions (Figure 9, Table B2).

The inverse models tested for the Olga and North Reservoir ASR systems suggest that reductive dissolution of iron oxyhydroxide minerals is feasible during recovery. However, phase mole-transfer values are exceedingly small (0.001 millimoles). Therefore, redox conditions in the aquifer can lead to reductive dissolution of iron oxyhydroxide and hence arsenic release during recovery. However, the mass of iron oxyhydroxide is minor, which suggests a limited capacity for aquifer material to sorb and desorb arsenic during cycle testing. Other reactions indicated by phase mole-transfer values are similar to those observed for the recharge flowpath, and uncertainties related to data quality also are true for these models. One difference between recharge and recovery models is that gypsum shows greater phase mole-transfer values, indicating significant gypsum dissolution in both Suwannee Limestone and Arcadia Formation aquifer materials. Gypsum was not identified in any sample by x-ray diffractometry, and bulk chemical data indicate that sulfur is present as a sulfide rather than sulfate (Tables A4 and A5). Dissolved sulfate concentrations

do increase during recovery. The inverse geochemical model infers gypsum as the “theoretical” sulfate source. In reality, advective mixing with native FAS water could also serve as the sulfate source, but combined mixing and redox geochemical models could not converge when the Olga cycle test data were used.

6 Conclusions

Geochemical models were developed to simulate water-quality changes that occurred during cycle tests at three representative potable water ASR systems that store water in different permeable zones of the upper Floridan aquifer system. At the Olga ASR system, water is stored in the Suwannee Limestone; at the North Reservoir ASR system, water is stored in the Arcadia Formation; and at the Eastern Hillsboro ASR system, water is stored in the Arcadia Formation/basal Hawthorn unit. ASR systems were chosen because of their proximity to proposed CERP ASR pilot systems. The following are major conclusions of this study.

Existing cycle test data sets generally are incomplete for development of quantitative geochemical models. Major dissolved species (those that occur at mg/L concentrations, such as calcium, magnesium, and sodium) are not measured. Calcium and magnesium concentrations are back-calculated from total and calcium hardness measurements, resulting in random error that is difficult to quantify. The lack of measured values for these species means that charge balance errors cannot be calculated, and thus there is no good estimate of integrity of analytical data beyond lab quality assurance/quality control data. Without charge balance errors, it is difficult to quantify uncertainty in geochemical models.

Also, errors associated with major ion concentrations are propagated in solubility indices for calcite, dolomite, and gypsum, making it difficult to characterize water-rock interactions during ASR cycle testing. In addition, there are few measurements of redox couples (sulfate/dissolved sulfide, or ferric/ferrous iron), or ORP values, so redox condition in the upper FAS is estimated based on measurements from other ASR systems in equivalent strata.

Geochemical models were developed to simulate mixing during recharge. Three types of geochemical models were 1) mixing models to simulate mixing between native groundwater and recharge water; 2) inverse models to simulate water-quality changes during storage; and 3) inverse models to simulate iron oxyhydroxide stability under changing redox conditions during recovery. Particular emphasis is placed on geochemical controls on arsenic mobility. Data sets are most complete for the Olga and

North Reservoir ASR systems, so most interpretations and conclusions are based on trends at these sites.

During recharge, mixing models and chloride breakthrough curves at monitor wells indicate that recharge water is transported differently at Olga (Suwannee Limestone) versus North Reservoir (Arcadia Formation) ASR systems. Hydraulic factors affect mixing behavior in the Suwannee Limestone, as indicated by mixing curves that deviate from the conservative mixing line, and by breakthrough curves that do not show an “ideal” sigmoid shape. In the Arcadia Formation, mixing curves follow more closely the conservative mixing line, and breakthrough curves are sigmoid shaped, suggesting plug flow through the aquifer.

During recovery, chloride concentration trends from ASR well samples generally do not follow conservative mixing lines, especially after successive cycles. This is expected because significant volumes (30 to 70 percent) of recharged water remain in the storage zones at Olga and North Reservoir ASR systems. Native upper FAS water is not recovered, so chloride concentrations of ASR well samples show freshening of the storage zone that results from successive ASR cycle tests.

Inverse geochemical models to simulate water-quality changes during storage. Inverse model simulations are beneficial prior to the development of a monitoring program for the following reasons: 1) to quantify the geochemical reactions that have the greatest effect on stored water quality; and 2) to focus subsequent sampling efforts. In this project, water-quality changes in different storage zones of the upper FAS can be compared: the Suwannee Limestone and Arcadia Formation (both of southwest Florida), and the basal Hawthorn unit (southeast Florida).

The geochemical reactions that account for the greatest mass changes (millimoles per kilogram water) during storage in both the Suwannee Limestone and Arcadia Formation of the upper FAS are pyrite oxidation with subsequent iron oxyhydroxide precipitation, and sulfate reduction and hydrogen sulfide production. These reactions proceed in a sequence, not simultaneously, and indicate that the redox evolution of the storage zone exerts a significant influence on stored water quality. This concept should be explored using better cycle test data sets. Data from the Eastern Hillsboro ASR system, where water is stored in the basal Hawthorn unit, are insufficient to support conclusions about changing redox environment.

Proposed hypothesis to explain arsenic mobility during ASR cycle testing. Additional data were obtained during this project to explain the geochemical conditions that facilitate arsenic transport, and to support more detailed geochemical model development. Additional data presented here are 1) bulk chemical data from two cores that span the lower Arcadia Formation and upper Suwannee Limestone in Hendry County, near the Olga ASR system; 2) major mineralogy from one core at this same site; 3) dissolved arsenic species concentrations from Olga and North Reservoir ASR systems. These data are used to support a guiding hypothesis that explains arsenic behavior throughout all phases (recharge-storage-recovery) during cycle testing. The hypothesis specifically examines why arsenic is detected rarely at monitor wells approximately 300 ft away from the point of recharge (ASR well), yet arsenic concentrations increase as 30 to 70 percent of the water returns to the ASR well during recovery of the same cycle.

The hypothetical controls on arsenic mobility during each phase of the ASR cycle test are highlighted below. Pyrite oxidation and subsequent arsenic release are well documented during recharge in the Suwannee Limestone by other researchers.

- **Recharge.** Arsenic is released during pyrite oxidation, primarily by dissolved oxygen in recharge water. Dissolved iron from recharge water, and iron released during pyrite oxidation, reprecipitates locally as amorphous iron oxyhydroxide. Arsenic occurs as a mixture of arsenate (AsV, as HAsO_4^-), and arsenite (AsIII, as H_3AsO_3^0), at pH values less than 9.1. Amorphous iron oxyhydroxide serves as a complexation surface to sequester all dissolved arsenic species, along the flowpath between the ASR and monitor well.
- **Storage.** Dissolved oxygen is consumed early during recharge and storage. Sulfate reduction resumes, as evidenced by dissolved hydrogen sulfide in stored water, and ORP measurements of -150 to -200 mV. Iron oxyhydroxide solids are not stable in this redox environment. Arsenate reduces to arsenite, either as a dissolved or sorbed species.
- **Recovery.** The aquifer redox environment declines to Eh values characteristic of sulfate-reducing conditions (approximately -200 mV). Amorphous iron oxyhydroxide, which precipitated presumably as grain coatings, undergoes reductive dissolution. Arsenic, complexed to this increasingly unstable solid phase, is also released into solution.

Arsenic and iron concentrations increase through recovery, reaching maxima between 30 and 70 percent recovery at the North Reservoir and Olga ASR systems. The proportion of arsenite (of total dissolved arsenic) increases as arsenic concentration increases, suggesting a redox gradient extending away from the ASR well.

These trends are best observed at the Olga ASR system, at which water is stored in the Suwannee Limestone. Arsenic concentrations remain much lower throughout three successive cycle tests at the North Reservoir ASR system, at which water is stored in the Arcadia Formation. Source waters are identical at both systems. Therefore, arsenic mobility likely is controlled by differences in trace mineralogy in the Arcadia Formation versus Suwannee Limestone. Lithologic or mineralogic differences are not indicated by bulk chemistry. Ferroan dolomite was identified in the Arcadia Formation. Its presence suggests a greater mass of iron-bearing minerals, and hence greater capacity for Arcadia Formation lithologies to complex dissolved arsenic.

Inverse geochemical models to simulate arsenic mobility during recovery. The release and transport of naturally occurring trace elements, specifically arsenic, during cycle testing represents a significant challenge to ASR feasibility. Inverse geochemical models were developed to simulate redox environmental control on arsenic mobility. Because trace concentrations of iron oxyhydroxides apparently exert a significant control on arsenic transport, it is important to establish stability of iron oxyhydroxide during recovery.

