APPENDIX C

Supporting documents for geochemical studies

1. **Mirecki, J.E., Bennett, M.W., and López-Baláez, M., 2012. Arsenic control during aquifer storage recovery cycle tests in the Floridan Aquifer. *Groundwater,* v. 51(4): 539-549.**

2. **Mirecki, J.E., 2004. Water-quality changed during cycle test at aquifer storage recovery (ASR) systems of south Florida. USACE Engineer Research and Development Center (ERDC) technical report TR-0408, 32 p. plus appendices.**

3. **Mirecki, J.E., 2006. Geochemical models of water-quality changes during aquifer storage recovery (ASR) cycle tests, Phase I: Geochemical models using existing data. USACE ERDC technical report TR-06-8, 66 p.**

Groundwater

Arsenic Control During Aquifer Storage Recovery Cycle Tests in the Floridan Aquifer

by June E. Mirecki[1], Michael W. Bennett[2], and Marie C. López-Baláez[3]

Abstract

Implementation of aquifer storage recovery (ASR) for water resource management in Florida is impeded by arsenic mobilization. Arsenic, released by pyrite oxidation during the recharge phase, sometimes results in groundwater concentrations that exceed the 10 μg/L criterion defined in the Safe Drinking Water Act. ASR was proposed as a major storage component for the Comprehensive Everglades Restoration Plan (CERP), in which excess surface water is stored during the wet season, and then distributed during the dry season for ecosystem restoration. To evaluate ASR system performance for CERP goals, three cycle tests were conducted, with extensive water-quality monitoring in the Upper Floridan Aquifer (UFA) at the Kissimmee River ASR (KRASR) pilot system. During each cycle test, redox evolution from sub-oxic to sulfate-reducing conditions occurs in the UFA storage zone, as indicated by decreasing Fe^{2+}/H_2S mass ratios. Arsenic, released by pyrite oxidation during recharge, is sequestered during storage and recovery by co-precipitation with iron sulfide. Mineral saturation indices indicate that amorphous iron oxide (a sorption surface for arsenic) is stable only during oxic and sub-oxic conditions of the recharge phase, but iron sulfide (which co-precipitates arsenic) is stable during the sulfate-reducing conditions of the storage and recovery phases. Resultant arsenic concentrations in recovered water are below the 10 μg/L regulatory criterion during cycle tests 2 and 3. The arsenic sequestration process is appropriate for other ASR systems that recharge treated surface water into a sulfate-reducing aquifer.

Introduction

Aquifer storage recovery (ASR) systems are important components of water resource management plans for regions that have appropriate subsurface permeability (Bloetscher et al. 2005; Dillon et al. 2005; Pyne 2005; National Academy of Sciences 2008; Maliva and Missimer 2010). In Florida, permitted ASR systems store treated surface (potable) water (Reese 2002; Mirecki 2004; Reese and Alvarez-Zarikian 2007) or reclaimed water (Clinton 2007) in the Floridan Aquifer during the wet season, for distribution back to surface water in the dry season. ASR serves as the largest component of new storage in the Comprehensive Everglades Restoration Plan (CERP; National Academy of Sciences 2001, 2002). Regional implementation of CERP ASR could capture approximately 1.6 billion gal/d (6056 megaliters/d) of surface water currently lost to tide directly through the St. Lucie Canal and Caloosahatchee River.

Arsenic mobilization during ASR cycle testing presents a significant challenge to expanded use of potable and reclaimed water ASR in Florida. The source and mechanism of arsenic mobilization during cycle testing in carbonate aquifers are well known through controlled laboratory leaching and column experiments (Fischler and Arthur 2010; Onstott et al. 2011), mineralogical characterization of aquifer matrix (Price and Pichler 2006; Pichler et al. 2011), and modeling studies (Mirecki 2006; Jones

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and Pichler 2007) at Floridan Aquifer ASR systems, and also from extensive field studies at Australian reclaimed water ASR systems (Herczeg et al. 2004; Dillon et al. 2005, 2008; Vanderzalm et al. 2010, 2011). Arsenic is released during oxidation of pyrite by dissolved oxygen as recharge water flows through permeable zones in the carbonate aquifer (Jones and Pichler 2007; Fischler and Arthur 2010). Resultant arsenic concentrations measured in groundwater during ASR cycle testing can exceed the Federal and state maximum contaminant level (10 μg/L). Once released into the aquifer, arsenic can: (1) be sequestered by sorption to iron oxyhydroxide phases that are stable under oxic or sub-oxic aquifer redox conditions (Vanderzalm et al. 2011); or (2) be transported as the dissolved complex arsenate (AsV) or arsenite (AsIII) under oxic to sub-oxic, iron-poor conditions (e.g. Höhn et al. 2006); or (3) co-precipitate as an iron sulfide phase under sulfate-reducing, iron-rich conditions. The third condition has not been documented at any ASR system, and has important implications for arsenic attenuation and also regulatory compliance during ASR cycle tests in the Floridan Aquifer.

Characterization and controls on arsenic transport and fate during ASR cycle testing have been impeded in the United States by the lack of extensive sampling. Most ASR system investigations are performed by water utilities at potable water ASR systems (Florida Department of Environmental Protection [FDEP] 2007). Water-quality datasets at utility ASR systems usually are limited to analytes required for permit compliance rather than geochemical characterization. Consequently, little is known of the magnitude and duration of arsenic mobilization, and factors that control arsenic transport and fate in the Floridan Aquifer. Without better assurance that ASR systems can perform in regulatory compliance, the future of ASR implementation is uncertain.

The overall objective of CERP ASR pilot system operations is to evaluate ASR feasibility at representative locations in south Florida. ASR feasibility is demonstrated by several factors including: (1) percent recovery of recharged surface water; (2) regulatory compliance with all state and Federal water-quality criteria; and (3) cost-effective subsurface storage. At the Kissimmee River ASR (KRASR) pilot system, three cycle tests have been completed with a groundwater monitoring program objective to evaluate water-quality changes.

Arsenic mobilization and subsequent attenuation are shown during three successive cycle tests at KRASR. In this report, the geochemical controls on arsenic transport and fate during ASR cycle testing in the Upper Floridan Aquifer (UFA) are defined. Our hypothesis is that arsenic, released by oxidation of pyrite during early portions of the recharge phase, is subsequently attenuated by co-precipitation in a stable iron sulfide phase during late recharge, storage, and recovery. The native UFA sulfate-reducing redox condition is disrupted only temporarily by dissolved oxygen introduced during recharge. Addition of dissolved (probably colloidal) iron and organic carbon in recharge (surface) water, mixing with sulfate-rich groundwater, provides abundant electron acceptors to re-establish microbe-mediated sulfate reduction, iron sulfide precipitation, and consequently arsenic attenuation. The result is that arsenic concentrations are nearly always below10 μg/L in all well samples collected weekly during the storage and recovery phases of successive cycles at KRASR.

Hydrogeologic Setting

At KRASR, the artesian UFA occurs within a thick sequence of interlayered marine calcareous and dolomitic limestones of Eocene and Oligocene age (Figure 1), and serves as the storage zone for ASR cycle tests. The UFA is confined by the overlying Intermediate Confining Unit, which consists of approximately 400 feet (122 m) of Hawthorn Group interlayered clays, silts, and fine sands (Scott 1988). Lower confinement of the UFA is provided by the Middle Confining Unit, which consists of 400 to 500 feet (122 to 152 m) of dolomitic limestone, dolomite, and dolostone (Reese and Richardson 2008). Hydrostratigraphic and lithostratigraphic characteristics are defined using geophysical logs, lithologic descriptions, and limited coring during construction of the ASR and monitoring wells (CH_2MHill 2004; Golder Associates 2007; Entrix 2010).

Water is stored in the UFA at depths between −543 and −856 feet (−166 and −261 meters, m) below the National Geodetic Vertical Datum of 1929 (NGVD29). However, permeability is not uniform with depth in the storage zone. Water will flow preferentially through zones of higher permeability that develop at or near unconformable formation contacts, and to a lesser extent, bedding planes. Permeability in the UFA is interpreted from geophysical logs in boreholes for the ASR and all storage zone monitor wells (SZMWs), and aquifer performance testing during construction of the ASR well. Static and dynamic flow logs were corrected for variations in borehole diameter from caliper logs, and interpreted to quantify the percent contribution of individual zones to total flow in the borehole that became the ASR well. Geophysical flow log interpretations indicate that 80% of flow occurs at the top of the storage zone, at depths between −546 and −609 feet (−166 and −186 m) NGVD29 (Figure 1). This preferential flow zone is consistent with an unconformable contact between the Arcadia Formation (lower part of the Hawthorn Group) sediments and the Ocala Limestone, and has been observed at a similar depth in all KRASR SZMWs, and commonly in UFA boreholes surrounding Lake Okeechobee (Reese and Richardson 2008). A smaller component of flow (12%) occurs below the base of the storage zone between −880 and −930 feet NGVD29. This preferential flow zone may occur near the formation contact between the Ocala Limestone and Avon Park Formation. An aquifer performance test of the entire storage interval at the ASR borehole resulted in a transmissivity value of 36,765 ft^2/d (CH_2MHill 2004).

A chloride-based conservative mixing model confirms extensive transport of recharge water along this

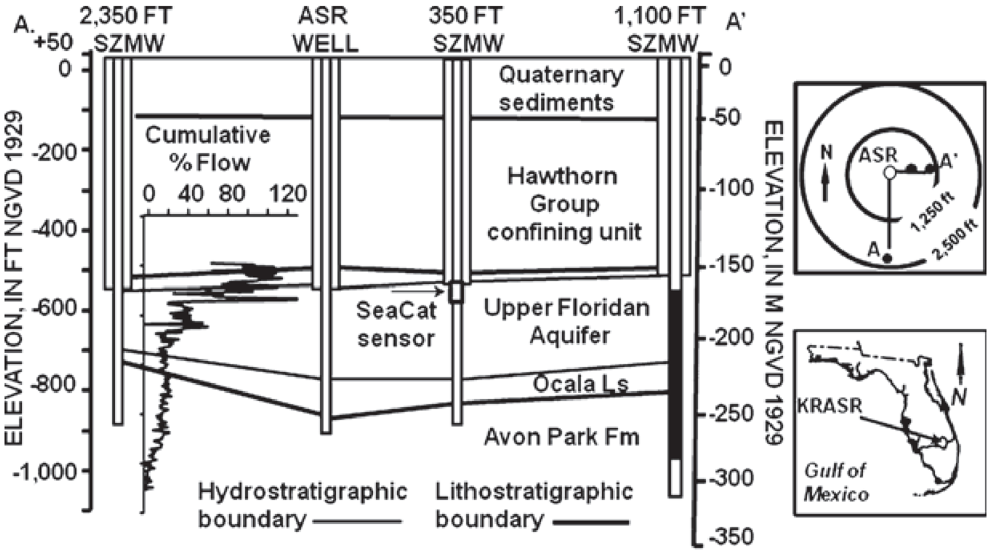

Figure 1. Hydrogeologic cross-section and plan view of the Kissimmee River ASR system. SZMW, storage zone monitor well; T, transmissivity. The 1100 feet SZMW is a dual zone well, but only upper zone sample data are presented. Horizontal axis in cross-section is not to scale. All distances are relative to the ASR well. Length conversions are: 350 feet (107 m); 1100 feet (335 m); 2350 feet (716 m); 4200 feet (1280 m).

upper preferential flow zone to the 1100 feet SZMW (Figure 2). Mixing fractions were calculated following the method of Herczeg et al. (2004) to show how the percentage of recharge water component changes throughout cycles 2 and 3 (Table S1, Supporting Information). After 1 or 2 months of recharge during cycles 2 and 3 (respectively), samples from the 1100 feet (335 m) SZMW consist of 90% or greater recharge water. This monitor well has a short open-interval (−544 to −583 feet; 166 to 178 m NGVD29) that intersects the preferential flow zone of the UFA. Interpretations of geophysical flow logs and the conservative mixing model support a conceptual hydrogeologic model in which most of the groundwater flow occurs in the a preferential flow zone of the uppermost UFA across the ASR wellfield.

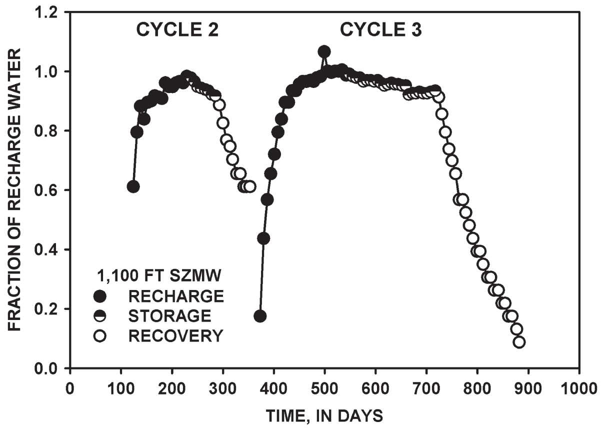

Figure 2. Conservative chloride mixing model for cycle tests 2 and 3 at the 1100 feet SZMW. Data are shown in Table S1.

The Kissimmee River ASR System and Cycle Testing History

The KRASR system is located on the eastern bank of the Kissimmee River near its confluence with Lake Okeechobee, Florida (Figure 1). The ASR system was designed for minimal pre-treatment of Kissimmee River source water prior to recharge into the UFA storage zone. Pre-treatment consists of pressurized media filtration and ultraviolet disinfection at a recharge rate of 5 million gal/d (MGD; 18.9 megaliters/d, MLD).

Groundwater is recovered at a rate of 5 MGD, with diversion of the first 0.3 million gallons (MG; 1.1 megaliters, ML) of turbid water to on-site storage ponds. When turbidity, pH, and specific conductance criteria are achieved, recovered water is re-oxygenated over a cascade aerator and returned to the Kissimmee River. More detailed information about system design and operation are found at US Army Corps of Engineers (USACE 2004, 2012).

Each ASR cycle test consists of recharge, storage, and recovery phases. Three cycle tests were completed at KRASR between 2009 and 2011 (Table 1). Each successive cycle test increased in duration and volume stored. Recovery exceeded 100% of the recharged volume during cycle 1 so that aquifer arsenic concentrations were returned to initial values (below 10 μg/L) prior to cycle 2. Interpretations are based primarily on data acquired during cycles 2 and 3 because these cycles represent intended ASR system operations.

Data Collection Effort

A single ASR well is surrounded by four SZMWs (Figure 1), designated by their lateral distances from the

Table 1
Recharge, Storage, and Recovery Pumping Rate, Durations, and Volumes During KRASR Cycle Tests

Phase	Start Date	End Date	No. of Days	Avg. Pumping Rate, in MGD (MLD)	Volume, in MG (ML)		Percent Volume Recovered
					Recharge	Recovery	
Cycle 1							
Recharge	January 12, 2009	February 9, 2009	28	4.7 (17.8)	128.5 (486.4)	—	—
Storage	February 9, 2009	March 9, 2009	28	—	—	—	—
Recovery	March 9, 2009	April 17, 2009	39	4.8 (18.2)	—	183.8 (695.7)	143%
Cycle 2							
Recharge	May 11, 2009	August 28, 2009	109	3.8 (14.4)	334.23 (1.27)	—	—
Storage	August 28, 2009	October 28, 2009	61	—	—	—	—
Recovery	October 28, 2009	January 2, 2010	66	4.0 (15.1)	—	331.5 (1255)	99%
Cycle 3							
Recharge	January 19, 2010	July 9, 2010	171	4.9 (18.5)	793.1 (3002)	—	—
Storage	July 9, 2010	January 4, 2011	178	—	—	—	—
Recovery	January 4, 2011	June 17, 2011	164	4.98 (18.9)	—	805.5 (3049)	102%

ASR well: 350 feet (107 m), 1100 feet (335 m), 2350 feet (716 m), and 4200 feet (1,280 m). Each monitor well has an open interval identical to that of the ASR well, between −543 and −856 feet (−166 and −261 m) NGVD29. Two SZMWs located farthest from the ASR well were constructed during cycle 2, so data were obtained at these distal wells only during cycle 3. All wells were sampled weekly at the wellhead for field parameters, major and trace inorganic constituents, nutrients, and microbes for the entire testing duration, using standard methods for groundwater sampling, laboratory analyses, and quality control (FDEP 2008). All analyses were performed at laboratories certified by the National Environmental Laboratory Accreditation Program. In addition to wellhead samples, the 350 feet SZMW is instrumented with a SeaCat 19plusV2Profiler, (Sea-Bird Electronics Inc., Bellevue, Washington), which is suspended downhole in the UFA preferential flow zone at −588 feet (−186 m) NGVD29. The SeaCat 19plusV2Profiler provided hourly in-situ measurements of pH, temperature, specific conductance, dissolved oxygen (DO), oxidation–reduction potential (ORP), and pressure through each cycle test. Because DO is the primary electron acceptor during pyrite oxidation, in-situ DO measurements at a location 350 feet away from the ASR well are particularly important to quantify proximal redox conditions in the storage zone. The SeaCat Profiler measures DO using a Clark polarographic membrane with a gold cathode, which is more stable and is not affected by dissolved hydrogen sulfide compared to sensors with a silver cathode (Sea-Bird Electronics Inc. 2012). The SeaCat Profiler was installed on January 25, 2009 (cycle 1 recharge), and checked during monthly data downloads. The DO sensor began to fail sometime during August 2009, so Cycle 2 DO values are not presented. Power supply issues caused interruption to the continuous record from this probe between 30 March and 22 August 2010. The SeaCat Profiler was recalibrated at the manufacturer between 13 February and 30 March 2010 (cycle 2) and between 1 June and 9 July 2011 (cycle 3).