Iron oxyhydroxide was found to be unstable under the redox conditions that prevail in the recovery flowpaths of the Arcadia Formation and Suwannee Limestone. However, the phase mole-transfer from solid to solution is quite small (micromoles per kilogram water). It is unclear whether these small masses of iron oxyhydroxide are sufficiently effective to sequester and release the arsenic concentrations measured during recovery. Subsequent reactive transport modeling will be helpful to confirm the proposed hypothesis.

References

- Arthur, J. D., A. A. Dabous, and J. B. Cowart. 2002. Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. *U.S. Geological Survey Artificial Recharge Workshop Proceedings*, G. R. Aiken and E. L. Kuniansky, ed., Sacramento, CA, April 2-4, 2002, U.S. Geological Survey Open-File Report 02-89, p. 47-50. Also available for download at http://water.usgs.gov/ogw/pubs/ofr0289/jda_mobilization.htm
- Bednar, A. J., J. R. Garbarino, J. F. Ranville, and T. R. Wildeman. 2002. Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples. *Environmental Science & Technology* 36(10), 2213-2218.
- Bednar, A. J., J. R. Garbarino, J. F. Ranville, and T. R. Wildeman. 2004. Methods of arsenic speciation and their application to natural water analysis. *Water Research* 38, 355-64.
- Bennett, M. W., P. F. Linton, and E. E. Rectenwald. 2001. *Hydrogeologic investigation of the Floridan Aquifer System West Hillsboro Basin, Palm Beach County, Florida*. South Florida Water Management District Technical Publication WS-8.
- Bethke, C. M. 1996. *Geochemical reaction modeling*. New York: Oxford University Press.
- Bethke, C. M. 2005. *Reference manual, The geochemist's workbench* © Release 6.0. Champaign, IL: University of Illinois.
- Brewster-Wingard, G. L., T. M. Scott, L. E. Edwards, S. D. Weedman, and K. R. Simmons. 1997. Reinterpretation of the peninsular Florida Oligocene: An integrated stratigraphic approach. *Sedimentary Geology* 108(1/4), 207-228.
- Castro, J. E. 1995. *Aquifer storage recovery Myrtle Beach, SC Phase II: A hydrologic, geochemical, and economic investigation*. Report 7. Columbia, SC: State of South Carolina Water Resources Division.
- Davis, S. N. 1988. Where are the rest of the analyses? *Ground Water* 26(1), 2-5.
- Dixit, S., and J. G. Hering. 2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environmental Science & Technology* 37, 4182-4189.
- Fetter, C. W. 2001. *Applied Hydrogeology*. 4th ed. Upper Saddle River, NJ: Prentice-Hall.
- Florida Administrative Code. 2005a. *Underground injection control*. F.A.C. 62-528, 87 pp. Accessed 10 November 2005. Also available for download at http://www.dep.state.fl.us/water/uic/docs/62-528_20NOV2002.pdf.
- Florida Administrative Code. 2005b. *Drinking water standards, monitoring, and reporting*. F.A.C. 62-550, 50 pp. Accessed 10 November 2005. Also available for download at <http://www.dep.state.fl.us/legal/rules/drinkingwater/62-550.pdf>

- Fritz, S. J. 1994. A survey of charge-balance errors on published analyses of potable ground and surface waters. *Ground Water* 32(4), 539-546.
- Goldberg, S., and C. T. Johnson. 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *Journal of Colloid and Interface Science* 254, 204-216.
- Hem, J. D. 1992. *Study and interpretation of the chemical characteristics of natural water*. 3rd edition, U.S. Geological Survey Water-Supply Paper 2254.
- Herczeg, A. L., K. J. Rattray, P. J. Dillon, P. Pavelic, and K. E. Barry. 2004. Geochemical processes during five years of Aquifer Storage Recovery. *Ground Water* 42(3), 438-445.
- Maliva, R. G., G. P. Kennedy, W. K. Martin, T. M. Missimer, E. S. Owosina, and J. A. D. Dickson. 2002. Dolomitization-induced aquifer heterogeneity: Evidence from the upper Floridan aquifer, southwest Florida. *Geological Society of America Bulletin* 114(4): 419-427.
- Manning, B. A., S. E. Fendorf, and S. Goldberg. 1998. Surface structures and stability of arsenic(III) on goethite: Spectroscopic evidence for inner-sphere complexes *Environmental Science & Technology* 32, 2383-2338.
- McNeal, M. 2005. Oral communication regarding monthly operating reports for City of Tampa, Rome Avenue ASR system, 25 July 2005.
- Mirecki, J. E. 2004. *Water-quality changes during cycle testing at aquifer storage recovery (ASR) systems of south Florida*. ERDC/EL TR-04-8. Vicksburg, MS: U. S. Army Engineer Research and Development Center. Available for download at <http://el.erdcl.usace.army.mil/elpubs/pdf/trel04-8.pdf>
- Mirecki, J. E., and J. R. Hendel. (in preparation). Native ground-water quality characterization of the Floridan Aquifer System of South Florida. USACE Technical Report.
- Mirecki, J. E., B. G. Campbell, K. L. Conlon, and M. D. Petkewich. 1998. Solute changes during aquifer storage recovery testing in a limestone/clastic aquifer. *Ground Water* 36(3), 394-403.
- Missimer, T. M. 2002. *Late Oligocene to Pliocene evolution of the central portion of the South Florida platform: Mixing of siliciclastic and carbonate sediments*. Florida Geological Survey Bull. 65.
- Missimer, T. M., and K. W. Martin. 2001. The hydrogeology of Lee County, Florida. *Geology and Hydrology of Lee County Florida, Durward H. Boggess Memorial Symposium*, T. M. Missimer and T. M. Scott, ed., Florida Geological Survey Special Publication 49.
- Missimer, T. M., W. Guo, C. W., Walker, and R. G. Maliva. 2002. Hydraulic and density considerations in the design of aquifer storage and recovery systems. *Florida Water Resources Journal* 30-36. Downloaded 3 January 2006 at http://www.fwrj.com/Articles%202002/FWRJ_2_02_1.pdf

- Nordstrom, D. K., and D. G. Archer. 2003. Arsenic thermodynamic data and environmental geochemistry. *Arsenic in ground water*. A. H. Welch and K. G. Stollenwerk, ed. Boston, MA: KluwerAcademic Publishers.
- Palm Beach County Water Utilities Department. 2003. *Eastern Hillsboro Canal – WTP No. 9 Aquifer Storage and Recovery Well Construction Report and Operational Testing Request (PBCWUD Project no. 98-66B)*. Prepared for Joseph May, Florida Department of Environmental Protection, August 2003.
- Palm Beach County Water Utilities Department. 2005. *Eastern Hillsboro ASR System Cycle Test No. 1 – Technical Memorandum*. (PBCWUD Project No. WUC-98-66). Prepared for Joseph May, Florida Department of Environmental Protection, April 18, 2005.
- Parkhurst, D. L., and C. A. Appelo. 1999. *User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Geological Survey Water-Resources Investigations Report 99-4259.
- Petkewich, M. D., D. L. Parkhurst, K. J. Conlon, B. G. Campbell, and J. E. Mirecki. 2004. *Hydrogeologic and geochemical evaluation of aquifer storage recovery in the Santee Limestone/Black Mingo aquifer, Charleston, South Carolina, 1998-2002*. U.S. Geological Survey Scientific Investigations Report 2004-5046. Available for download at <http://water.usgs.gov/pubs/sir/2004/5046/>
- Price, R. E., and T. Pichler. 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock Interaction. *Chemical Geology* 228, 44-56.
- Prommer, H., and P. J. Stuyfzand. 2005. Identification of temperature-dependent water quality changes during a deep well injection experiment in a pyritic aquifer. *Environmental Science & Technology* 39(7), 2200-2209.
- Reese, R. S. 2000. *Hydrogeology and the distribution of salinity in the Floridan Aquifer System, southwestern Florida*. U.S. Geological Survey Water-Resources Investigations Report 98-4253.
- Reese, R. S. 2002. *Inventory and review of aquifer storage and recovery in southern Florida*. U.S. Geological Survey Water-Resources Investigations Report 02-4036.
- Reese, R. S. and S. J. Memberg. 2000. *Hydrogeology and the distribution of salinity in the Floridan Aquifer, Palm Beach County, Florida*. U.S. Geological Survey Water-Resources Investigations Report 99-4061.
- Reese, R. S., and E. Richardson. 2006. Oral communication, January 20, 2006. "Preliminary Hydrogeologic Framework Report. Report in review for SFWMD and U.S. Army Corps of Engineers – Jacksonville District.
- Rye, R. O., W. Back, B. B. Hanshaw, C. T. Rightmire, and F. J. Pearson, Jr. 1981. The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas. *Geochimica et Cosmochimica Acta* 45, 1941-1950.

- Scott, T. M. 1988. *The Lithostratigraphy of the Hawthorn Group (Miocene) of Florida*. Florida Geological Survey Bulletin 59.
- South Florida Water Management District. 2004. *Geophysical logs for wells LM-6615, LM-6210, and LM-6208*. Downloaded in 2004 at <http://www.sfwmd.gov/org/ema/dbhydro/index.html>
- South Florida Water Management District and Water Resource Solutions, Inc. 2005. *Berry Groves Class V, Group 9 Exploratory Well and EXBRY-1 Caloosahatchee River ASR pilot project well completion report*. Technical Publication.
- U.S. Geological Survey. 2005. PHREEQC geochemical model. Software, accessed 15 November 2005 at http://www.wbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html
- Vacher, H. L., W. C. Hutchings, and D. A. Budd. 2006. Metaphors and models: The ASR bubble in the Floridan aquifer. *Ground Water* 44(2), 144-153.
- Vanderzalm, J. L., J. Le Gal La Salle, J. L. Hutson, and P. J. Dillon. 2002. Water quality changes during aquifer storage and recovery at Bolivar, South Australia. *Management of aquifer recharge for sustainability*. P. J. Dillon, ed. Lisse, Belgium: AA Balkema Publishers.
- Vink, V. W. 1996. Stability relations of antimony and arsenic compounds in light of revised and extended Eh-pH diagrams. *Chemical Geology* 130, 21-20.
- Water Resource Solutions, Inc. 2002a. *Olga ASR system Cycle 1 report, July 2002*. Prepared for Lee County Utilities Department, Fort Myers, FL.
- Water Resource Solutions, Inc. 2002b. *North Reservoir ASR system Cycle 1 report, July 2002*. Prepared for Lee County Utilities Department, Ft. Myers, FL.
- Water Resource Solutions, Inc. 2003a. *Olga ASR system Cycle 2 report, September 2003*. Prepared for Lee County Utilities Department, Ft. Myers, FL.
- Water Resource Solutions, Inc. 2003b. *North Reservoir ASR system Cycle 2 report, September 2003*. Prepared for Lee County Utilities Department, Ft. Myers, FL.
- Water Resource Solutions, Inc. 2004. *North Reservoir ASR system Cycle 3, August 2004*. Prepared for Lee County Utilities Department, Ft. Myers, FL.
- Wedderburn, L. A., M. S. Knapp, D. P. Waltz, and W. S. Burns. 1982. *Hydrogeologic reconnaissance of Lee County Florida, Part I – Text and Part II – Atlas*. Technical Publication 82-1, South Florida Water Management District, West Palm Beach, FL.
- Wicks, C. M., J. S. Herman, A. F. Randazzo, and J. L. Jee. 1995. Water-rock interactions in a modern coastal mixing zone. *Geological Society of America Bulletin* 107(9), 1023-1032.
- Zhu, C., and C. Anderson. 2002. *Environmental applications of geochemical modeling*. Cambridge United Kingdom: Cambridge University Press.

Appendix A: Mineralogy and Chemical Data from Cores CCBRY-1 and EXBRY-1

Selected samples of the Arcadia Formation and Suwannee Limestone were analyzed for major mineralogy by x-ray diffraction methods in core CCBRY-1 (Berry Groves; Florida Geological Survey core W-18594). Unpublished bulk chemical and trace element data from Arcadia Formation and Suwannee Limestone samples in cores CCBRY-1 (W-18594) and EXBRY-1 (W-18464) were provided by Dr. Jonathan Arthur, Florida Geological Survey.

Table A1. Mineralogy of selected samples from the Arcadia Formation and Suwannee Limestone in core CCBRY-1

Sample Interval, in feet below land surface	Lithostratigraphic Formation	Abbreviated Lithologic Log Description ¹	Mineralogy, by X-Ray Diffraction ²
421.5-421.8	Arcadia	Marl with abundant fine phosphate	calcite, quartz, ferroan dolomite, carbonate-hydroxylapatite
500.5-501.0	Arcadia	Limestone (mudstone to wackestone), poor to moderate induration	calcite, quartz, ferroan dolomite, carbonate-hydroxylapatite
523.5-524.0	Arcadia	Limestone (wackestone to packstone), moderate induration, shell fragments	calcite, quartz, ferroan dolomite, carbonate-hydroxylapatite
539.5-540.0	Arcadia	Marly limestone (mudstone to packstone), friable	calcite, quartz, ferroan dolomite
545-547	Arcadia	Dolomitic limestone (wackestone to packstone), moderate induration	
553 -554	Arcadia	Sandy limestone (packstone), moderate induration	
563.0-563.5	Arcadia	Sandy clay, abundant very fine to fine quartz, trace phosphate and shell	montmorillonite, quartz, calcite, ferroan dolomite
632.0-632.5	Suwannee Ls	Limestone (fossil packstone) variably indurated	quartz, calcite
637-638	Suwannee Ls	Limestone (fossil packstone), variably indurated	
640.0-640.5	Suwannee Ls	Limestone (wackestone), moderate to poor induration, minor quartz sand and phosphate	quartz, calcite
661	Suwannee Ls	Limestone (wackestone), moderate to poor induration, with fine quartz, very fine phosphate	quartz, calcite
661-662	Suwannee Ls	Limestone (wackestone), moderate to poor induration, with fine quartz, very fine phosphate	
709-710	Suwannee Ls	Limestone (grainstone), moderate to poor induration, fine quartz sand phosphate	

728-729	Suwannee Ls	Limestone (fossil packstone), moderately well indurated, medium to coarse grained, marly, very fine phosphate	
757.0-757.5	Suwannee Ls	Limestone (grainstone), moderate to poor induration, fine quartz sand and phosphate	calcite, quartz, carbonate-hydroxylapatite
761-762	Suwannee Ls	Limestone (grainstone), moderate to poor induration, fine quartz sand and phosphate	
782-783	Suwannee Ls	Sandstone, quartz, moderate to poor induration, fine grained, subrounded, fine phosphate with abundant shell fragments	
798.0-798.2	Suwannee Ls	Sandstone, moderate to poor induration, fine phosphate, common shell fragments	calcite, quartz, carbonate-hydroxylapatite
827-828	Suwannee Ls	Limestone (fossil packstone), moderately well indurated, fine to coarse grained, marly, fine phosphate	
829.0-830.0	Suwannee Ls	Limestone (fossil packstone), moderately well indurated, fine to coarse grained, marly, fine phosphate	quartz, calcite
847.5-847.7	Suwannee Ls	Limestone (fossil packstone), moderately well indurated, minor quartz sand, phosphate	quartz, calcite
849-850	Suwannee Ls	Limestone (fossil packstone), moderately well indurated, fine to very coarse grained, variably marly, fine phosphate	
860-861	Suwannee Ls	Limestone (wackestone), well indurated, fine phosphate, variably fine quartz sand	
915-916	Suwannee Ls	Limestone (wackestone), moderately well to well indurated, fine to very coarse grained, chalky very fine phosphate	
954-955	Suwannee Ls	Limestone (wackestone), well indurated, fine to very coarse grained, marly, fine phosphate, trace quartz	
1000-1001	Suwannee Ls	Limestone (mudstone), well indurated, variably chalky, very fine phosphate, trace quartz	

¹ Lithologic log by Water Resource Solutions, Inc.

² X-Ray Diffractometry performed by Charles W. Weiss, Jr., GSL-ERDC.