Source Water and Native Floridan Aquifer Water Quality

The Kissimmee River is the source of recharge water, and water-quality data reflect dry and wet season conditions through the cycle tests (Table 2). Recharge water quality is characterized using samples from the ASR wellhead during the recharge phase of all cycle tests. Recharge water is oxic, and has neutral pH, low carbonate alkalinity, low total dissolved solids (TDS) concentrations, and relatively high concentrations of total and dissolved organic carbon, iron, phosphorus, and color; and low to non-detectable concentrations of nitrate and manganese (Table 2).

The native UFA at this location is relatively fresh as indicated by low chloride and TDS concentrations and specific conductance values (Table 2). Native UFA groundwater at KRASR is characterized as sulfate-reducing and has slightly alkaline pH, moderate carbonate alkalinity and sulfate concentrations, and low concentrations of metals including iron. Arsenic concentrations generally are less than 3 μg/L.

Geochemical Calculations

Geochemical characterization was performed using public domain codes developed by the U.S. Geological Survey. The aquifer redox condition was evaluated using the Redox Processes Workbook by Jurgens et al. (2009). Mineral saturation indices and charge balance errors for each complete water quality analysis was performed using PHREEQC, version 2.17 with the Wateq4f database (Parkhurst and Appelo 1999), with data entry facilitated with the Excel interface NetpathXL (Parkhurst and Charlton 2008). The choice of controlling redox couple in PHREEQC will determine mineral stabilities. In each water sample, if DO concentration is greater than 0.05 mg/L (the field detection limit), the dissolved oxygen (O^{-2}/O^0) couple is used; if DO is below

Table 2
Recharge Water Quality and Native Floridan Aquifer Water Quality

		Recharge Water Quality				Native UFA Water Quality at KRASR			
Constituent or Parameter	**Unit**	**Mean**	**Std Dev**	**Median**	***N***	**ASR WELL**	**1100 feet SZMW**	**2350 feet SZMW**	**4200 feet SZMW**
Temperature	°C	25.3	6.0	28.3	46	25.5	25.2	24.3	24.9
Specific conductance	µS/cm	227	46	204	46	1347	1300	983	1404
pH	std. units	6.7	0.4	6.6	46	7.80	7.97	7.95	8.05
Oxidation–reduction potential	mV	130	59	114	46	−283	−179	−430	−249
Dissolved oxygen	mg/L	4.5	2.5	3.5	46	0.3	0.02	0.52	0.82
Color	PCU	91	32	90	44	5	10	—	—
Calcium	mg/L	19.2	4.9	17.0	44	51.5	47	28	27
Magnesium	mg/L	4.8	0.9	4.7	44	38.7	33	30	33
Sodium	mg/L	16.1	3.8	14.0	45	152	150	59	110
Potassium	mg/L	4.0	0.6	4.1	44	8.3	7.2	4.7	8.3
Sulfate	mg/L	15.6	6.5	14.0	45	198	150	170	200
Sulfide	mg/L	0.1	0.3	0.01	44	0.8	<1.0	1.1	1.2
Chloride	mg/L	31.1	7.5	28.0	45	242	260	140	160
Total alkalinity as $CaCO_3$	mg/L	50	51	36	45	91	84	80	87
Dissolved organic carbon	mg/L	15.3	1.5	15.5	14	—	1.2	—	—
Total organic carbon	mg/L	16.3	1.0	17.0	13	<1.0	1.3	—	—
Arsenic	µg/L	0.9	0.5	0.8	45	<2.6	1.6	0.81	1.2
Iron	µg/L	226	68	230	45	28	65	23	<2.4
Manganese	µg/L	4.5	2.8	3.6	45	<3.8	4.3	1.1	0.57
Nitrate	mg/L	0.142	0.101	0.100	29	0.100	<0.025	<0.003	<0.003
Phosphorus	µg/L	64	32	54	43	0.010	<0.008	—	—

Note: Concentrations reported as "less than" are below the method detection limit. Recharge water data are measured at the ASR wellhead. Native UFA data are from single samples obtained prior to cycle testing. *N* is number of samples.

detection, the sulfur (S^{-2}/S^{+6}) couple is used for Eh calculations.

Results

Redox Environment of the Native Floridan Aquifer System

The sulfate-reducing redox environment is the native condition of the KRASR storage zone as interpreted from groundwater redox couple concentrations. Chapelle et al. (2009) proposed geochemical criteria to distinguish iron-reducing from sulfate-reducing conditions in groundwater using the Fe^{2+}/H_2S mass ratio, when dissolved oxygen, nitrate, and manganese are absent. The native redox environment in the UFA storage zone at KRASR is sulfate-reducing on the following bases: (1) that low to non-detectable concentrations of dissolved oxygen, nitrate, and manganese species do not contribute significantly to redox condition; and (2) that the Fe^{2+}/H_2S mass ratio in native UFA samples collected at the KRASR system is <0.3 (Table 3).

Redox Evolution During ASR Cycle Tests

Redox evolution in the UFA during cycle testing is defined in space and time. The spatial component is defined by reactions along the flowpath from the point of recharge (ASR well) to the 350 feet SZMW and the 1100 feet SZMW. No water-quality changes were detected at distal SZMWs (2350 and 4200 feet; Tables S3 and S4) during cycles 2 and 3, so data from these SZMWs serve as background (Table 3). The temporal component is defined through time-series presentation of groundwater data at a single monitor well through recharge, storage, and recovery phases during cycle tests 2 and 3. Interpretations will show redox evolution in both space and time.

Redox evolution in the UFA during cycle tests 2 and 3 is interpreted similarly to that of the native UFA, using (1) Fe^{2+}/H_2S mass ratios from ASR well and SZMW samples (Figure 3); and (2) wellhead and SeaCat Profiler measurements of DO and ORP at depth in the 350 feet SZMW (Figure 4).

The recharge phase of an ASR cycle test introduces DO, organic carbon, and ferric iron into the UFA, which shows low native concentrations of these solutes (Table 2). Source water (Kissimmee River, as measured during recharge at the ASR well) concentrations of redox-sensitive species vary seasonally: DO ranges from 1.6 to 8.8 mg/L; organic carbon ranges from 12 to 18 mg/L; and total iron ranges from 0.060 to 0.360 mg/L (Table 2; Tables S2 through S4). Ferric iron probably is complexed to organic carbon in source water rather than as a particulate phase, as recharge water is highly colored and shows total suspended solids concentrations typically less than the detection limit at 5.0 mg/L. ASR well clogging

Table 3
Characterization of Sulfate-Reducing Redox Environment in the Native UFA (mg/L)

Well	ORP	Nitrate	Manganese	Iron	Sulfate	Sulfide	Fe^{2+}/H$_2$S	Arsenic	Location
Chapelle et al. (2009) criteria[1]	—	<0.5	<0.05	≥0.1	>0.50	—	<0.30	0.010[2]	—
ASR Well (May 5, 2004)	−283	0.10	<0.0038	0.028	200	0.8	0.035	<0.026	KRASR
2350 feet SZMW (January 6, 2010)	−430	<0.0030	0.0011	0.028	170	1.1	0.025	0.0008	KRASR
4200 feet SZMW (January 6, 2010)	−249	<0.0030	<0.001	0.024	200	1.2	0.020	0.0012	KRASR
OKF-101 (November 18, 2010)[3]	−146	<0.015	0.0025	0.060	230	1.8	0.033	0.0047	5 mi. east of KRASR
HIF-42 (April 4, 2008)[3]	—	0.11	0.0024	0.036	200	0.38	0.095	<0.005	5 mi. north of KRASR

[1] Criterion for sulfate-reducing redox environment. All values are in mg/L.
[2] Arsenic criterion is the Maximum Contaminant Level from the Safe Drinking Water Act.
[3] Nearby background UFA monitor wells of the South Florida Water Management District.

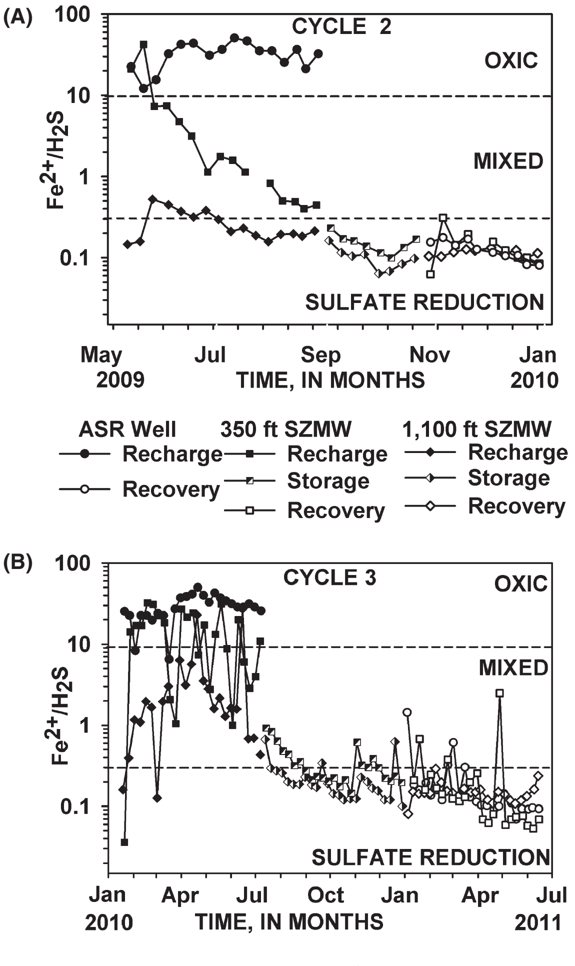

Figure 3. Redox evolution of the ASR storage zone (upper FAS) during cycle tests 2(A) and 3(B) as shown by Fe^{2+}/H$_2$S values as indicators of redox environment. SZMW, storage zone monitor well. Data are shown in Tables S3 and S4.

from mineral precipitation was not observed during three cycle tests. Recharge water also dilutes and displaces native UFA sulfate concentrations (Table 2).

During cycles 2 and 3 recharge, SZMW samples show Fe^{2+}/H$_2$S values greater than 0.3 (Figure 3A and 3B) indicating that the aquifer redox environment is sub-oxic, and is characterized by both ferric iron- and sulfate-reduction reactions. These reactions likely are coupled to oxidation of organic carbon by native and recharge water microbes (Vanderzalm et al. 2006). Native sulfate-reducing conditions in the storage zone are perturbed temporarily, resulting from iron, organic carbon, and DO transport through a sulfate-reducing UFA redox environment. Farther from the ASR well at both 350 and 1100 feet SZMWs, Fe^{2+}/H$_2$S values decrease, indicating that mixed ferric iron- and sulfate-reduction redox couples dominate as DO is depleted along the flowpath.

SeaCat Profiler data and wellhead sample data from the 350 feet SZMW show redox evolution in the UFA at a proximal position away from the ASR well (Figure 4A and 4B). In particular, these data quantify DO transport and fate during recharge because the SeaCat Profiler is deployed directly in the upper preferential flow zone of the UFA at −588 feet NGVD29. Pyrite oxidation will continue as long, and as far away from the ASR well, as DO persists. As recharge water flows away from the ASR well, DO concentrations diminish from a range of 2 to 8 mg/L at the ASR wellhead, to 0.01 to 1.5 mg/L at the 350 feet SZMW, and <0.25 mg/L at the 1100 feet SZMW (Tables S3 and S4). DO and positive ORP values are detected in 350 feet SZMW wellhead samples approximately 2 weeks after the onset of recharge in cycles 1 and 3, resulting in an apparent horizontal flow velocity of 25 ft/d to the east. During later recharge, DO concentrations and ORP values in all SZMW wellhead samples decrease to <0.06 mg/L and <-100 mV respectively. Iron and organic carbon concentrations also decline along the flowpath during recharge (Tables S3 and S4).

SeaCat Profiler and wellhead sample data obtained during cycle 1 at the 350 feet SZMW show that

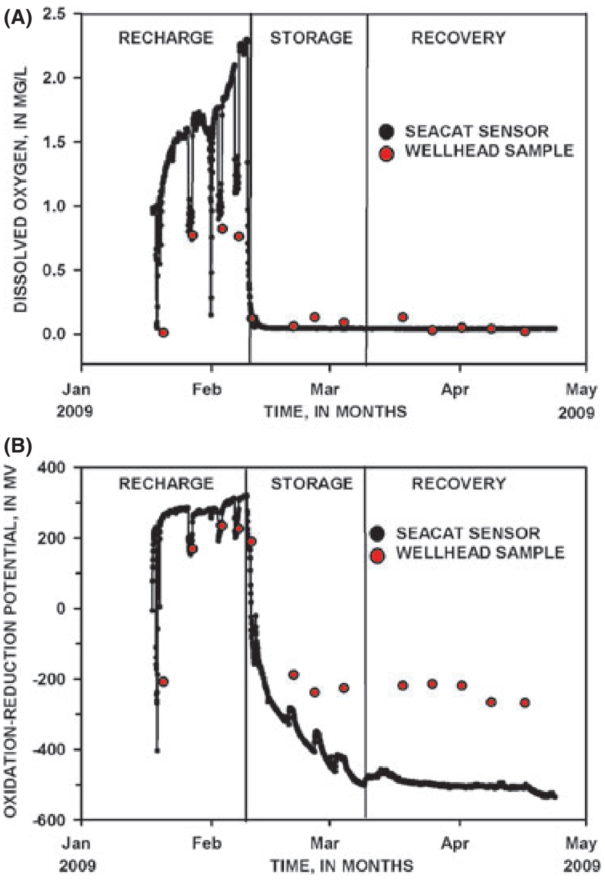

Figure 4. Dissolved oxygen (A) and ORP values (B) measured during cycle test 1 by the SeaCat Profiler suspended in the 350 feet SZMW at −588 feet (−186 m) NGVD29.

perturbation of the aquifer redox environment during recharge is temporary (Figure 4). During recharge, DO is detected in-situ at higher concentrations (∼1.5 to 2.5 mg/L) compared to wellhead samples (0.01 to 1.5 mg/L). Upwelling of deeper, low DO water during well purging and sampling results in lower wellhead DO concentrations (Figure 4). Similarly, SeaCat Profiler ORP values also are slightly more positive than wellhead values. SeaCat Profiler data clearly show the rapid decay of DO at a single location once recharge ends. DO declines from an average concentration of 1.6 mg/L ($n = 384$ readings) during cycle 1 recharge, to below detection (0.05 mg/L) within 5 d. A conservative half-life ($t^{1/2}$) calculated for DO reduction is 25 h.

A few weeks after initiating cycles 2 and 3 recharge, redox conditions in the storage zone evolve from sub-oxic to mixed iron- and sulfate-reducing redox conditions (Figure 3). Fe^{2+}/H$_2$S values continue to decline below 0.3 at all SZMWs during late recharge and storage of cycles 2 and 3. The native UFA is iron-poor in this area (<24 µg/L; see 2350 and 4200 feet SZMW "background" data in Table S4), so ferric iron reduction does not contribute significantly to native UFA redox equilibria. Introduction of iron-rich recharge water into the sulfate-reducing UFA allows a new redox couple to react in the storage zone.

During storage and recovery, DO is depleted, and the aquifer redox environment continues to evolve such that sulfate reduction becomes the dominant redox reaction. Fe^{2+}/H$_2$S values decline below 0.3 in all SZMWs, and equilibrate during the first two months of cycles 2 and 3 storage (Figure 3). SeaCat Profiler ORP values are very negative (−400 to −500 mV; Figure 4), more so than wellhead samples (−280 to −300 mV). This disparity may result from a pressure effect on dissolved hydrogen gas equilibrium.

Arsenic Trends During ASR Cycle Tests

Arsenic concentration trends through three cycle tests show several common characteristics when data from all wellhead samples are compared (Figure 5). Maximum arsenic concentrations were measured during cycle 1 in all wells, when the initial exposure of the aquifer to DO occurred. Subsequent cycles show arsenic concentration maxima occurring in SZMW wellhead samples during recharge or early storage, then declining through late storage and recovery. This pattern reflects reactive transport (during recharge) and reactions (during storage) of iron and arsenic as the aquifer redox environment evolves from a sub-oxic to sulfate-reducing condition. Arsenic concentration maxima, and concentrations that exceed the 10 µg/L regulatory criterion, coincide with mixed ferric iron- and sulfate-reduction redox environment in the UFA (Figure 5 and Tables S3 and S4). The duration that arsenic exceeds the MCL in the aquifer is approximately 150 d (cycle 2: 3-month recharge, 241-d cycle), and 290 d (cycle 3: 6-month recharge, 513-d cycle), and these exceedances only occur during recharge and early storage phases.

Arsenic concentration trends observed during the static conditions of storage result primarily from geochemical reactions, rather than reactive transport. Declining arsenic concentrations measured at the 350 and 1100 feet SZMWs during cycle 3 storage (Figure 5) suggest that in-situ geochemical reactions are sequestering arsenic in a solid phase, coincident with sulfate-reducing conditions. During cycle tests 2 and 3 storage, arsenic concentrations declined below the 10 µg/L regulatory criterion, prior to the onset of the recovery phase. Consequently, with the exception of one sample in cycle 3 (Figure 5A), all recovered water is in compliance with the Safe Drinking Water Act arsenic criterion. Arsenic exceedances are temporary in the UFA, occurring only during late recharge and storage.

The chloride-based conservative mixing model (Figure 2) supports the geochemical sequestration interpretation. There is little to no change in the fraction of recharge water (>90%) at the 1100 feet SZMW through cycle test 2 and 3 storage, concurrent with declining arsenic concentration. Under static (non-pumping) conditions of storage, groundwater flow in the UFA does not cause significant mixing of native and recharge water over the durations of cycle tests 2 and 3 (at least in proximal positions in the wellfield), so that concentration trends are not affected by advective transport.

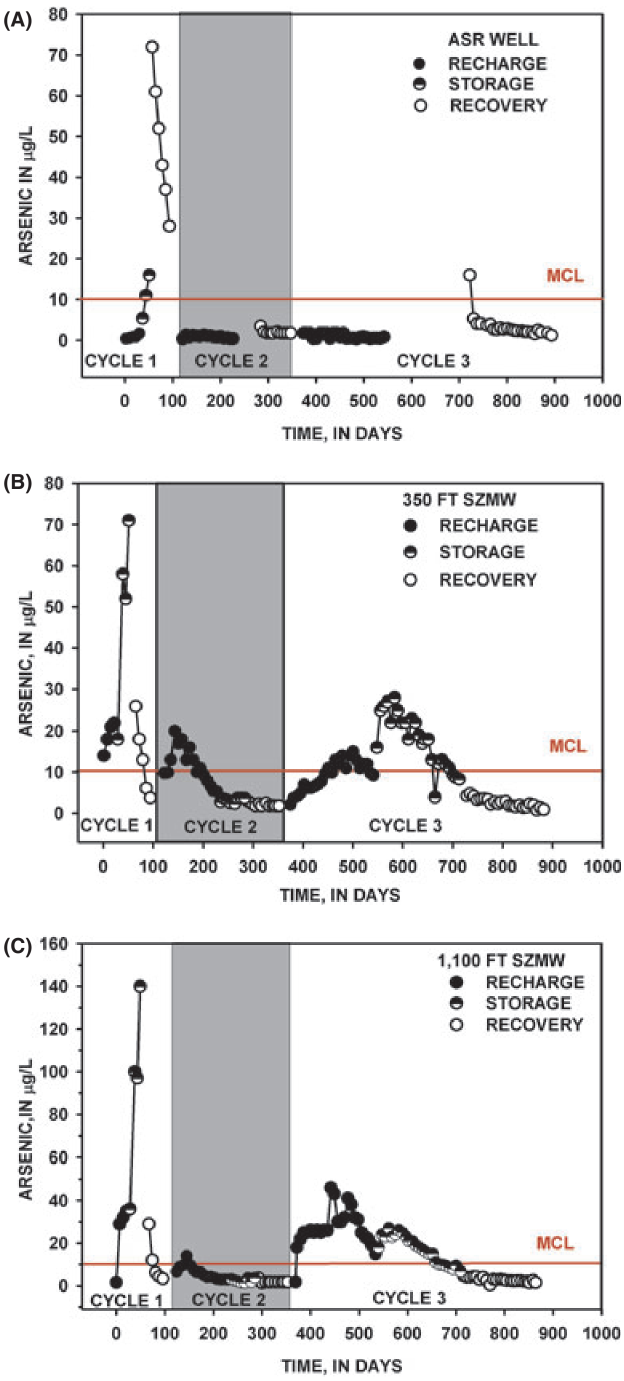

Figure 5. **Arsenic concentrations measured in wellhead samples during cycle tests 1 through 3 at the ASR well (A), the 350 feet SZMW (B), and the 1100 feet SZMW (C).**

Discussion

Iron Mineral Stabilities During ASR Cycle Tests

Mineral saturation indices (SI) were calculated for each wellhead sample collected during cycle tests 2 and 3. Because both cycle tests show identical trends, only SI values from cycle 3 are presented (Figure 6). Two mineral phases are considered: amorphous iron oxyhydroxide ($FeOH_3(a)$), which is stable under oxic and sub-oxic conditions; and amorphous iron sulfide (FeS), which is the initial iron sulfide phase to precipitation under sulfate-reducing conditions (Schoonen 2004). Mineral stabilities are interpreted at two locations in the storage zone away from the ASR well: the 1100 feet SZMW that is affected by recharge, and the 2350 feet SZMW that represents native UFA conditions. Saturation indices do not change throughout the cycle at the 2350 feet SZMW, confirming that recharge water has not been transported to this distal location in the UFA. Calculated SI values are tabulated in Table S5 for all samples.

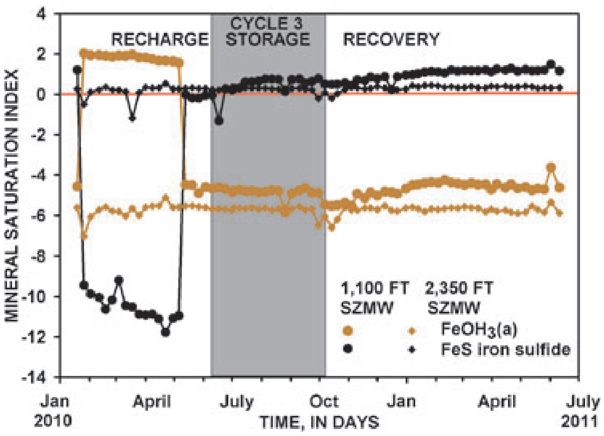

Figure 6. **Mineral saturation indices (SIs) calculated from wellhead sample data at the 1100 and 2350 feet (background) storage zone monitor wells (SZWMs) during cycle test 3. Positive SIs indicate that the mineral will precipitate or is stable in contact with groundwater. Negative SIs indicate that the mineral will dissolve or is unstable in contact with groundwater. Data are shown in Table S5.**

The recharge portion of a cycle test shows the greatest change in native mineral stabilities (Figure 6). In the presence of DO in the storage zone, amorphous iron oxyhydroxide is stable as a solid as shown by positive SI values. Iron sulfide is not stable, as shown by negative SI values. During late storage and recovery, the UFA redox environment shifts from sub-oxic, to mixed iron- and sulfate-reduction, and ultimately pure sulfate-reducing conditions. Amorphous iron oxyhydroxide is lost through reductive dissolution under sulfate-reducing conditions. Negative SI for values for iron oxyhydroxide appear late in recharge and continue through the end of the cycle. Simultaneously, amorphous iron sulfide SI values become positive, indicating stability through the end of the cycle, as native sulfate-reducing redox conditions are re-established.

Arsenic Sequestration During KRASR Cycle Tests

Iron mineral stabilities control the appearance, transport, and fate of arsenic in an aquifer. The testable hypothesis for arsenic sequestration during KRASR cycle tests is: if geochemical concentrations and redox conditions that favor precipitation of a stable iron sulfide phase are established during storage and recovery, then dissolved arsenic will be sequestered in the iron sulfide phases. Arsenic sequestration in iron sulfide phase is preferable to that of iron oxyhydroxide, because the former more closely represents native UFA mineralogy in which arsenic occurs at concentrations generally <3 μg/L.

During recharge, iron-rich recharge water plus iron released during pyrite oxidation can precipitate as amorphous iron oxyhydroxide ($Fe(OH)_3(a)$). Iron oxyhydroxide is stable under oxic to sub-oxic redox conditions that characterize the storage zone during early recharge. Dissolved arsenic is released during pyrite oxidation, and subsequently can be is sequestered by co-precipitation, sorption, or complexation to the iron oxyhydroxide surface (Waychunas et al. 1993; Dixit and Hering 2003). Unfortunately, arsenic sequestration by iron oxyhydroxide surfaces is only temporary, occurring during the oxic redox conditions of recharge of each cycle test.

During late recharge and early storage, the storage zone evolves to sub-oxic and mixed ferric iron- and sulfate-reducing conditions. Iron oxyhydroxide undergoes reductive dissolution by dissolved sulfide, and sorbed arsenic is released again into groundwater (O'Day et al. 2004; Poulton et al. 2004; Onstott et al. 2011). Ferrous iron (Fe^{2+}) is released into groundwater where it is transported during late recharge along with arsenic. Thus, in sub-oxic aquifer redox environments, or in the presence of nitrate (a competing electron acceptor with ferric iron), arsenic will remain in solution. A sequence of arsenic sequestration and release under sub-oxic redox conditions (in the presence of nitrate) was demonstrated during cycle tests at the Bolivar reclaimed water ASR system (Vanderzalm et al. 2011).

During storage, sulfate-reducing conditions are re-established in the UFA storage zone, which favors the stability of iron sulfide minerals. Sufficient dissolved iron, sulfide, and the absence of nitrate and manganese are required for iron sulfide precipitation to proceed (Wilkin and Barnes 1997; Butler and Rickard 2000). Concomitant co-precipitation of arsenic in the new iron sulfide phase has been documented in other aquifers (Rittle et al. 1995; Kirk et al. 2004; Root et al. 2009), but has not been documented at any other ASR system to date.

At KRASR, arsenic sequestration is demonstrated by the synchronous evolution of sulfate-reducing redox conditions in the storage zone, accompanied by decreasing arsenic concentrations in all SZMWs during storage and recovery of cycle tests 2 and 3. As each cycle test proceeds from recharge to recovery, arsenic concentrations and Fe^{2+}/H_2S mass ratios decline. The simultaneous decline in these geochemical characteristics in all SZMW samples supports the arsenic sequestration hypothesis at KRASR wellfield.

Conclusions

Arsenic mobilization at Florida ASR systems has slowed implementation of subsurface storage because water managers are hesitant to invest in facilities that may not operate in regulatory compliance. Extensive water-quality monitoring at the Kissimmee River ASR system during three cycle tests shows that arsenic mobilization is a temporary process. Arsenic is transported primarily when the aquifer redox environment is characterized by sub-oxic or mixed iron- and sulfate-reducing conditions during recharge, concomitant with Fe^{2+}/H_2S values >0.3. Arsenic concentrations can exceed the Safe Drinking Water Act regulatory standard (10 μg/L) under these aquifer redox conditions. As a cycle test proceeds through storage and recovery phases, the redox environment of the UFA is re-established as the native, sulfate-reducing condition ($Fe^{2+}/H_2S < 0.3$) that favors arsenic sequestration in iron sulfide solids. Amorphous iron sulfide mineral stability is indicated by positive mineral saturation indices in SZMWs during storage and recovery. Co-precipitation of arsenic with iron sulfide in recovered water during cycles 2 and 3 results in arsenic concentrations that are in compliance with the Safe Drinking Water Act regulatory standard (<10 μg/L).

The mechanism for arsenic sequestration defined here is appropriate for ASR systems having the following characteristics: (1) recharge water that has sufficient iron and organic carbon to stimulate aquifer microbes; (2) recharge water that has negligible concentrations of other electron acceptors (manganese and nitrate) that inhibit sulfate reduction; and (3) a native sulfate-reducing aquifer redox environment.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1.	Mixing Model
Table S2.	Cycle Test 1
Table S3.	Cycle Test 2
Table S4.	Cycle Test 3
Table S5.	Mineral Saturation Indices Cycle Test 3

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Water-Quality Changes During Cycle Tests at Aquifer Storage Recovery (ASR) Systems of South Florida

June E. Mirecki

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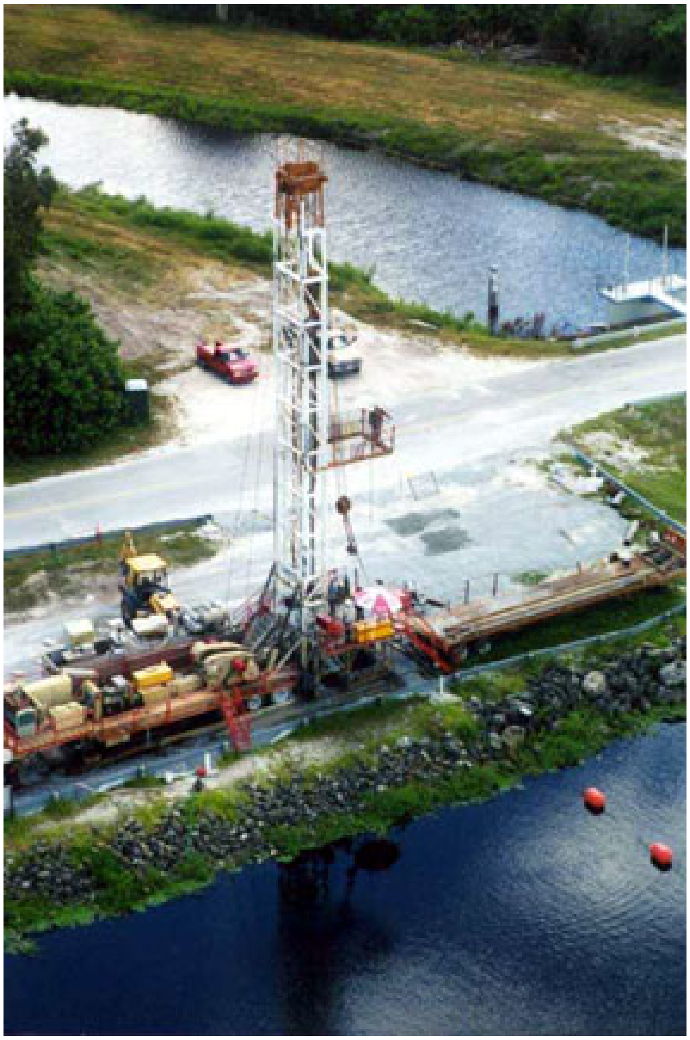

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Water-Quality Changes During Cycle Tests at Aquifer Storage Recovery (ASR) Systems of South Florida

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Final report

Prepared for U.S. Army Engineer District, Jacksonville
Jacksonville, FL 32207

ABSTRACT: Water-quality changes were interpreted from existing cycle test data obtained from 11 treated surface-water Aquifer Storage Recovery (ASR) systems located in South Florida. Six ASR systems are located along the lower east coast (Palm Beach and Broward Counties), and five ASR systems are located in Lee and Collier Counties. These diverse data sets were the basis for interpretations of water-quality changes during ASR cycles in different regions. These data sets were interpreted to provide guidance for cycle test performance at Comprehensive Everglades Restoration Plan (CERP) ASR pilot sites. ASR and monitoring well data were interpreted for trends in water-quality changes. Estimates of reaction rates or half-lives are based only on data obtained from monitoring wells during storage. Analytes that are reactants or products in major geochemical reactions are: dissolved oxygen, nitrate and ammonia, sulfate and hydrogen sulfide, gross alpha radioactivity and radium isotopes, and total trihalomethanes. Concentrations of these solutes in recovered water samples from recharge/recovery wells were compared to state and Federal water quality regulations to identify regulatory exceedences. Concentrations of arsenic and gross alpha in recovered water sometimes exceeded regulatory criteria at ASR sites in Southwest Florida.

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COVER PHOTOGRAPH: Aerial view of test well operations at the Moore Haven Aquifer Storage Recovery pilot site, September 2002. Cover photo by Tom Teets, Sough Florida Water Management District.