[illegible]

Table A3. Bulk chemistry of selected samples from the Arcadia Formation and Suwannee Limestone in core EXBRY-1¹

Sample Interval, ft bls	Lithostratigraphic Fm	As, mg/kg	CaO, weight percent	SiO ₂ , weight percent	MgO, weight percent	Fe ₂ O ₃ , weight percent	Al ₂ O ₃ , weight percent	K ₂ O, weight percent	Na ₂ O, weight percent	P ₂ O ₅ , weight percent	TiO ₂ , weight percent
556-557	Arcadia	2	52.19	4.27	0.72	0.19	0.40	0.13	0.14	2.17	0.030
558-559	Arcadia	<1	53.50	2.15	0.96	0.08	0.25	0.05	0.08	1.11	0.017
560-561	Arcadia	<1	39.38	27.48	0.45	0.33	0.51	0.09	0.06	0.35	0.103
756-757	Suwannee	4	42.50	15.41	2.57	0.26	1.46	0.41	0.44	4.24	0.063
759-760	Suwannee	2	35.76	33.05	0.47	0.30	0.73	0.13	0.05	0.32	0.144
902-903	Suwannee	2	53.93	1.49	0.65	0.06	0.10	-0.01	0.02	0.07	0.009
905-906	Suwannee	2	53.41	2.49	0.60	0.59	0.12	0.01	-0.01	0.06	0.017
909-910	Suwannee	2	54.36	1.11	0.59	0.07	0.08	-0.01	-0.01	0.05	0.009
1094-1096	Suwannee	<1	53.85	0.41	1.12	0.04	0.13	-0.01	0.02	0.02	-0.001

¹ Bulk chemical data from Jon Arthur, Florida Geological Survey. Minimum detection limit (MDL) for arsenic - 1 ppm by neutron activation analysis; MDL for all oxide data is 0.01 wt % by FUS-inductively coupled plasma spectroscopy.

Table A4. Selected major and trace element concentrations in Arcadia Formation and Suwannee Limestone samples from core CCBRY-1¹

Depth, ft bls	Formation ²	Arsenic, ppm	Organic Carbon, weight percent	Total Sulfur, weight percent	Sulfate, weight percent
545-547	Arcadia	6	<0.05	0.12	<0.05
553-554	Arcadia	2	<0.05	0.02	<0.05
637-638	Suwannee	2	<0.05	0.05	<0.05
661-662	Suwannee	2	<0.05	0.04	<0.05
709-710	Suwannee	<1	<0.05	0.03	<0.05
728-729	Suwannee	1	<0.05	0.02	<0.05
761-762	Suwannee	5	<0.05	0.03	<0.05
782-783	Suwannee	8	<0.05	0.09	<0.05
827-828	Suwannee	5	<0.05	0.04	<0.05
849-850	Suwannee	3	<0.05	0.05	<0.05
860-861	Suwannee	5	0.07	0.04	<0.05
915-916	Suwannee	4	<0.05	0.03	<0.05
954-955	Suwannee	2	<0.05	0.04	<0.05
1000-1001	Suwannee	1	0.05	0.02	<0.05
Minimum detection limit		1	0.05	0.01	0.05

¹ Unpublished data provided by Jon Arthur, Florida Geological Survey. FGS core code W-18594.

² Contact between Arcadia and Suwannee Fm at point where gamma log intensity diminishes (560 ft bls in Core CCBRY-1).

Table A5. Selected major and trace element concentrations in Arcadia Formation and Suwannee Limestone samples from core EXBRY-1¹

Depth, ft bls	Formation ²	Arsenic, ppm	Organic Carbon, weight percent	Total Sulfur, weight percent	Sulfate, weight percent
556-557	Arcadia	2	<0.05	0.16	<0.05
558-559	Arcadia	<1	<0.05	0.12	<0.05
560-561	Arcadia	<1	<0.05	0.04	<0.05
756-757	Suwannee	4	0.07	0.23	<0.05
759-760	Suwannee	2	<0.05	0.04	<0.05
902-903	Suwannee	2	<0.05	0.06	<0.05
905-906	Suwannee	2	<0.05	0.07	<0.05
909-910	Suwannee	2	<0.05	0.07	<0.05
1094-1096	Suwannee	<1	0.13	0.08	<0.05
Minimum detection limit		1	0.05	0.01	0.05
¹ Unpublished data provided by Jon Arthur, Florida Geological Survey. FGS core code W-18464. This core located 1000 ft east of CCBRY-1. ² Contact between Arcadia and Suwannee Fm at point where gamma log intensity diminishes (630 ft bls in core EXBRY-1; SFWMD & WRS, 2005).					

Table A6. X-ray diffractograms of Arcadia Formation and Suwannee Limestone samples from core CCBRY-1.

Peaks that are identified as “ankerite” $[\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2]$ are interpreted to be ferroan dolomite

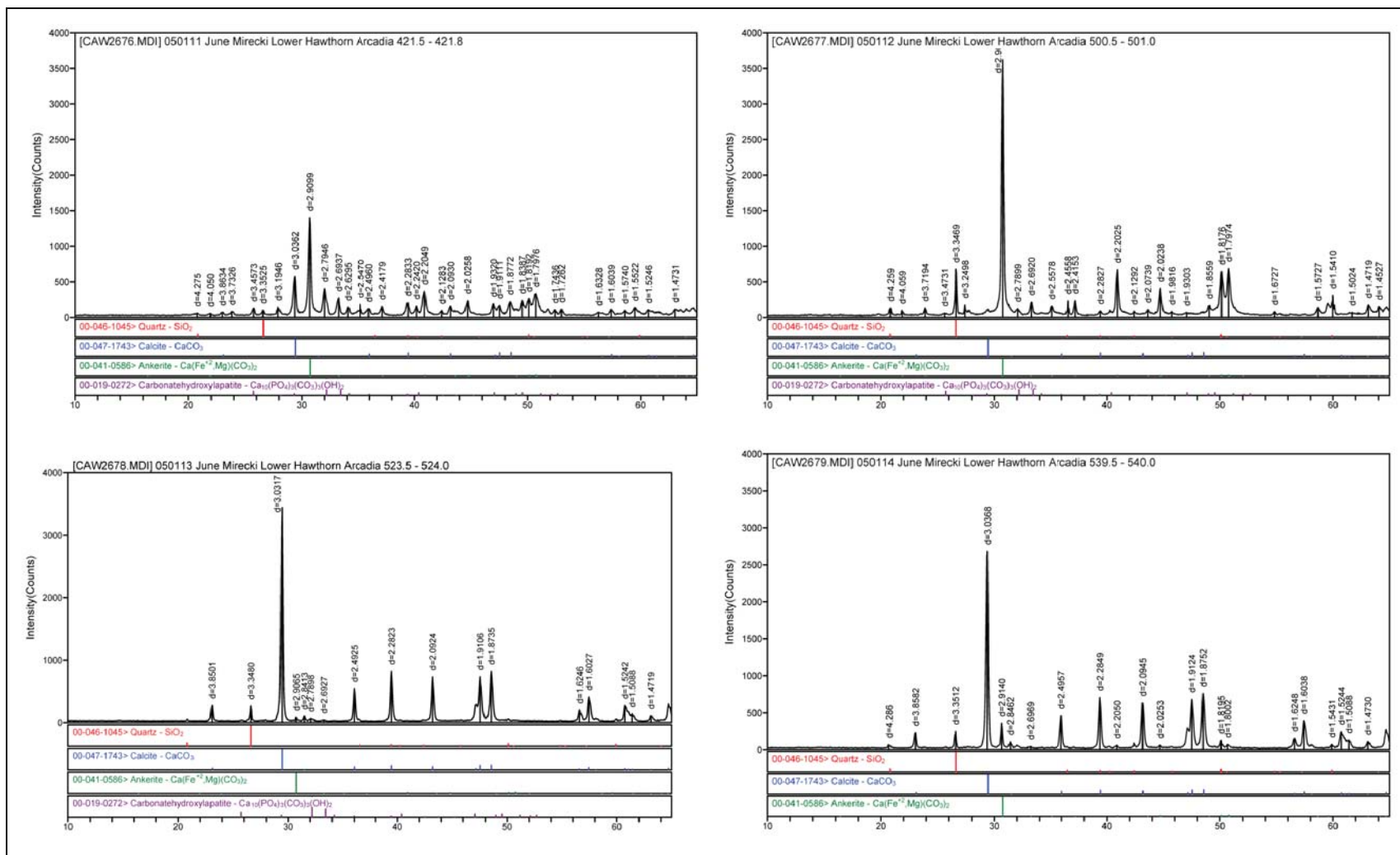


Table A6. (Continued).