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Preface

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

This report was reviewed by Dr. Stacy Howington, Coastal and Hydraulics Laboratory (CHL), ERDC, Mr. Danny Harrelson, Geotechnical and Structures Laboratory (GSL), ERDC, Drs. Manjiang Zhang and Lisa Gued (CESAJ-EN-GG, USAED, Jacksonville), Mr. Pete Kwiatkowski (South Florida Water Management District), and Mr. Mark McNeal (CH2M HILL, Inc., Gainesville, FL). The study was conducted under the direct supervision of Dr. Richard E. Price, Chief, EPED, EL, ERDC, Dr. Edwin A. Theriot, Director, and Dr. Elizabeth Fleming, Acting Director, EL, ERDC.

The author gratefully acknowledges the following colleagues for their time, insight, and willingness to provide data for the Aquifer Storage Recovery (ASR) systems described in this report: Mr. Peter Mazzella, City of Boynton Beach ASR system; Drs. Thomas Missimer and Kirk Martin, CDM/Missimer International, Fort Myers; Mr. John Cargill, C.E. Fiveash Regional Water Treatment Plant, Fort Lauderdale; Messrs. Bell Beddow, Mark McNeal, and Steve Gong, CH2M HILL, Inc.; Mr. n'Detenga n'Gurumo, Delray Beach Environmental Services Laboratory; Mr. Doug Stryjek, Delray Beach Water Treatment Plant; Messrs. Richard Orth, Joe Haberfield, Joe May, and Len Fiskin, Florida Department of Environmental Protection; Messrs. Paul Mattaush, Peter Schalt, and Howard Brogdon, Manatee Road ASR system, Collier County; Mr. Clint Oakley, Miami – Dade Water and Sewer Department; Mr. Ronald Reese, U.S. Geological Survey, Miami; and Messrs. Lloyd Horvath, Dan Acquaviva, and Mike Weinberg, Water Resource Solutions, Inc., Coral Springs.

COL James R. Rowan, EN, was Commander and Executive Director of ERDC, and Dr. James R. Houston was Director.

Summary

Water-quality changes were interpreted from existing cycle test data obtained from 11 treated surface-water Aquifer Storage Recovery (ASR) systems located in South Florida. Six ASR systems are located along the lower east coast (Palm Beach and Broward Counties), and five ASR systems are located in Lee and Collier Counties. These diverse data sets were the basis for interpretations of water-quality changes during ASR cycles in different regions. These data sets were interpreted to provide guidance for cycle test performance at Comprehensive Everglades Restoration Plan (CERP) ASR pilot sites. ASR and monitoring well data were interpreted for trends in water-quality changes. Estimates of reaction rates or half-lives are based only on data obtained from monitoring wells during storage. Analytes that are reactants or products in major geochemical reactions are: dissolved oxygen, nitrate and ammonia, sulfate and hydrogen sulfide, gross alpha radioactivity and radium isotopes, and total trihalomethanes.

Dissolved oxygen (DO) is reduced during cycle testing at ASR systems in Lee and Collier Counties, from 4- to 8-mg/L saturation to approximately 2-mg/L, as measured throughout cycle tests in ASR well samples. Apparently, DO is consumed along the flowpath prior to reaching the monitoring well during recharge and storage. Half-lives calculated for DO are 1 day (Fort Myers – Winkler Avenue) and 23 days (Lee County – Olga).

Nitrate reduction to ammonia (denitrification) is suggested from increasing ammonia concentrations during storage, as measured at two ASR systems. Ammonia concentrations in recovered water samples from the ASR wells at Boynton Beach and Fiveash ASR systems exceeded the Florida Classes I and III surface water-quality criterion (0.020 mg/L), although concentrations of volatile ammonia likely will diminish by degassing during postrecovery water treatment. Where measured (one site, Springtree – City of Sunrise), nitrate concentrations in all cycle test samples were well below the Federal maximum contaminant level (MCL) of 10 mg/L.

Sulfate concentrations vary during cycle testing at all ASR systems. However, the processes that control sulfate concentration probably differ among all sites considered. Although sulfate concentration increases through the cycle test, concentrations of recovered water in ASR well samples do not exceed the Federal MCL of 250 mg/L.

Limited hydrogen sulfide data (two ASR systems) suggest that microbe-mediated sulfate reduction occurs during storage. It may be necessary to use

laboratory methods rather than a field test kit for hydrogen sulfide data, because concentrations are likely to be near or below the detection limit (0.10 mg/L) for the field test method.

Gross alpha radioactivity and radium isotope activities show pronounced regional trends. Elevated gross alpha radiation and radium isotope activity occurred at those ASR systems in Southwest Florida that stored water within the phosphate-rich Lower Hawthorn Group, and to a lesser extent in the Suwannee Limestone. Gross alpha activity exceeded the Federal MCL (15 picocuries/L) in some recovered water samples from ASR wells at all ASR systems in Lee and Collier Counties except Corkscrew and North Reservoir. Radium isotope activity data are not as abundant. However, radium isotope activities measured in recovered water samples from ASR wells exceeded the Federal MCL at two ASR systems in Lee and Collier Counties. No gross alpha data, and only limited radium isotope data were available for ASR systems located in Palm Beach and Broward Counties. Radium isotope activity measured in recovered water samples from the Delray Beach ASR well was below the Federal MCL.

Trends in total trihalomethanes (TTHMs) concentrations reflect water treatment strategies applied at each ASR system. Generally, TTHM concentrations decline through the cycle test, so that concentrations are below the Federal MCL (80 µg/L) in recovered water samples from both ASR and monitoring wells.

Arsenic concentrations in recovered water samples at the ASR well typically are below the newly promulgated arsenic MCL (10 µg/L) at all sites except Lee County – Olga. Arsenic concentrations were interpreted in the context of specific analytical method and its respective minimum detection limit (MDL). Of the 11 ASR systems considered in this report, arsenic was analyzed in cycle test samples at 7 of the systems. All seven ASR systems analyzed arsenic using the graphite furnace atomic absorption method, with an MDL of 3 to 5 µg/L. Of those seven ASR systems using the appropriate analytical method, one ASR system (Lee County – Olga) showed arsenic concentrations in recovered water samples that exceeded the arsenic MCL. The Marco Lakes – Expanded ASR system has three ASR wells, of which two showed arsenic concentrations that sometimes exceeded the MCL during recovery.

Data and interpretations presented here provide qualitative guidance for sampling design and analysis during CERP ASR pilot cycle tests. However, there are some limitations to these data sets, identified as follows:

a. Major dissolved anions and cations are not analyzed consistently in each sample of a cycle test; therefore, charge balance errors cannot be calculated for quality assurance.

b. Qualitative trends in regional water-quality changes can be inferred from these data, but only for radium isotopes and gross alpha radioactivity. Sulfate concentrations increase during cycle testing because of gypsum dissolution, mixing of native and recharged water, and microbe-mediated sulfate reduction. It is not possible to identify the controlling mechanism for sulfate variation with these data. A quantitative understanding of sulfur cycling will require sulfur isotope analyses of specific phases in water and rock.

c. Few data sets comprise samples from both ASR and monitoring wells through a complete cycle test. Ideally, reaction rates of major geochemical reactions are calculated from data obtained during storage from monitoring wells, so that concentration variations that result from rapid flow rates are minimized. Reaction rates could only be estimated for dissolved oxygen reduction at a few sites, owing to insufficient data for quantitative analysis.

Major recommendations for further work to support CERP pilot sites are as follows:

a. As site-specific hydrogeologic data are obtained from CERP pilot site drilling operations, datasets from nearby ASR system operations should be used to guide CERP cycle test performance.

b. The geochemical evolution of the Upper Floridan aquifer during cycle tests is not well-defined with respect to redox condition. Because redox condition affects microbiology, metal mobility, and hence recovered water quality, efforts should be made to better characterize the redox condition of the aquifer environment as oxygenated recharged water mixes with anoxic native ground water.

c. Radium isotopes and gross alpha activity exceed MCLs in recovered water samples at many ASR systems of Southwest Florida. Particular focus on discrete flow zones (Intermediate aquifer system, and permeable zones within the Lower Hawthorn Group and Suwannee limestone) should be initiated at the Caloosahatchee ASR pilot site.

d. Preliminary data presented here indicate that total trihalomethanes concentrations do not increase during storage, and decrease throughout cycle tests in ASR systems surveyed here. However, because total trihalomethanes concentrations are a sensitive issue, it would be prudent to ensure that cycle tests confirm the hypothesis of natural attenuation.

1 Introduction

Objectives

Aquifer Storage Recovery (ASR) systems have been in development and operation throughout South Florida since the early 1980s (Pyne 1994), and many systems have expanded through the addition of recharge/ recovery (or ASR) wells and distribution infrastructure. Some Comprehensive Everglades Restoration Plan (CERP) ASR pilot sites will be located near existing ASR facilities, or will operate in similar hydrogeologic or hydraulic conditions. Therefore, water-quality data obtained from existing ASR systems ideally can have a beneficial predictive value to guide cycle test development at the CERP ASR pilot sites. The objectives of this report are:

a. To compile all relevant existing water-quality data obtained during ASR cycle tests conducted in the Upper Floridan Aquifer in South Florida.

b. To provide preliminary interpretations of water-quality changes that occur during ASR testing at South Florida ASR systems.

c. To identify data gaps in the water-quality data sets, in preparation for a subsequent geochemical modeling efforts.

ASR Systems Surveyed in this Report

This report summarizes water-quality data collected during cycle testing at 11 potable water ASR systems in South Florida (Table 1). ASR systems are arranged by county, but also represent two distinct hydrogeologic regions. Five sites are located along the lower east coast of Florida (Palm Beach and Broward Counties), and six sites are located in Southwest Florida (Lee and Collier Counties).

Description of Water-Quality Data Sets from ASR Systems

Water-quality analyses are performed during cycle tests primarily to assess ASR system performance and also to ensure that recovered water meets state and Federal drinking-water-quality criteria. ASR system performance is quantified

Table 1
Water-Quality Parameters, Analytes, Sampling Frequency, and Well Types at ASR Systems in South Florida

County	Site	Temperature	pH	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Chloride	Fluoride	Sulfate	Nitrite + Nitrite	Phosphorus	Ammonia	Iron	Manganese	Arsenic	Mercury	Dissolved O2	Dissolved H2S	Tot. Org. Carbon	TTHMs	Radium 226+228	Gross Alpha	Wells Sampled	Sampling Frequency	No. of Cycles	Source Water
Palm Beach	Boynton Beach	X	X	X	X	X	-	-	X	-	X	(X)	-	X	(X)	-	-	-	-	(X)	O	X	O	O	ASR well only	weekly	15	Treated drinking water
	Delray Beach	X	X	X	X	X	(X)	-	X	X	X	(X)	X	(X)	X	O	(X)	X	O	(X)	X	X	X	O	ASR well only	weekly/daily	7	Treated drinking water
Broward	BCOES WTP 2A	X	X	X	X	X	-	-	X	-	-	-	-	-	X	-	-	-	-	-	-	-	-	-	ASR & MW	daily	3	Raw Biscayne
	Fiveash WTP	X	X	X	X	X	X	-	X	-	X	(X)	X	X	X	-	-	-	O	X	-	(X)	O	-	ASR & MW	weekly	5	Raw Biscayne
	Sunrise/Springtree	X	X	X	X	X	X	-	X	-	X	X	X	X	X	-	-	-	O	(X)	-	X	-	-	ASR well only	weekly	6	Potable Biscayne
Dade	MDWASD West	X	X	-	-	-	X	-	X	-	X	(X)	X	X	X	-	-	-	X	X	-	-	-	-	ASR & MW	weekly	0	Potable Biscayne
Lee	Bonita Spr/San Carlos Estates	X	X	-	-	-	X	-	X	-	X	-	-	-	-	X	(X)	-	X	-	-	X	X	X	ASR & MW	daily during recovery	2	Treated drinking water
	Corkscrew ASR	X	X	X	X	X	-	-	X	X	X	-	(X)	-	X	(X)	-	-	X	-	-	X	-	X	ASR & MW	monthly (limited)	3	Treated drinking water
	Corkscrew – Expanded	X	X	X	X	X	-	-	X	X	X	O	-	-	X	-	(X)	-	X	(X)	-	X	-	X	ASR & MW	weekly/ bimonthly	2	Treated drinking water
	Fort Myers – Winkler Avenue	X	X	X	X	X	X	-	X	X	X	-	-	-	(X)	(X)	(X)	-	X	(X)	-	X	X	X	ASR & MW	daily during recovery	1	Treated drinking water
	North Reservoir	X	X	X	X	X	-	-	X	-	X	-	-	-	X	-	(X)	-	X	-	-	X	-	X	ASR & MW	weekly	2	Treated drinking water
	Olga	X	X	X	X	X	-	-	X	-	X	-	-	-	X	-	X	-	X	-	-	X	-	X	ASR & MW	weekly	2	Treated drinking water
Collier	Manatee Road	-	X	-	-	-	-	-	X	X	X	X	-	-	-	-	O	-	-	-	-	X	-	-	ASR & MW	quarterly/ annual	0	Treated drinking water
	Marco Lakes	-	X	-	-	-	-	-	X	-	X	-	-	-	(X)	-	-	-	X	-	X	X	-	X	ASR & MW	weekly	6	Treated surface water
	Marco Lakes – Expanded	X	X	-	-	-	-	-	X	-	X	-	-	-	X	-	X	-	X	-	-	(X)	-	0	ASR & MW	weekly	1	Treated surface water

Note: MW = Monitoring well; ASR = recharge/recovery well; TTHMs = total trihalomethanes; X = analyte measured in all samples; (X) = greater than 80 percent of all concentrations reported are below the minimum detection limit; 0 = limited (less than 5) analyses during a single cycle; - = not analyzed.

during cycle testing as recovery efficiency, which is the percentage of recharge water recovered at the ASR well that meets numerical state and Federal drinking-water-quality standards. Typically, recovery efficiency is the volume of water recovered that meets the Federal Maximum Contaminant Level (MCL) for chloride (250 mg/L; Code of Federal Regulations (CFR) 2002). Other analytes are measured during cycle testing to ensure that recovered water concentrations are less than MCLs. Arsenic, fluoride, nitrate, nitrite, total trihalomethanes, radium isotopes, and gross alpha radioactivity have enforceable primary MCLs, although these are not analyzed at all ASR systems. Chloride, iron, manganese, and sulfate have nonenforceable secondary MCLs (primarily for aesthetics), and also are not analyzed at all ASR systems. All water-quality data reported here were measured at laboratories certified by either the Florida Department of Health, or by the U.S. Environmental Protection Agency (USEPA), National Environmental Laboratory Accreditation Conference (NELAC). The types of water-quality analytes, sampling frequency, and sampling location (ASR and/or monitoring well) are compiled in Table 1.

Sampling and Analysis Strategies

The strategy for sampling and analysis of water quality during cycle testing at ASR systems varies by site and through time. Because analyses are costly, most cycle test sampling strategies are designed to:

a. Fulfill state and Federal Underground Injection Control permitting requirements for Class V wells.

b. Quantify recovery efficiency.

c. Address site-specific water-quality issues related to analytes that have primary MCLs.

Generally, it is not the goal for ASR system performance studies to address geochemical or microbiological changes that occur in the storage zone during cycle testing. Typically in these data sets, ground water was sampled at the start and end of storage, so that geochemical changes are inferred from limited initial and final data. However, storage samples were collected at a few ASR systems from both ASR and monitoring wells. These data are most useful for quantifying geochemical changes and reaction rates that occurred during cycle tests.

Interpretations of water quality can differ between ASR (recharge/recovery) well data and monitoring well data. ASR well samples are best to show the characteristics of stored water for drinking-water treatment and to fulfill permit requirements. However, monitoring well samples are better suited for an analysis of physical and chemical changes that occur in the aquifer during cycle testing and to provide a more quantitative basis for modeling efforts. Degassing of volatile constituents and well-bore mixing (Campbell et al. 1997) during recovery in the ASR well can obscure the in situ composition of recharge water in the aquifer. For this reason, quantitative interpretations of water-quality evolution in the aquifer are best made from monitoring well data. Data from both well types (as available) are presented in this report.

Data Set Characteristics

Characteristics of the ideal data set to interpret water-quality changes during cycle testing are:

a. Samples are obtained weekly or semimonthly from both ASR and monitoring wells during recharge, storage, and recovery.

b. Storage duration is long, at least 1 month.

c. Samples are analyzed for all major dissolved cations and anions to permit calculation of charge-balance error for each sample.