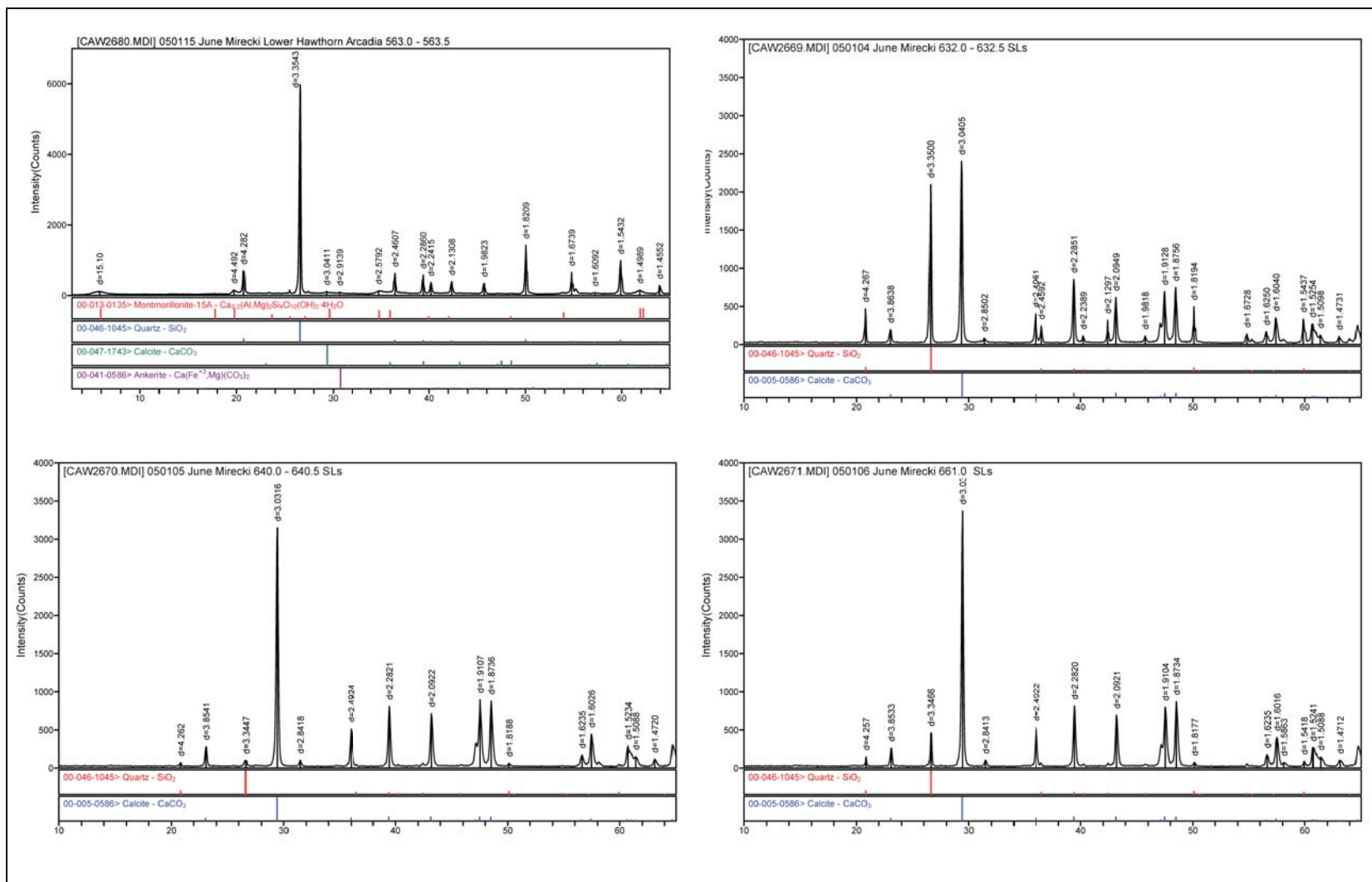
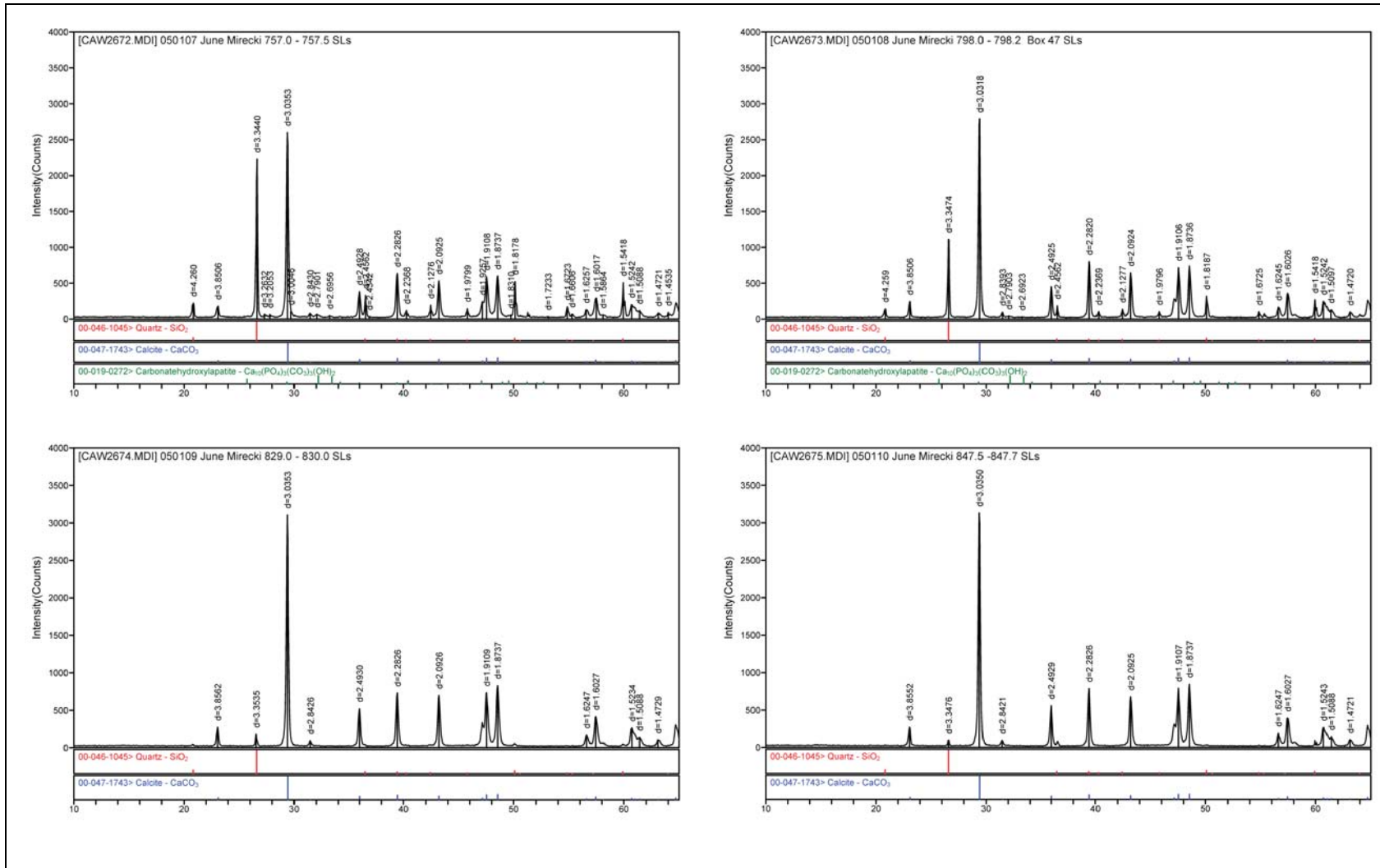


Table A6. (Concluded).



Appendix B: PHREEQC Input Files

Mixing models

The script cited below is the input for a model of conservative mixing of two end members at the Olga ASR system. Similar scripts were developed for North Reservoir ASR system, using end member (recharge water and native upper FAS water) at each site. Mixing models are described in section 2.

```
DATABASE C:\Program Files\USGS\Phreeqc Interactive
2.12.5\llnl.dat
TITLE Olga Cycle 1 Mixing Curve
SOLUTION 1 Recharge water from ASR well
    temp      26.6
    pH        7.2
    pe        4
    redox     O(-2)/O(0)
    units     mg/l
    density   1
    Alkalinity 74.2
    Ca        71.3
    Mg        3.3
    Cl        78.1
    S(6)      100.2
    Fe        0.04
    Na        50      # estimated for charge balance
    O(0)      6.1
    -water    1 # kg
SAVE solution 1
END
```

Mixing models – continued.

```
SOLUTION 2 NATIVE UFA LM-6615
    temp      28.3
    pH        7.9
    pe         4
    redox      S(-2)/S(6)
    units      ppm
    density    1
    Alkalinity 189
    Ca         180
    Mg         25.9
    Cl         1110
    S(6)       357
    Fe         0.11
    Na         900 # estimated for charge balance
    O(0)       0
    S(-2)      1
    -water     1 # kg
SAVE solution 2
END

TITLE MIXING CURVE
MIX 1 80 % recharge
    1      0.8
    2      0.2
SAVE solution 3
END
MIX 2 60% recharge
    1      0.6
    2      0.4
Save solution 4
END
MIX 3 40% recharge
    1      0.4
    2      0.6
SAVE SOLUTION 5
END
MIX 4 20% recharge
    1      0.2
    2      0.8
SAVE SOLUTION 6
END
```