Surprisingly, no ASR system considered here fulfills all criteria (Table 1). Despite this, regional trends of water-quality changes can be inferred because sufficient data were obtained from cycle tests at several ASR systems in a region (lower east coast of Florida and Southwest Florida). Miami – Dade County is not represented because the Miami – Dade Water and Sewer Department (MDWASD) – West well field water-quality data set is incomplete at this writing. Collier County is represented by the Marco Lakes data sets, because the Manatee Road ASR system is sampled only on a quarterly basis.

In South Florida, ASR systems are an increasingly common means for water-supply management, facilitated by abundant surface water (or Biscayne aquifer water) resources for recharge during the wet season. Consequently, many facilities are expanding to become large-volume systems with multiple ASR wells. Unfortunately, the growth of these systems has not resulted in more detailed, complete water-quality data sets. This compilation represents data sets from diverse operations at which sampled wells, sample frequency, and analytes varied. Therefore, limited interpretations of temporal changes in water-quality are proposed.

Data Set Criteria

To compare diverse ASR systems, data sets were focused using the following criteria:

a. Use of early cycle test (usually cycle 1 or 2) data.

b. Use of early cycle tests that have long (greater than 30 days) storage durations.

c. Comparison of water-quality data obtained from ASR and monitoring well samples at each site.

Interpreting cycle test data that fulfill these criteria will enable estimates of regional water-quality changes that occur over time, in permeable zones within the upper Floridan aquifer. Estimated reaction rates are offered where storage data are sufficient. Well field configurations for ASR systems reported here are shown in Table 2. ASR cycle test schedules and recovery efficiencies are tabulated in Appendix A.

Table 2
Well Configurations at ASR Systems in South Florida

County	Site	ASR Well(s)	Cycle 1 Typical Recharge and Recovery Rate in ASR Well (MGD)	Storage Zone, ft[1]	Monitoring Wells	Depth, ft[1], below land surface	Distance Between ASR and Monitoring Well, ft[1]	Hydro - stratigraphic Unit
Palm Beach	Boynton Beach	ASR-1	1 - 1.3	804 - 909 ft UFA	MW-1-	300 - 320 ft	50 ft S of ASR well	Hawthorn
	Delray Beach	ASR Well	2.7	1,016 - 1,200 ft UFA	--	--	--	--
Broward	BCOES WTP 2A	ASR-1	2.5 - 3.5	995 - 1,200 ft UFA	MW-1	1: 990 - 1,200 ft	MW 275 ft W of ASR	Upper Floridan
	Fiveash WTP	ASR-1	1.3 - 1.8	1,055 - 1,200 ft UFA	FMW-1	1: 1,055 - 1,175 ft	MW 350 ft W of ASR	Upper Floridan
	Sunrise/Springtree	ASR-1	1	1,110 - 1,270 ft UFA	--	--	--	--
Dade	MDWASD West	ASR-1	1 - 3	--	--	--	--	--
Lee	Bonita Springs/San Carlos Estates	ASR TPW-1	1 - 2	650 - 701 ft Lower Hawthorn	SMW-1 SZMW-1R	1: 234 - 321 ft 1R: 659 - 721 ft	SMW-1 100 ft E of TPW-1 MW 217 ft S of TPW-1	Mid-Hawthorn Lower Hawthorn
	Corkscrew ASR	ASR-1 LM-3982	0.3	328 - 397 ft Hawthorn Zone I	MW-A	A: 340 - 402 ft	MW-A 450 ft E of ASR1	Hawthorn Zone I
		ASR-2 LM-4267	2.5	337 - 397 ft Hawthorn Zone I	MW-B MW-C	B: 452 - 504 ft C: 330 - 400 ft	MW-B 250 ft SW of ASR1 MW-C 250 ft W of ASR1	Hawthorn Zone II Hawthorn Zone I
	Corkscrew — Expanded	ASR-3	2.5	285 - 347 ft Hawthorn Zone I	MW-1	1: 358 - 410 ft	MW-1 6,000 ft S of ASR 3	Hawthorn Zone I[2]
		ASR-4	2.5	310 - 368 ft Hawthorn Zone I	MW-2	2: 283 - 354 ft	MW-2 250 ft N of ASR 3	Hawthorn Zone I
		ASR-5	2.5	253 - 291 ft Hawthorn Zone I	MW-3	3: 355 - 411 ft	MW-3 2,000 ft N of ASR 3	Hawthorn Zone I
	Fort Myers — Winkler Avenue	ASR-1	0.72	455 - 553 ft Lower Hawthorn	MHMW-1	1: 150 - 200 ft	MW 80 ft S of ASR	Mid-Hawthorn
					SZMW-1	1: 455 - 553 ft	MW 200 ft SW of ASR	Lower Hawthorn
	North Reservoir	ASR-1 LM-6210	0.5	540 - 642 ft UFA Arcadia Fm	MW-1 LM-6208	1: 537 - 615 ft	MW 250 ft S of ASR	Upper Floridan
	Olga	ASR-1 LM-6086	0.5	859 - 920 ft UFA Suwannee Fm	OBS-1 LM-6209	1: 850 - 895 ft	MW 350 ft W of ASR	Upper Floridan
					OBS-3 LM-6615	3: 864 - 945 ft	MW 400 ft SW of ASR	Upper Floridan
Collier	Marco Lakes	ASR-1 CO-2428	2 - 5[3]	745 - 790 ft UFA	SZ-1 (Shallow)	1: 293 - 350 ft	750 ft SE of ASR 1	Mid-Hawthorn
					DZ-1(ASRZMW1)	1: 745 -811 ft	750 ft SE of ASR 1	Upper Floridan
	Marco Lakes — Expanded	ASR-2	1 - 2[3]	735 - 780 ft UFA Arcadia Fm	SZ-2 (MHZ2MW)	2: 440-470 ft	1,000 ft NE of ASR 1	Mid-Hawthorn
		ASR-3	1 - 2[3]	736- 780 ft UFA Arcadia Fm	DZ-2 (ASRZMW2)	2: 725 - 774 ft	2,750 ft NE of ASR 1	Upper Floridan

Note: ASR = recharge/recovery well; MW = monitor well; UFA = Upper Floridan Aquifer; MGD = million gallons per day; -- = no data available.

[1] To convert feet to meters, multiply by 0.3048.

[2] Wells at the expanded Corkscrew ASR site may be screened in the Intermediate aquifer system, which occurs in part within Lower Hawthorn Group sediments (Plate 9, Reese 2002).

[3] Recharge/recovery rates cited for Cycle 1E, when recharge occurred through all three ASR wells.

2 Results

Water-Quality Changes During ASR Cycle Tests

Significant water-quality changes that occur during ASR cycle tests will be described using single analytes. These data form the basis for preliminary interpretations of regional and temporal trends in water quality. Table 3 summarizes relevant Florida and Federal water-quality standards for comparison.

Table 3
Florida and Federal Water-Quality Standards

Analyte	Unit	US EPA Maximum Contaminant Level (MCL)	Florida Class I Surface Water Criteria	Florida Class III Surface Water Criteria	Note
Alkalinity	mg/L as $CaCO^3$	--	>20	>20	
Ammonia, un-ionized	mg/L as NH_3	--	<0.02	<0.02	
Total Arsenic	µg/L	10	10	10	Effective Jan 1, 2005, in Florida. Federal MCL effective Jan 2006
Chloride	mg/L	250	250	--	Secondary Federal MCL
Dissolved Oxygen	mg/L	--	>5.0	>5.0	Normal surface water fluctuations maintained
Fluoride	mg/L	4	<1.5	<10	
Total Trihalomethanes	µg/L	80	<100	--	Federal MCL effective 31 Dec 2003
Iron	mg/L	0.3	<0.3	<1.0	Secondary Federal MCL
Manganese	mg/L	0.05	--	--	Secondary Federal MCL
Nitrate	mg/L	10	<10	--	See nutrient regulations for FL Class III criteria
pH	standard units	6.5 -8.5	6 - 8.5 or <1 unit from background		
Phosphorus	mg/L	--	--	--	
Sulfate	mg/L	250	--	--	Secondary Federal MCL
$Ra^{226} + Ra^{228}$	picocuries/L	5	<5	<5	
Gross Alpha	picocuries/L	15	<15	<15	

Note: -- = no standard exists.

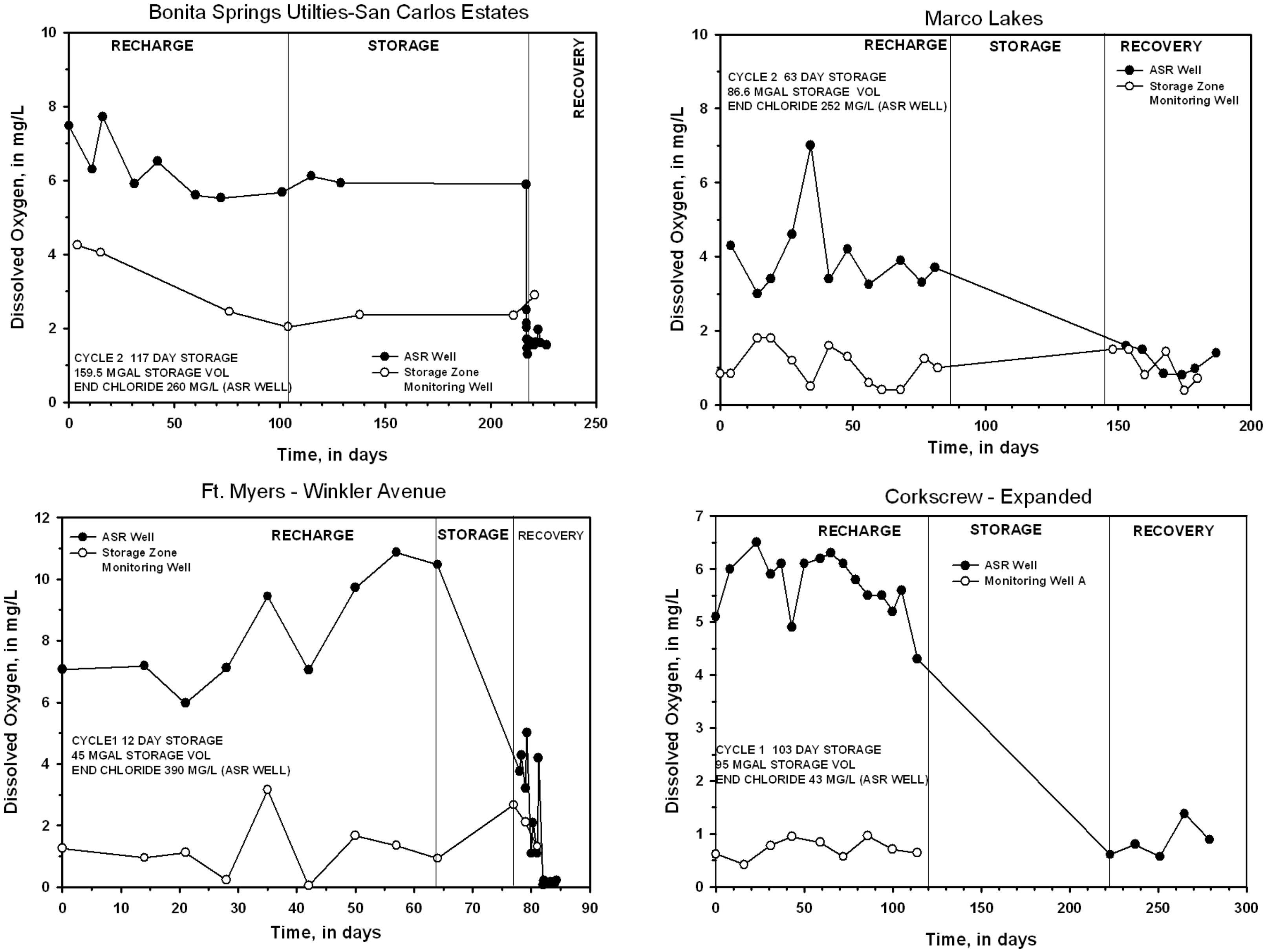
Dissolved Oxygen

The first significant water-quality change to occur during ASR cycle testing is reduction of dissolved oxygen (DO). Determining spatial and temporal trends of DO reduction is significant, because an oxic versus anoxic conditions in the aquifer will control major inorganic and microbial reactions. In this report, only ASR systems in Lee and Collier Counties had sufficient DO data for interpretation (Figure 1).

DO concentrations should decline away from the ASR well and also throughout the cycle test. During recharge, DO concentrations will be higher in ASR than monitoring well samples, reflecting proximity to oxygen-saturated recharge water. DO concentrations diminish at both wells during storage, although well-bore mixing may allow oxygen diffusion unless wells are completely purged and the sampling method excludes contact with the atmosphere. In the presence of oxidizable material or aerobic bacteria, DO should be consumed as it travels along a flowpath from the ASR well during cycle testing. During recovery, DO concentrations in both wells should converge to an approximate concentration (less than 1 mg/L DO) that reflects native ground-water conditions. These trends are exemplified in cycle test data sets from Lee and Collier Counties (Figure 1).

The DO concentration in fresh surface water at standard conditions (25 °C, 1 atm pressure) is approximately 8 mg/L (Appelo and Postma 1993). The DO concentration of recharge water in ASR well samples at all sites ranges between 4 and 8 mg/L, which reflects differences in saturation from seasonal and/or temperature differences. After recharge, oxygen-saturated water encounters oxidizable material in the aquifer (for example, pyrite and organic carbon) and perhaps aerobic bacteria, which diminish DO concentration and reduce Eh of the aquifer environment. ASR systems shown here have the following configurations: the distance between ASR and monitoring well ranges between 0.61 and 229 m (200 and 750 ft); recharge rate ranges between 0.5 and 3 MGD; and storage duration ranges between 12 and 168 days (Table 2, Figure 1). By the completion of storage during these cycle tests, DO concentrations throughout the subsurface system converge at concentrations of approximately 2 mg/L. It appears that under typical pumping conditions and aquifer material composition, DO does not persist as it travels along the flowpath toward monitoring wells. The Eh of the aquifer will reduce at some distance away from the ASR well. At ASR systems considered here, DO is reduced before reaching the monitoring well.

Temporal trends observed in DO concentration data can provide an estimate of reduction rate in the aquifer environment. Ideal data for calculation of reduction rate would be those samples measured throughout storage, to avoid concentration changes that result from ground-water flow. Because significant changes in DO concentration are not observed in the monitoring well samples, an estimate of DO reduction rate must come from ASR well samples. Only the Lee County – Olga and Fort Myers – Winkler Avenue sites have sufficient storage data for rate estimates. Assuming that oxygen reduction proceeds as a first-order reaction, half-lives calculated from Fort Myers – Winkler Avenue (k = -0.73 day^{-1}) and Lee County – Olga (k = -0.03 day^{-1}) data sets are 1 day, and 23 days, respectively.



Bonita Springs Utilties-San Carlos Estates

Marco Lakes

Ft. Myers - Winkler Avenue

Corkscrew - Expanded

Figure 1. Dissolved oxygen concentrations measured during cycle tests in ASR and monitoring well samples (Continued)

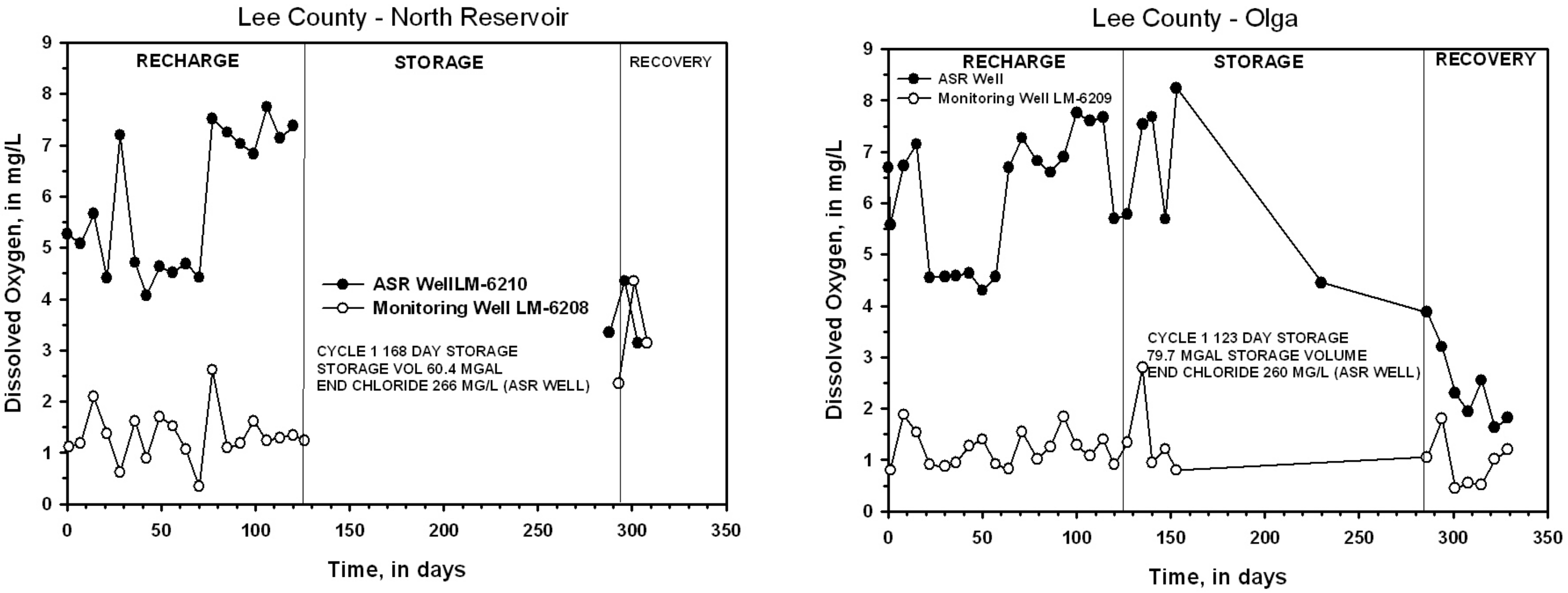


Figure 1. (Concluded)

Theoretically, there should be no dissolved oxygen detected in distal monitoring well samples, particularly after long-storage durations. The detection of DO at 1-2 mg/L concentrations may be because of the following factors:

a. Absence of oxidizable material and/or aerobic bacteria in the Upper Floridan aquifer.

b. Measurement of DO in the well bore using an uncalibrated DO probe.

c. Atmospheric oxygen diffusion into the well bore, well-head flow-cell, or sample bottles during sample acquisition.

d. Episodic recharge during storage.

Finally, it is important to note that the use of oxidation-reduction probes do not provide a good estimate of redox state, especially in oxic waters (Lindberg and Runnells 1984). Field measurements of Eh in oxic waters ranged from approximately 0 to +0.5 volts, probably because probe surfaces are not electro-active toward O_2 molecules. DO concentration measurements (by Winkler titration in the field; APHA (1998a)) are preferred for estimation of Eh values in oxic waters. In situ measurement of DO will be very important supporting data for microbial ecology and pathogen survival studies.

Ammonia and Nitrate

After dissolved oxygen reacts, the next constituent to be reduced is nitrate. The reduction of nitrate (denitrification) by electron donors such as organic matter, ferrous (Fe^{2+}) iron, or hydrogen sulfide has been observed in reclaimed water ASR systems in Florida and South Australia, (Pyne 2002; Vanderzalm et al. 2002). Typically, nitrate will reduce through a series of reactions to either N_2 or ammonia (NH_3). ASR systems that recharge with treated surface or Biscayne aquifer water show much lower nitrate concentrations than reclaimed water systems, so the effect of nitrate reduction on the aquifer redox environment is not as significant. The primary drinking-water MCL for nitrate is 10 mg/L (CFR 2002). The Florida Class I and Class III surface water-quality criterion for nitrate is less than 10 mg/L, and for ammonia is less than 0.02 mg/L (Florida Department of Environmental Protection (FDEP) 2003)

Few ASR systems measure nitrate or ammonia during cycle testing. Ammonia was analyzed at five ASR systems surveyed here but was detected only at Boynton Beach, Fiveash, and Springtree – City of Sunrise sites. Nitrate was analyzed at six ASR systems but was detected only at the Springtree – City of Sunrise site (Table 1, Figure 2). Ammonia concentrations in all wells at Boynton Beach, Fiveash, and Springtree – City of Sunrise ASR systems suggest that denitrification occurs at some point during the cycle test, resulting in ammonia concentrations that exceed the State of Florida surface-water quality criterion.

Ammonia evolution during storage is suggested from monitoring well data at the Fiveash and Boynton Beach ASR systems (Figure2). Ammonia concentrations increase to nearly 1.0 mg/L throughout cycle test 6 at Boynton Beach

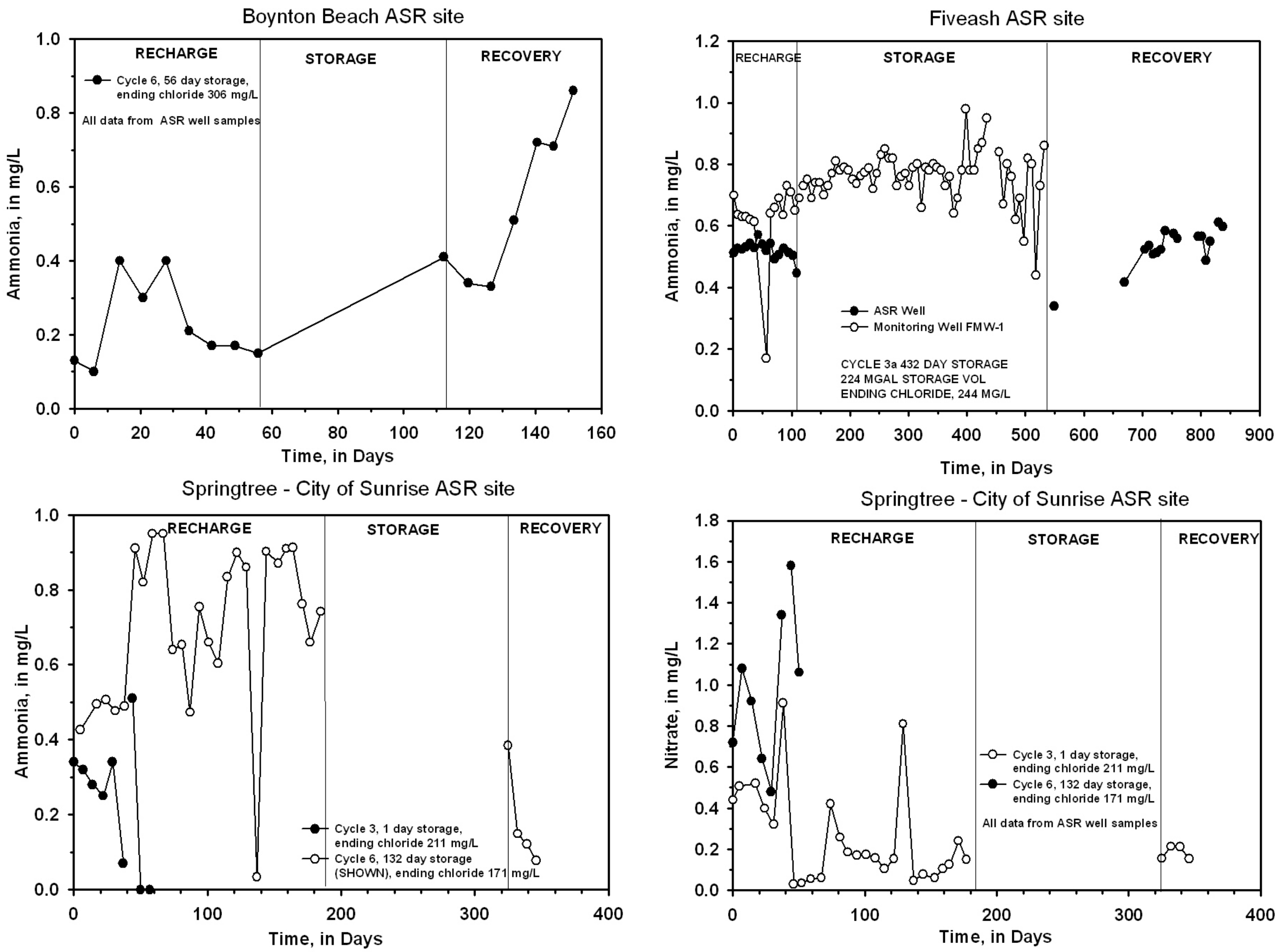


Figure 2. Dissolved ammonia and nitrate (Springtree only) concentrations measured during cycle tests in ASR and monitoring well samples

(cycle test 6 was the first operational test that had a storage period greater than 1 week). At the Fiveash ASR system, ammonia concentrations from monitoring well FMW-1 suggest ammonia evolution in the aquifer. However, linear regression of ammonia concentrations versus time in those storage samples shows no statistical significance ($r^2 = 0.02$). Episodes of recharge (20 to 40 days in duration) were performed throughout the 432-day storage period. It is possible that ground-water flow resulted in the variable ammonia concentrations during storage in the Fiveash data set.

Nitrate concentration data are rare in these South Florida data sets, with detectable nitrate occurring only at the Springtree – City of Sunrise ASR system (Figure 2). Maximum nitrate concentration at Springtree – City of Sunrise was 2.0 mg/L during all cycle tests. State and Federal water-quality criteria were never exceeded at this site.

Sulfate

Quantifying changes in dissolved sulfate during cycle testing will be important because sulfate in recovered water may contribute to sulfur loading in Everglades surface water. Higher sulfate concentrations in surface water can stimulate sedimentary sulfate-reducing bacteria and enhance mercury methylation in the process (Marvin-Dipasquale and Oremland 1998). Sulfate concentrations in northern Everglades surface-water range between 10 and 200 mg/L (Bates et al. 2002), with higher values reflecting the addition of sulfur amendments in the Everglades Agricultural Area. Sulfate concentrations in recovered water samples can increase (compared to recharged water) as the result of two processes: (a) mixing with brackish native water of the Upper Floridan aquifer in some areas (sulfate concentrations range between100 and 1,000 mg/L (Reese and Memberg 2000; Reese 2000)); and (b) gypsum ($CaSO_4$) dissolution in aquifer material (Reese 2000; Wicks and Herman 1996). Sulfate concentrations in recovered water samples can diminish because of microbial sulfate reduction in the Upper Floridan aquifer, which will proceed in the absence of DO (Katz 1992). Recovered water is not expected to exceed the sulfate secondary MCL of 250 mg/L (CFR 2002).

Spatial variations of sulfate concentration are observed in the cycle test data sets, although the specific basis for variation (geologic versus hydrologic) cannot be identified. Sulfate concentrations measured in ASR well samples increased through each cycle test at all sites, except for Corkscrew – Expanded ASR system (Figure 3). Sulfate concentrations in samples from ASR wells were below the MCL at completion of recovery.

Native sulfate concentrations in the upper brackish zone of the Upper Floridan aquifer do show spatial variations. In Southwest Florida, minimum sulfate concentrations (generally less than 300 mg/L) are observed in wells at central Lee County, with increasing concentrations toward the south and west (Reese 2002). In Palm Beach County, sulfate concentrations in the upper brackish zone of the Upper Floridan aquifer (depths 198 to 305 m (650 to 1,000 ft) below land surface) range between 100 and 500 mg/L (Reese and

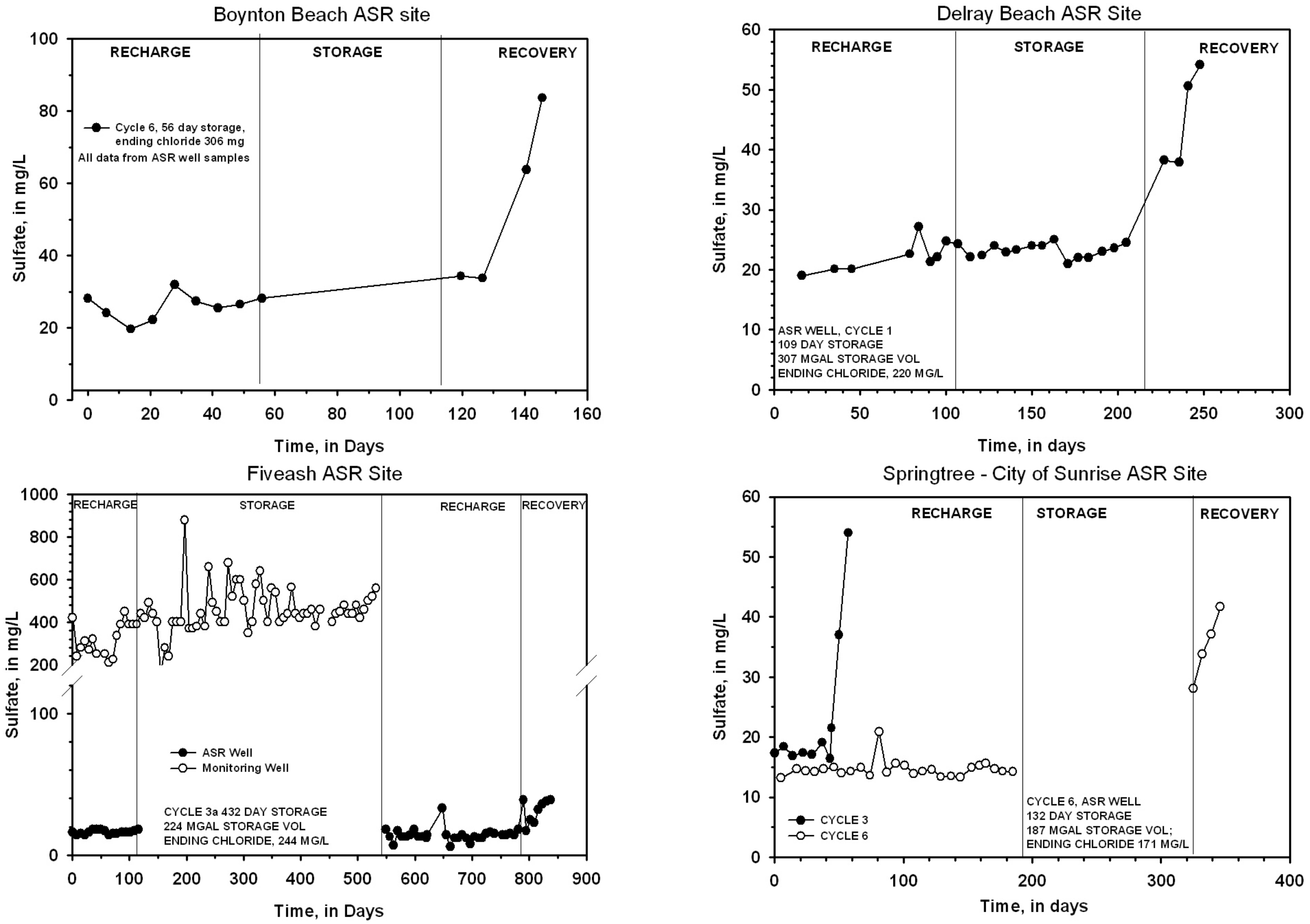
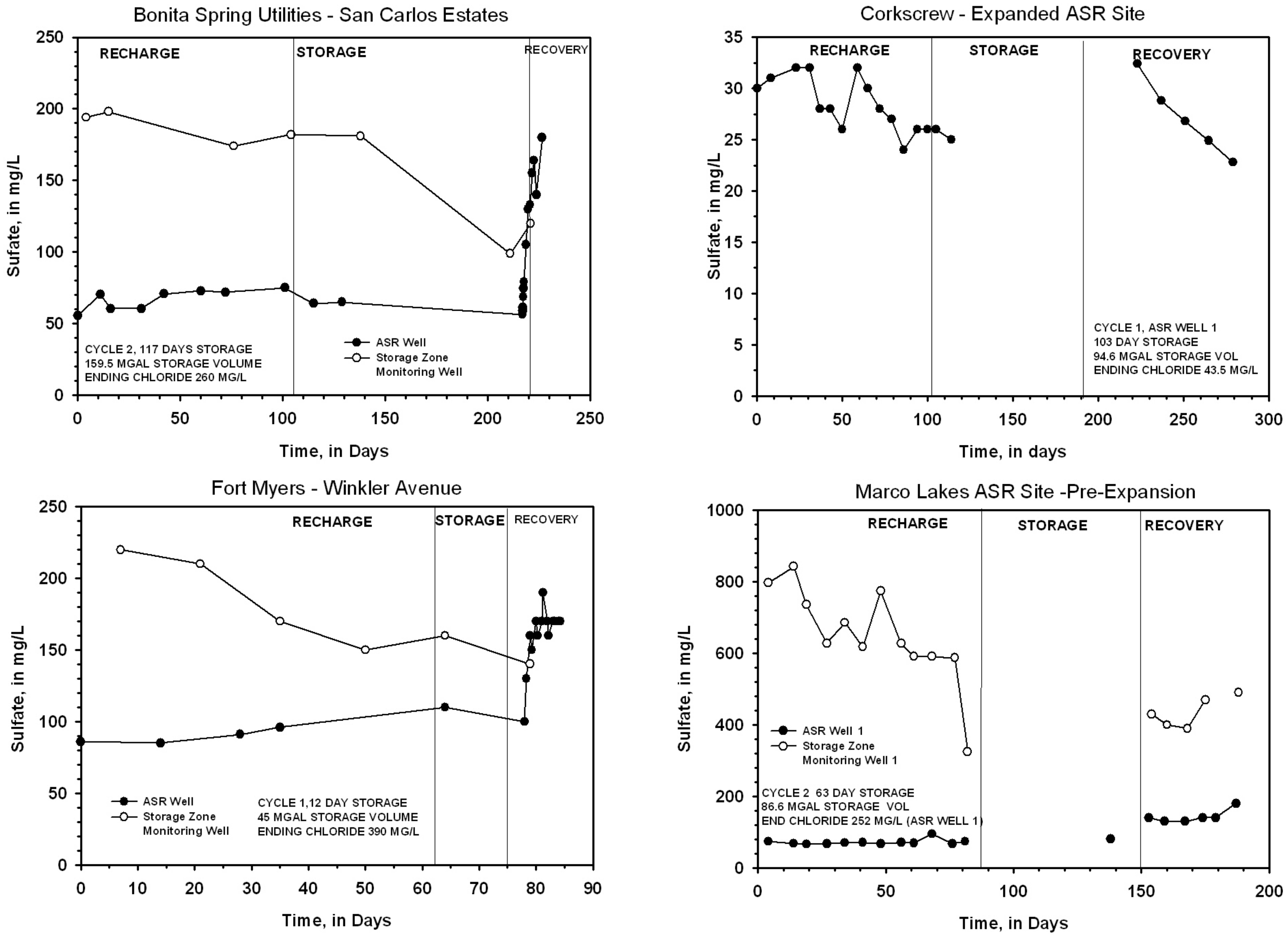