Inverse geochemical model of water-quality changes during storage

The code below shows PHREEQC v. 2.15 input for inverse geochemical models to describe major geochemical reactions during storage. Output (phase mole-transfer values) for all models is listed in Table B1. Positive values indicate dissolution (mass entering water); negative values indicate precipitation (mass leaving water).

```
DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.12.5\phreeqc.dat
SOLUTION 1 Final Recharge Water from ASR well
  units mg/L
  pH 7.7
  temp 24.9
  redox O(0)/O(-2)
  Ca      101
  Mg      1.9 #Ca and Mg concentration calculated from total hardness
  Na      70 #Na concentration estimated for low %CBE
  Cl      136
  Fe      0.04
  S(6)    88.6
  S(-2)   0.0
  Alkalinity      159.7 as HCO3
  O(0)      5.69
SAVE SOLUTION 1
END
SOLUTION 2 Initial Recovered Water from ASR well
  units mg/L
  temp 25.4
  redox S(6)/S(-2)
  pH 7.8
  Ca      101
  Mg      4.9 #Mg is calculated from total hardness
  Na      85 #Na concentration is estimated for low %CBE
  Cl      130
  Fe      0.14
  S(6)    118
  S(-2)   0.3
  Alkalinity 180.4 as HCO3
  O(0)    0.0
SAVE SOLUTION 2
INVERSE_MODELING 1
-solutions 1 2
-phases
  halite
  dolomite
  H2S(g)
  gypsum
  calcite
  pyrite diss
  Fe(OH)3(a) pre
-range
-minimal
-multiple_precision
-Mineral_water false
-balance Cl 0.07
END
```

Table B1. Inverse geochemical models showing water quality changes during storage.

ASR System	Storage, days	Phase Mole Transfers, millimoles							Model Evaluation Criteria			Input Data Source
		Halite	Calcite	Dolomite	Gypsum	Pyrite	Iron Oxy-hydroxide	H ₂ S gas	No. of models	Sum of Residuals	Uncertainty, %	
Olga Cycle 1	123	0.35	no rxn	0.11	0.14	0.05	(-0.05)	no rxn	2	9.6	7	WRS, 2002a
Olga Cycle 2	98	0.16	0.41	0.08	no rxn	1	(-1.0)	(-0.18)	1	9.5	7	WRS, 2003a
Olga Cycle 3	181	0.50	0.80	(-0.12)	no rxn	1.6	(-1.6)	(-2.9)	1	8.2	7	MORs
North Reservoir Cycle 1	174	1.7	1.0	(-0.25)	(-0.6)	5.6	(-5.6)	(-10.5)	1	5.4	7	WRS, 2002b
North Reservoir Cycle 2	50	1.1	1.1	(-0.26)	0.27	no rxn	(-1.6)	1.6	1	5	7	WRS, 2003b
North Reservoir Cycle 3	133	0.43	0.71	0.12	(-0.51)	3.3	(-3.3)	(-6.2)	1	5.9	7	WRS, 2004
Eastern Hillsboro Cycle 1	13	2.2	no rxn	0.04	0.16	0.001	no rxn	(-0.012)	1	6.5	7	PBC WUD, 2005
Note: Positive phase mole transfer values indicate dissolution; negative values indicate precipitation. Abbreviations: no rxn, no phase mole transfer reaction; WRS, Water Resource Solutions, Inc.; MORs, monthly operating reports; PBCWUD, Palm Beach County Water Utility District.												

Inverse geochemical model: Reductive dissolution of iron oxyhydroxides during recovery

The code below shows PHREEQC v. 2.15 input for a preliminary inverse geochemical model to describe the redox environment of arsenic transport during recovery. Output (phase mole-transfer values) for this model is listed in Table B2. Positive values indicate dissolution (mass entering water); negative values indicate precipitation (mass leaving water). This model supports arsenic mobilization resulting from reductive dissolution of iron oxyhydroxide.

```
TITLE Olga C1 Inverse Model_RedDiss_Recovery
SOLUTION 1 Initial Recovered Water from ASR well
units mg/L
temp 23.1
pe 0.0 #approx Eh with no DO
pH 7.8
Ca      101
Mg       5
Na      90  #estimated
Cl      130
Fe       0.14
S(6)    118
S(-2)   0.1
#S(-2) concentration is estimated
Alkalinity 180 as HCO3
C       0.4  #DOC is estimated
O(0)    0.2
SAVE SOLUTION 1
End
```

```
SOLUTION 2 Final Recovered Water from ASR well
units mg/L
temp 27.2
pe -3.3 # approx Eh of -0.2, sulfate reduction
pH 7.9
Ca      135
Mg       0.5
Na     140 #estimated
Cl      260
Fe       0.04
S(6)    166
S(-2)   0.19 # estimated
Alkalinity 139 as HCO3
C       0.1  #DOC is estimated
O(0)    0.0
SAVE SOLUTION 2
End
```

```
PHASES
```


Appendix C: Selected Water-Quality Data from Cycle Tests

Arsenic and chloride concentrations (among other constituents) were measured weekly during recharge and recovery during three successive cycle tests at both Olga and North Reservoir ASR systems (WRS 2002 a, b; 2003 a, b, 2004; plus MORs; Tables C1 through C6). Few arsenic data are available from the Eastern Hillsboro site. Two samples from the ASR well during Cycle 1 recharge showed total dissolved arsenic concentrations of 3.8 and 4.5 µg/L; two samples from the Floridan Aquifer monitor well during recharge showed total dissolved arsenic concentrations of 5.3 and 3 µg/L (PBCWUD 2005; Table C7). These data are the basis for Figures 2, 3, and 5.

In addition, arsenic species were measured during Cycle 3 recovery at Olga and North Reservoir ASR systems (Tables C8 and C9). These samples were analyzed at the Engineer Research and Development Center (ERDC) for total dissolved arsenic, arsenic species (AsIII or arsenite, and AsV or arsenate), and methyl arsenical species. Total dissolved arsenic concentration was measured using graphite furnace atomic absorption spectroscopy, with a method detection limit of 1.0 µg/L. Arsenate (AsV), arsenite (AsIII), and methyl arsenicals were separated using high-performance liquid chromatography (HPLC), and quantified by inductively coupled plasma-mass spectroscopy (ICP-MS) following the methods of Bednar et al. (2002, 2004). HPLC/ICP-MS method detection limits were 0.6 or 1.8 µg/L. No methyl arsenical species (monomethyl arsonate and dimethyl arsenate) were detected in any sample from these systems. Statistically identical ($r^2=0.98$, $n=46$) total dissolved arsenic concentrations were obtained when data reported previously (WRS 2004 and MORs) are compared with arsenic concentrations measured at ERDC for Olga and North Reservoir Cycle Test 3.

Table C1. Arsenic and chloride concentrations from Cycle Test 1 at Olga ASR system. Data from WRS (2002a).

Phase of Cycle Test	Time, days	ASR Well LM-6086		Monitor Well LM-6209		Monitor Well LM-6615	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	1	1	84	<3	1100	<3	940
Recharge	8	82.8	80	<3	1040	<3	870
Recharge	15	154	64	<3	1040	<3	860
Recharge	22	153	64	<3	1020	<3	840
Recharge	30	<3	68	<3	1000	<3	800
Recharge	36	<3	74	<3	920	<3	760
Recharge	43	<3	64	<3	940		740
Recharge	50	<3	64	<3	900	<3	720
Recharge	57	25.6	59	<3	860	<3	720
Recharge	64	21.7	50	<3	820	<3	690
Recharge	71	25.8	52	<3	800	<3	640
Recharge	79	23.1	65	<3	820	<3	640
Recharge	86	22.6	64	<3	680	<3	580
Recharge	93	21.4	78	<3	740	<3	580
Recharge	100	20.5	70	<3	720	<3	580
Recharge	107	16.1	70	<3	700	<3	580
Recharge	114	20.6	80	<3	740	<3	560
Recharge	120	29.8	80	<3	680	<3	560
Recharge	127	24.9	90	<3	640	<3	540
Recharge	135	24.8	108	<3	620	<3	530
Recharge	140	30.9	112	<3	620	<3	520
Recharge	147	27.5	118	<3	620	4	500
Recharge	153	29.9	136	<3	620	<3	495
Storage	162	37	220				
Storage	230	41	120				
Recovery	286	55.8	130	<3	600	<3	640
Recovery	294	9.8	156	<3	680	<3	660
Recovery	301	5.2	168	<3	680	<3	680
Recovery	308	4.8	182	<3	740	<3	660
Recovery	315	3.6	202	<3	740	<3	700
Recovery	322	3.1	224	<3	780	<3	700
Recovery	329	1.9	260		780	7	660

Table C2. Arsenic and chloride concentrations from Cycle Test 2 at Olga ASR system. Data from WRS (2003a).