Figure 3. Dissolved sulfate concentrations measured during cycle tests in ASR and monitoring well samples (Sheet 1 of 3)



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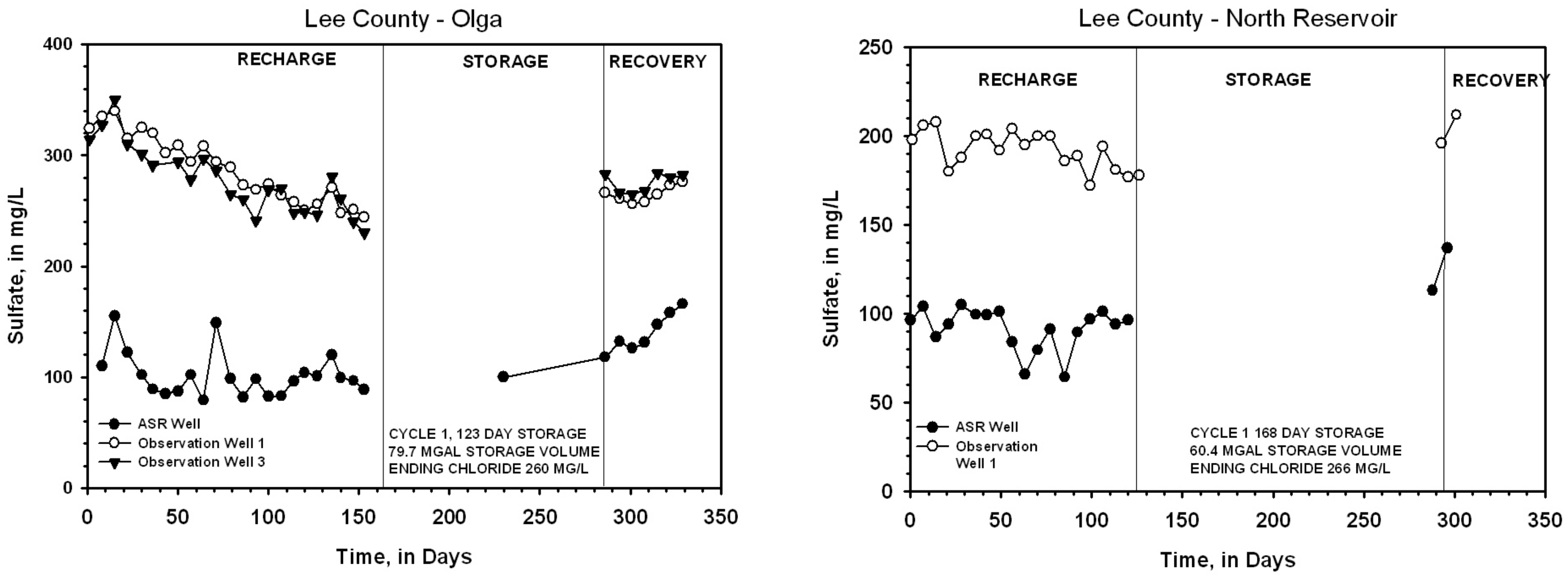

Figure 3. (Sheet 3 of 3)

Memberg 2000). Pumping during recovery results in mixing between recharged and native ground waters to increase sulfate concentration at coastal facilities.

Temporal trends in sulfate concentration during storage can result from two competing processes: gypsum dissolution to increase sulfate concentration; and sulfate reduction to decrease concentration. The flux of sulfate from gypsum dissolution likely exceeds that from sulfate reduction, so it is not possible to infer sulfate reduction rate from sulfate concentrations data alone. Three ASR systems have sufficient sulfate concentration data collected during storage to interpret temporal trends: Delray Beach, Fiveash, and Bonita Springs/San Carlos Estates (Figure 3). Linear regression of sulfate concentrations versus time shows no statistical relationship, except in monitoring well data from Bonita Springs/San Carlos Estates. There, sulfate concentration declines during storage, as measured in monitoring well (but not ASR well) samples. Diminished sulfate concentration during storage could result from gypsum precipitation, sulfate reduction, or mixing between native ground water and fresher recharge water. Hydrogen sulfide and mineralogical data are not available at this site, so it is not possible to interpret declining sulfate concentrations unequivocally.

Because sulfate geochemistry is complex, it will be necessary to constrain sulfate and hydrogen sulfide data with isotopic measurements to support any conclusion. The sulfur isotopic composition ($\delta^{34}S$) is characteristic of a sulfur source (Bates et al. 2002), whether sulfate appears from gypsum dissolution, pyrite oxidation, seawater mixing, or surface water affected by agricultural runoff. Similarly, hydrogen sulfide generated during subsurface microbial sulfate reduction also has characteristic $\delta^{34}S$. Concentration data presented here indicate that many processes contribute to increased sulfate concentration during cycle testing; however, the dominant mechanism of increased sulfate concentration cannot be specified with these data.

Dissolved Hydrogen Sulfide

Dissolved hydrogen sulfide evolves most likely from microbe-mediated sulfate reduction in the Upper Floridan aquifer (Katz 1992). Although there is no MCL for dissolved hydrogen sulfide, this compound would contribute to the total odor number (TON) that is measured during water treatment. Typically, sulfate-reducing bacteria produce hydrogen sulfide and increased alkalinity during oxidation of organic matter. Decreased sulfate and increased hydrogen sulfide and alkalinity were observed during storage in the Bolivar (South Australia) reclaimed water ASR system, which is developed in a limestone aquifer (Vanderzalm et al. 2002). Hydrogen sulfide was measured only at two ASR systems during cycle testing: Fiveash (Broward County) and the Corkscrew (Lee County) (Figure 4).

It is not possible to infer spatial trends in hydrogen sulfide concentration because site-specific data are limited. Also, microbial sulfate reduction may show patchy distribution, occurring where redox conditions, carbon source, and ground-water flow rate are optimum for bacterial metabolism.

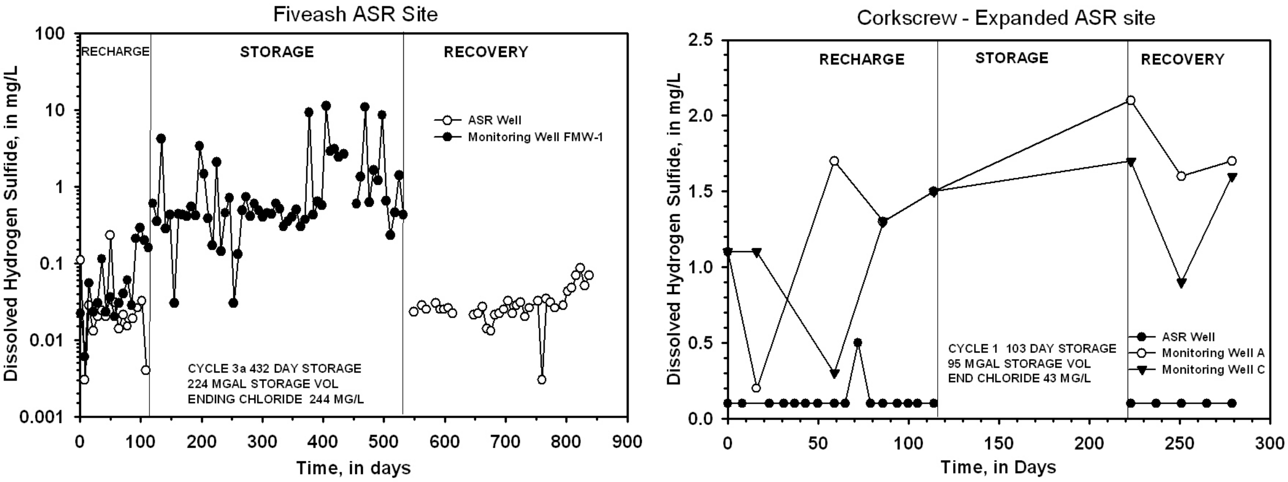

Figure 4. Dissolved hydrogen sulfide concentrations measured during cycle tests in ASR and monitoring well samples

Hydrogen sulfide evolution during storage is suggested from monitoring well data at the Fiveash ASR system. However, linear regression of hydrogen sulfide concentrations in storage samples versus time shows no statistical significance ($r^2 = 0.075$). As was observed with ammonia concentration data, episodic recharge during storage probably obscured temporal trends of this constituent.

At many ASR systems, hydrogen sulfide concentrations are measured colorimetrically, using a field test kit based on the methylene blue method (APHA 1998b). Minimum detectable hydrogen sulfide concentration is 0.1 mg/L when a color wheel (rather than spectrophotometer) is used. This method may not be suitable for conditions encountered during cycle testing at the CERP pilot sites, because detection of very low dissolved hydrogen sulfide concentrations will be necessary.

Gross Alpha Radioactivity and Radium Isotopes

Gross alpha radioactivity is a bulk measurement of the alpha particle activity emitted during decay of uranium-series isotopes. Important daughter products are radium, thorium, and uranium (Osmond and Cowart 2000), polonium 210 (Oural et al. 1988), but not radon 222, which occurs as a gas. Radium-226 (half-life 1,600 yr; alpha emitter) and radium-228 (half-life 5.75 yr, beta emitter) are daughters in the decay sequences of uranium-238 and thorium-232, respectively. Radium isotopes in drinking water are of particular interest because of their relatively long half-lives, health implications of high-energy alpha particle emission, and that radium coprecipitates in carbonate and bone/apatite. Radium isotopes are a significant component of gross alpha activity in the Floridan aquifer (Osmond and Cowart 2000). Bioaccumulation of radium-226 has been documented in unionid mussels living in Round Lake (Hillsborough County), which is augmented by Upper Floridan aquifer water (Brenner et al. 2000). The drinking-water MCLs are 15 picocuries per liter (pCi/L) for gross alpha, and 5 pCi/L for radium 226+228. Florida surface-water quality criteria are ≤15 pCi for gross alpha, and ≤5 pCi/L for radium 226+228 (FDEP 2003).

There are pronounced spatial variations in gross alpha activity among ASR systems. Elevated gross alpha radiation occurs at sites where storage is within permeable zones of the Lower Hawthorn Group, and these sites typically occur in Southwest Florida (Figure 5). Sediments of the Lower Hawthorn Group are characterized by zones of abundant phosphate (>3 percent; Reese 2000), which are enriched in uranium and daughter isotopes. Trace to abundant phosphate also has been observed in sediments of the upper Suwannee Limestone in Lee Counties (Reese 2000). In Lee and Collier Counties, the Lower Hawthorn unit occurs generally at depths between 122 to 244 m (400 and 700 ft) below land surface, stratigraphically underlain by the Suwannee Limestone. All ASR systems in Lee and Collier Counties reported here use permeable zones within the Lower Hawthorn Group for storage, with the exception of the Olga, North Reservoir, and Corkscrew sites. At these sites, recharge is within permeable zones of the Suwannee Limestone (Olga and North Reservoir), or the Intermediate aquifer systems (Corkscrew; Table 2). Gross alpha activity exceeded the state and Federal MCL (15 pCi/L) in some recovered water samples from ASR wells at all ASR systems in Lee and Collier Counties except Corkscrew and North Reservoir (Figure 5).

Gross alpha activity data are not collected frequently from ASR systems on the lower east coast of Florida. There, recharge occurs into permeable zones of the Lower Hawthorn Group and "Eocene Group," which consist of the Suwannee, Ocala, and Avon Park limestones (Reese 2000), depending on location. Apparently, phosphate is not abundant in these lithologies, so corresponding gross alpha radiation is low. Gross alpha data were reported only from the Fiveash ASR system (Broward County), which showed mean values of <1.0 +/- 0.5 pCi/L at monitoring well MW-1 (n = 2, sample collected at the beginning of recharge) and 3.6 +/- 1.4 pCi/L at the ASR well 1 (n = 2; sample collected at the beginning of recharge).

Radium isotope (Ra^{226} + Ra^{228}) data are rare compared to gross alpha data. Radium isotope data were measured only at three sites (Figure 6), and most of these data were measured during recovery at the ASR well. Spatial trends in radium isotope activity are similar to those shown by gross alpha data. Highest activities are observed in ASR systems of Lee County that stored water in permeable zones of the Lower Hawthorn Group. Recovered water show radium isotope activities that exceeded the state and Federal MCL at the Bonita Springs Utilities – San Carlos Estates and Fort Myers – Winkler Avenue ASR systems. Considering ASR systems of the lower east coast, radium isotope data are reported at one site. Delray Beach (Palm Beach County) showed radium isotope activities in recovered water that are below the state and Federal MCL. A localized occurrence of elevated Ra^{226} was reported for soil and shallow ground water in Dade County (Moore and Gussow 1991), but there is no indication that this is related to Floridan aquifer isotope activities.