Phase of Cycle Test	Time, days	ASR Well LM-6086		Monitor Well LM-6209		Monitor Well LM-6615	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	0	<3	96				
Recharge	7	<3	106	<3	740	<3	660
Recharge	14	<3	80	<3	660	5	620
Recharge	21	<3	82	<3	660	4	600
Recharge	28	<3	86	<3	620	4	560
Recharge	35	<3	82	<3	520	<3	520
Recharge	42	<3	88	<3	600	6	500
Recharge	49	<3	86	<3	560	<3	500
Recharge	56	<3	86	<3	560	<3	460
Recharge	63	<3	94	<3	580	<3	520
Recharge	70	<3	68	<3	560	<3	420
Recharge	77	<3	78	<3	520	<3	400
Recharge	84	<3	74	<3	520	<3	400
Recharge	91	<3	58	<3	520	<3	460
Recharge	96	<3	66	<3	540	<3	400
Recharge	103	<3	74	<3	520	<3	380
Recharge	110	<3	72	<3	380	<3	500
Recharge	117	<3	74	<3	500	<3	360
Recharge	124	<3	66	<3	480	<3	380
Recharge	131	<3	64	<3	340	<3	340
Recharge	138	<3	64	<3	460	<3	340
Recharge	145	<3	76	<3	480	<3	380
Recharge	152	<3	66	<3	500	<3	360
Recharge	160	<3	60	<3	480	<3	340
Recharge	167	<3	68	<3	480	<3	380
Recharge	174	<3	104	<3	480	<3	340
Recharge	182	<3	94	<3	460	<3	340
Recharge	189	<3	82	<3	440	<3	380
Recharge	194	<3	100	<3	440	<3	360
Recharge	201	<3	88	<3	440	<3	360
Recharge	208	<3	80	<3	420	<3	340
Storage	215	<3	92	<3	480	<3	280
Storage	258	<3	68				
Recovery	320	4	90	<3	580	<3	440
Recovery	327	4	98	<3	600	<3	460

Recovery	334	7	108	<3	600	<3	480
Recovery	341	7	120	7	600	<3	480
Recovery	348	<3	130	5	640	<3	520
Recovery	355	4	136	<3	600	<3	500
Recovery	362	27	146	<3	620	<3	520
Recovery	370	<3	152	<3	620	<3	560
Recovery	377	28	164	<3	660	<3	540
Recovery	384	28.6	180	3	440	3	500
Recovery	391	38	178	32	640	<3	600
Recovery	397		202				

Table C3. Arsenic and chloride concentrations from Cycle Test 3 at Olga ASR system. Data from Monthly Operating Reports.

Phase of Cycle Test	Time, days	ASR Well LM-6086		Monitor Well LM-6209		Monitor Well LM-6615	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	7	<3	59	5	546	490	5
Recharge	14	<3	47	<3	563	432	<3
Recharge	21	<3	50	<3	448	317	<3
Recharge	28	<3	55	<3	479	334	8
Recharge	35	<3	57	<3	510	326	6
Recharge	42	<3	66	<3	475	310	5
Recharge	49	RP	62	<3	505	295	<3
Recharge	56	<3	60	<3	465	285	<3
Recharge	63	<3	56	<3	490	267	<3
Recharge	70	<3	60	<3	452	292	<3
Recharge	87	<3	67	<3	449	304	<3
Recharge	94	<3	66	<3	402	269	<3
Storage	100						
Recovery	281						
Recovery	288	8.1	77	<3	478	354	<1
Recovery	295	8.5	85	<3	506	384	1.6
Recovery	302	9.3	178	2	481	360	2
Recovery	316	12.1	111	1.2	494	402	1.6
Recovery	323	14.3	124	1.4	527	453	1.7
Recovery	330	16.4	134	1.5	515	448	1.5
Recovery	337	22.8	138	1.6	506	390	<1
Recovery	344	34	160	2.54	550	490	1.68
Recovery	351	23.3	169	1.3	524	470	<1
Recovery	358	31.7	183	1.7	530	480	1
Recovery	365	35.9	184	1.4	533	493	<1
Recovery	387	66	194	1.2	530	446	1.1
Recovery	394	68	200	1.5	611	381	5.2
Recovery	401	62	204	2	552	369	6.2

Table C4. Arsenic and chloride concentrations from Cycle Test 1 at the North Reservoir ASR system. Data from WRS (2002b).

Phase of Cycle Test	Time, days	ASR Well LM-6210		Monitor Well LM-6208	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	1	Not avail	93	<3	710
Recharge	7	<3	90	<3	650
Recharge	14	<3	81	<3	710
Recharge	21	<3	68	<3	630
Recharge	28	<3	58	<3	590
Recharge	36	<3	51	<3	560
Recharge	42	<3	52	<3	560
Recharge	49	<3	60	<3	560
Recharge	56	<3	56	<3	480
Recharge	63	<3	59	<3	460
Recharge	70	<3	48	<3	430
Recharge	77	<3	52	<3	360
Recharge	85	<3	54	<3	320
Recharge	92	<3	52	<3	300
Recharge	99	<3	72	<3	300
Recharge	106	<3	58	<3	250
Recharge	113	<3	62	<3	240
Recharge	120	<3	74	<3	220
Recharge	126	<3	Not avail	<3	208
Recovery	293	10	146	<3	200
Recovery	301	5	208	3	520
Recovery	308	9	266	8	540

Table C5. Arsenic and chloride concentrations from Cycle test 2 at the North Reservoir ASR system. Data from WRS (2003b).

Phase of Cycle Test	Time, days	ASR Well LM-6210		Monitor Well LM-6208	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	0	<3	92	<3	360
Recharge	8	<3	82	<3	220
Recharge	15	<3	62	<3	280
Recharge	22	<3	78	<3	180
Recharge	29	<3	84	<3	180
Recharge	36	<3	84	<3	140
Recharge	43	<3	66	<3	200
Recharge	50	<3	74	<3	144
Recharge	57	<3	96	<3	120
Recharge	64	<3	64	<3	128
Recharge	71	<3	70	<3	124
Recharge	78	<3	72	<3	120
Recharge	85	<3	64	<3	116
Recharge	92	<3	62	<3	112
Recharge	99	<3	66	<3	114
Recharge	106	<3	70	<3	114
Recharge	113	<3	78	<3	110
Recharge	120	<3	66	<3	102
Recharge	127	<3	66	<3	104
Recharge	134	<3	66	<3	104
Recharge	141	<3	66	<3	98
Recharge	148	<3	68	<3	100
Recharge	155	<3	54	<3	98
Recharge	155	<3	60	<3	92
Recharge	162	<3	68	<3	94
Recharge	169	<3	94	<3	94
Recharge	177	<3	78	<3	96
Recharge	184	<3	86	<3	102
Recharge	189	<3	76	<3	100
Recharge	196	<3	80	<3	100
Recharge	203	<3	80	<3	102
Recharge	210	<3	76	<3	90
Recharge	218	<3	80	<3	96
Recharge	225	<3	82	<3	102
Recharge	232	<3	88	<3	100

Recharge	239	<3	96		
Storage	254	<3	75		
Recovery	295	<3	134	<3	252
Recovery	302	<3	160	7	318
Recovery	309	<3	182	6	376
Recovery	316	<3	200	6	420
Recovery	323	6	204	3	460
Recovery	330	5	218	7	440
Recovery	338	9	246	7	480
Recovery	345	3	242	<3	480
Recovery	352	3	248	4	460
Recovery	367		272		460

Table C6. Arsenic and chloride concentrations from Cycle Test 3 at the North Reservoir ASR system. Data from WRS (2004).

Phase of Cycle Test	Time, days	ASR Well LM-6210		Monitor Well LM-6208	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	0	<3	70	11.3	420
Recharge	7	<3	60	11.4	360
Recharge	14	<3	74	8.0	300
Recharge	21	<3	60	<3	260
Recharge	28	<3	62	<3	200
Recharge	35	<3	56	<3	160
Recharge	42	<3	72	<3	154
Recharge	49	<3	68	<3	128
Recharge	56	<3	76	<3	116
Recharge	63	<3	78	<3	112
Recharge	70	<3	74	<3	104
Recharge	77	<3	66	<3	104
Recharge	84	<3	76	<3	96
Recharge	91	<3	78	3.6	94
Recharge	99	<3	82	<3	92
Recharge	105	<3	82	<3	92
Recharge	112	<3	76	<3	86
Recharge	119	<3	80	<3	86
Recharge	126	<3	82	<3	98
Recharge	133	<3	80	<3	84
Recharge	140	<3	90	<3	84

Recharge	146	<3	90	<3	88
Storage			106		
Recovery	279	5.3	102	< 3	94
Recovery	286	2.0	164	2.5	176
Recovery	293	2.7	190	3.7	278
Recovery	300	3.9	212	5.3	314
Recovery	307	4.8	216	5.4	340
Recovery	314	5.0	228	5.8	340
Recovery	321	5.3	240	6.9	360
Recovery	328	5.6	238	4.9	360
Recovery	335	6.1	250	5.5	380
Recovery	342	6.9	254	5.4	380

Table C7. Arsenic and chloride concentrations from Cycle Test 1 at the Eastern Hillsboro ASR system. Data from PBCWUD (2005).

Phase of Cycle Test	Time, days	ASR Well		Floridan Aquifer Monitor Well	
		Arsenic, µg/L	Chloride, mg/L	Arsenic, µg/L	Chloride, mg/L
Recharge	0	3.8	51.1	5.27	1580
Recharge	20	4.5	52.6	3	3080
Recharge	27		53		2890
Recharge	34		51.2		2590
Recharge	40		51.2		2480
Recharge	47		52.2		2380
Recharge	54		53		2290
Recharge	61		53.7		2180
Recharge	68		53.8		2130
Recharge	75		53.7		2080
Recharge	82		53.2		2032
Recharge	89		51.9		2348
Recharge	97		54.1		2130
Recovery	109		34.5		2460
Recovery	116		137		1260
Recovery	118		252		1390

Table C8. Dissolved arsenic species concentrations from Cycle Test 3 recovery at the Olga ASR system (ERDC data). All concentrations reported in µg/L.

Percent Volume Recovered Cycle 3	Olga ASR System								
	ASR Well LM-6086			Monitor Well LM-6209			Monitor Well LM-6615		
	AsIII	AsV	Total As	AsIII	AsV	Total As	AsIII	AsV	Total As
10.7	1.1	6.7	8.6	1.6	<0.6	<1.0	3.1	<0.6	2.8
15.5	no data	no data	no data	<1.0	<0.6	<1.0	1.7	1.8	2.6
25.0	<0.6	13	13	<0.6	<0.6	3.0	2	0.8	3.0
30.6	<0.6	14	14	<0.6	<0.6	3.0	<0.6	<0.6	3.0
36.3	2	17	18	1.0	<0.6	3.0	1.0	0.8	3.0
41.4	5	17	22	<1.8	<1.8	4.0	<1.8	<1.8	4.0
45.8	8	15	25	<1.8	<1.8	4.0	<1.8	<1.8	4.0
57.8	16	14	33.8	<1.8	<1.8	2.1	<1.8	<1.8	2.0
63.1	22	14	37	<1.8	<1.8	2.5	<1.8	<1.8	2.1
66.1	54	13	60	<1.8	<1.8	2.0	<1.8	<1.8	2.5
69.4	52	15	58.3	<1.8	<1.8	2.6	6.0	<1.8	7.5

Table C9. Dissolved arsenic species concentrations from Cycle Test 3 recovery at the North Reservoir ASR system (ERDC data). All concentrations reported in µg/L.

Percent Volume Recovered Cycle 3	North Reservoir ASR System					
	ASR Well LM-6210			Monitor Well LM-6208		
	AsIII	AsV	Total As	AsIII	AsV	Total As
1.5	2.4	2.7	3.4	2.9	1.6	3.4
3.3	2.7	2.0	4.0	5.4	<0.6	5.2
6.0	3.4	1.5	4.2	6.1	<0.6	5.7
7.5	4.4	1.2	5.2	6.4	<0.6	6.0
8.2	1.0	7.6	8.9	no data	no data	no data
8.9	4.0	3.0	6.0	6.0	2.0	7.0
10.3	5.0	2.0	6.0	7.0	0.7	7.0
11.7	5.0	2.0	7.0	6.0	0.8	6.0
13.1	5.0	<1.8	7.0	6.0	<1.8	7.0
14.5	5.0	<1.8	8.0	4.0	<1.8	8.0

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) September 2006		2. REPORT TYPE Final report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Geochemical Models of Water-Quality Changes During Aquifer Storage Recovery (ASR) Cycle Tests, Phase I: Geochemical Models Using Existing Data				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) June E. Mirecki				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Environmental Laboratory U.S. Army Engineer Research and Development Center 3909 Halls Ferry Road Vicksburg, MS 39180-6199				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/EL TR-06-8	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Corps of Engineers Jacksonville, FL				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Geochemical models were developed using existing water-quality data sets from three permitted, potable-water Aquifer Storage Recovery (ASR) systems in south Florida. All three systems store and recover water in different permeable zones of the upper Floridan Aquifer System (FAS). At the Olga ASR system, water is stored in the Suwannee Limestone; at the North Reservoir ASR system, water is stored in the Arcadia Formation of the lower Hawthorn Group. Both sites are located in Lee County, along the southwest Gulf Coast of Florida. At the Eastern Hillsboro ASR system, water is stored in the basal Hawthorn unit; this system is located in Palm Beach County near the southeastern Atlantic Coast of Florida. The objectives of this study are to use geochemical modeling methods to simulate 1) mixing between native water of the upper FAS and recharge water during cycle testing; 2) geochemical reactions that occur during the storage phase of cycle tests in different lithologies; and 3) controls on arsenic transport and fate during ASR cycle testing. Existing cycle test data sets were developed for permitting purposes, not research; therefore, concentrations of some major dissolved constituents are estimated. Quantitative uncertainty that resulted from the use of incomplete water-quality datasets is defined for these geochemical models. (Continued)					
15. SUBJECT TERMS		Arsenic	Comprehensive Everglades	Florida	Ground water quality
Aquifer Storage Recovery		ASR	Restoration Plan	Floridan Aquifer System	Groundwater quality
Arcadia Formation		CERP	Everglades	Geochemical modeling	Suwannee Limestone
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 66	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code)

14. ABSTRACT

Mixing of recharge and native groundwater end members during cycle testing is simulated using chloride as a conservative tracer. Mixing models show that low-chloride groundwater mixes to different extents during recharge in the Arcadia Formation and Suwannee Limestone. At the North Reservoir ASR system (Arcadia Formation), recharge water is transported as plug flow, as shown by sigmoid-shaped breakthrough curves in monitor wells, and chloride trends that resemble conservative mixing lines. In contrast, at Olga ASR system, recharge water is affected by hydraulic factors because breakthrough curves at the monitor well are not sigmoidal, and chloride trends deviate from conservative mixing curves. Data were insufficient to simulate mixing at the Eastern Hillsboro ASR system.

Inverse geochemical models quantified phase mole-transfer between water and rock, which controls water quality during the storage phase of a cycle test. The greatest phase mole-transfer values resulted from reactions of iron and sulfur at the Olga and North Reservoir ASR systems. Specifically, these reactions included pyrite oxidation with subsequent iron oxyhydroxide precipitation, and sulfate reduction with hydrogen sulfide production. These reactions should proceed in a sequence, not simultaneously, and suggest that the redox evolution of the storage zone exerts a significant influence on stored water quality.

Arsenic mobility is a major challenge to ASR feasibility, so inverse geochemical models were developed to simulate redox conditions that facilitate arsenic mobility during ASR cycle testing. Trends in arsenic concentrations measured at ASR and monitor wells, along with additional water-quality data, arsenic speciation analyses, and bulk chemistry and major mineralogy in core samples from the Arcadia Formation and Suwannee Limestone constrain these models. The stability of iron oxyhydroxide phases changes as the storage zones evolve from oxic (during recharge) to sulfate-reducing (during storage and recovery). Because iron oxyhydroxide is an effective sorption surface for arsenic, the stability of this mineral is an important control. The onset of sulfate-reducing conditions causes reductive dissolution of iron oxyhydroxide, with subsequent release of sorbed arsenic. The instability of iron oxyhydroxide during recovery is supported by inverse geochemical models at Olga and North Reservoir ASR systems. However, phase mole-transfer values are small (micromoles/kilogram water), and it is unclear if this mass of iron is sufficient for effective arsenic sequestration.