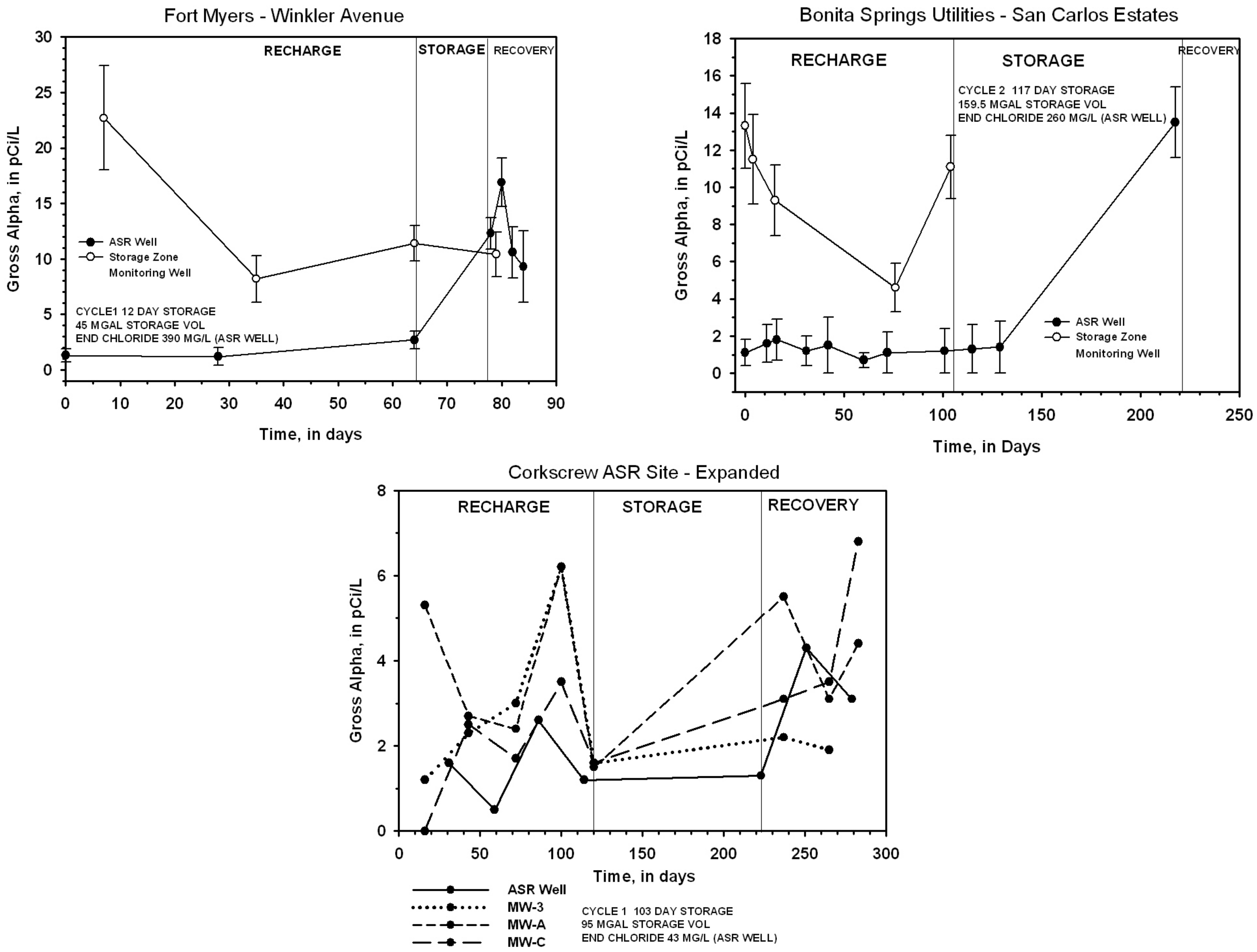

Figure 5. Gross alpha activities measured during cycle testing in ASR and monitoring well samples from sites in Lee and Collier Counties, Florida. Some ASR systems report standard deviations about gross alpha values. If reported, standard deviation about the measured gross alpha value is shown (Continued)

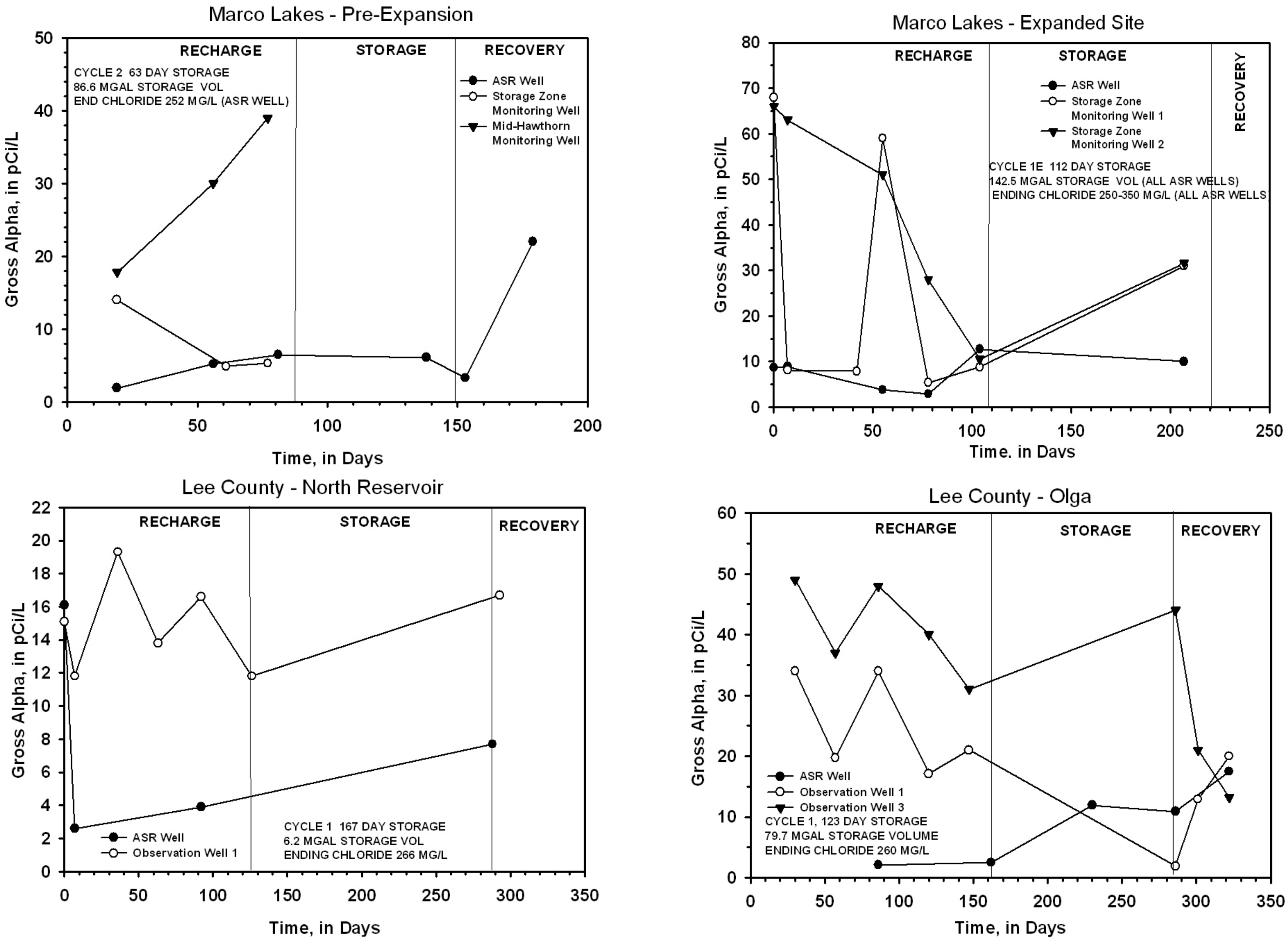

Figure 5. (Concluded)

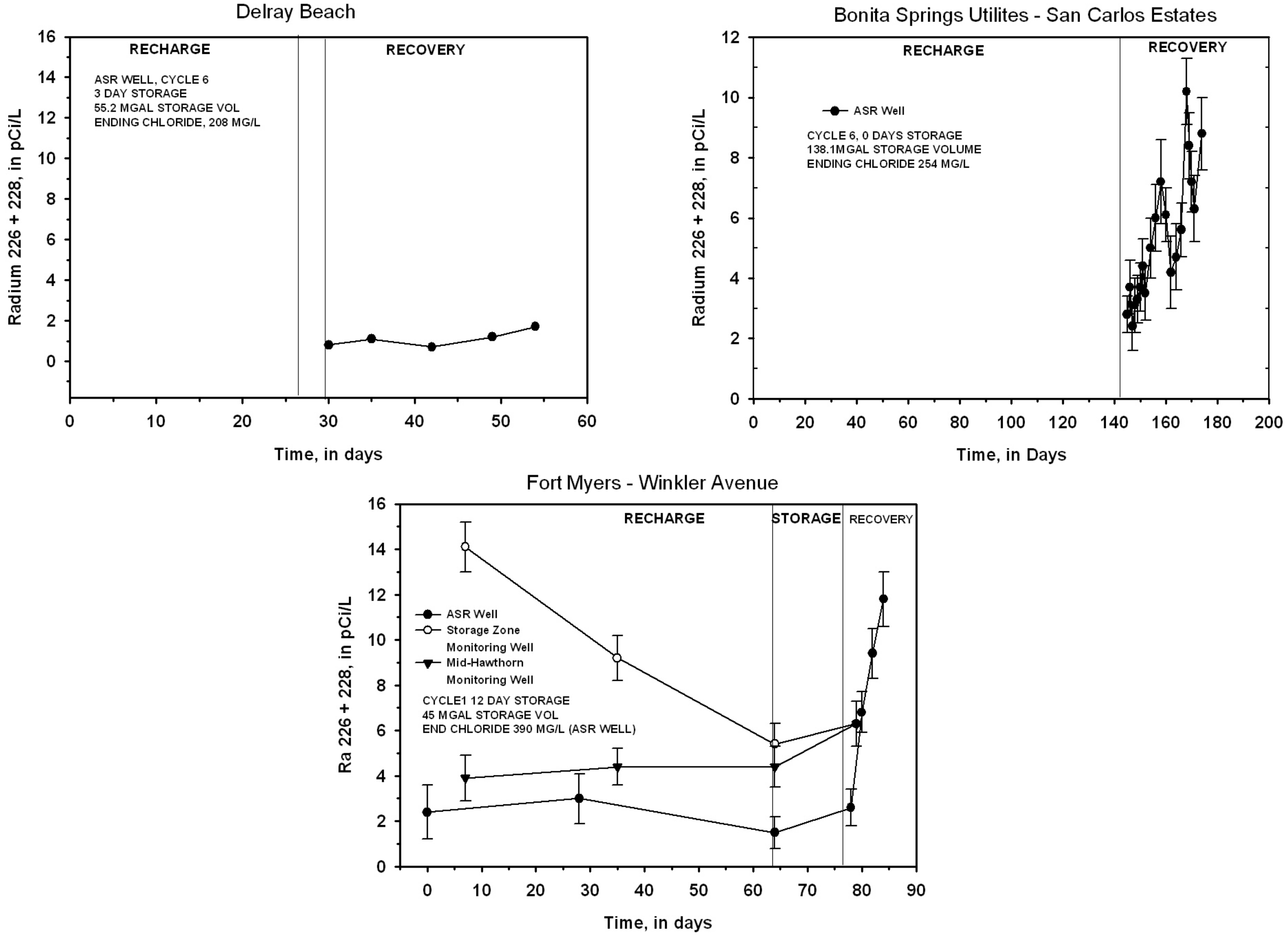

Figure 6. Radium isotope activity measured during cycle tests in ASR and monitoring well samples

Arsenic

Arsenic concentrations that exceeded past and present Federal MCLs have been documented at ASR systems operating to the North of this study area, in Hillsborough and Charlotte Counties (Arthur et al. 2001; Williams et al. 2002). Arsenic analyses have been performed at many ASR systems surveyed here, particularly in Lee and Charlotte Counties where hydrogeologic and lithologic characteristics may be similar to more northern sites. Effective January 2005, the State of Florida criterion for arsenic in Class I and Class III waters will decrease from 50 µg/L to 10 µg/L. The Federal MCL for arsenic also will decrease to 10 µg/L effective January 2006 (Code of Federal Regulations 2001). In preparation, most Florida water treatment plants are revising arsenic analysis methodology to quantify lower arsenic concentrations.

Three analytical methods have been used during the past decade to quantify arsenic concentrations in drinking water:

a. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES); USEPA method 200.7), with which arsenic can be quantified at low concentrations (approximately 10 to 20 µg/L) on certain instruments.

b. ICP-Mass Spectrometry (ICP-MS); USEPA method 200.8), with which arsenic can be quantified at the parts per trillion level.

c. Graphite furnace atomic absorption (GFAA); USEPA methods 206.2 and 206.3), with which arsenic can be quantified below 5 µg/L.

The USEPA has withdrawn standard method 200.7 (ICP-AES) for analysis of arsenic in drinking water, effective 2006.

To estimate whether arsenic concentrations exceed the new drinking-water MCL (10 µg/L) during cycle tests at South Florida ASR systems, existing data must be interpreted in the context of analytical method and its reported minimum detection limit (MDL) (Table 4). An analysis that is reported as "below detection level" may still exceed the arsenic MCL if that analysis was performed using ICP-AES with relatively high MDL. In contrast, if arsenic was not detected using the GFAA or ICP-MS methods, with MDLs at or below 5 µg/L, then it can be reasonably concluded that arsenic concentrations are in compliance with the drinking-water MCL.

Of the eleven (11) ASR systems considered in this report, arsenic was analyzed in cycle test samples at seven (7) (Table 4). All seven ASR systems analyzed arsenic using the graphite furnace atomic absorption method, with an MDL of 3 to 5 µg/L. Of those seven ASR systems using the appropriate analytical method, two ASR systems (Lee County – Olga and Marco Lakes, Collier County; Figure 7) showed arsenic concentrations in recovered water samples that exceeded the arsenic MCL. The Marco Lakes – Expanded ASR system has three ASR wells, of which two showed arsenic concentrations that sometimes exceeded the MCL during recovery.

Table 4
Comparison of Analytical Methods for Arsenic and Minimum Detection Limit Among Sites Reporting Arsenic Concentrations

County	Site	Arsenic Detections	Method of Arsenic Analysis	Reported Minimum Detection Limit	Dates of Analyses	Note
Palm Beach	Boynton Beach		Not analyzed	--	1993-2000	
	Delray Beach	(X)	GFAA; USEPA 206.2	0.5 ppb	2000-2001	
Broward	BCOES WTP 2A	O	GFAA; USEPA 206.2	10 ppb	1996-1997	Background WQ only
	Fiveash WTP	O	GFAA; USEPA 206.3	2.2 ppb	1998	Recharge WQ only
	Sunrise/Springtree		Not analyzed	--	1997-2002	
Dade	MDWASD West	O	ICP-AES; USEPA 200.7	50 ppb	1998	Background WQ only
	MDWASD Southwest	(X)	GFAA; USEPA 206.2	10 ppb	1998	Background WQ only
Lee	Bonita Springs/San Carlos Estates	(X)	GFAA; USEPA 206.2	3.2 ppb	1999-2001	
	Corkscrew ASR		Not analyzed	--	1995-1996	
	Corkscrew – Expanded	(X)	GFAA; USEPA 206.3	3 ppb	2001-2002	
	Fort Myers – Winkler Avenue	(X)	GFAA; USEPA 206.3	10 ppb (5 ppb)	1999 (2001)	
		(X)	ICP-MS; USEPA 200.8	0.4 ppb	1999	
	North Reservoir	(X)	GFAA; USEPA 206.3	3 ppb	2001-2003	
	Olga	(X)	GFAA; USEPA 206.3	3 ppb	2001-2003	
Collier	Manatee Road	O	ICP-AES; USEPA 200.7	50 ppb	2002-2003	Recharge WQ only
	Marco Lakes	O	GFAA; USEPE 206.2	3.2 ppb	1998-1999	Recharge & Background WQ only
	Marco Lakes – Expanded	(X)	GFAA; USEPA 206.2	3.2 ppb	2001-2002	

Note: All data were obtained during cycle tests except those designated O, which are represented by a limited (<5) number of analyses. (X) = 88% of all reported concentrations are below minimum detection limit. MW = monitoring well; ASR = recharge well; WQ = water quality; GFAA = graphite furnace atomic absorption; ICP-AES = inductively coupled plasma-atomic emission spectroscopy; ICP-MS = inductively coupled plasma-mass spectroscopy.

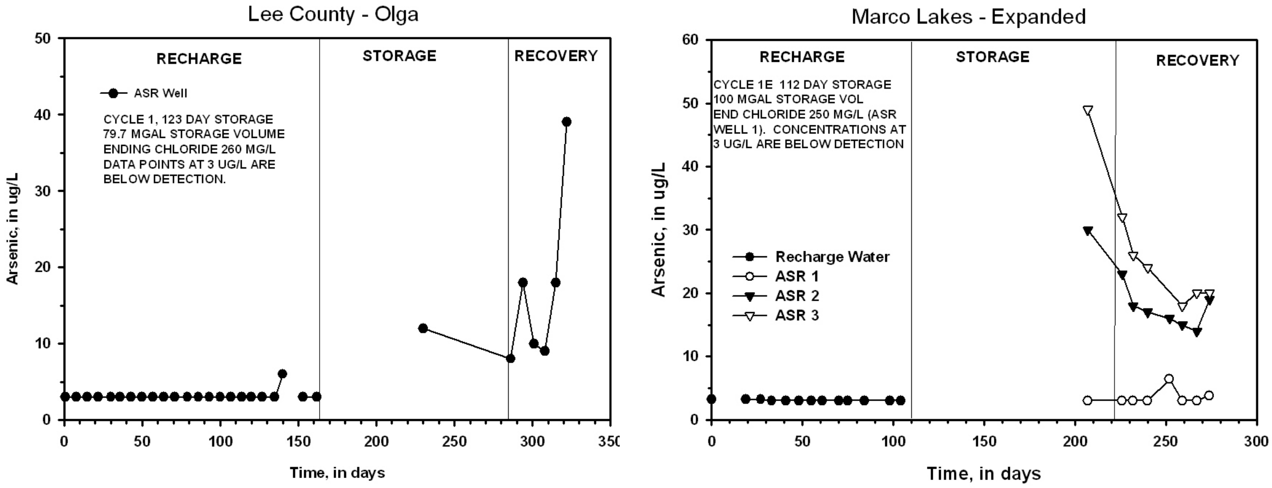

Figure 7. Arsenic concentrations measured during cycle tests in ASR well samples

Total trihalomethanes

Total trihalomethanes (TTHMs) are a class of disinfection by-products (DBPs). TTHM molecules are formed during the water treatment process by the reaction of halogen gases (bromine and chlorine) with naturally occurring dissolved organic matter. TTHM concentration is the sum of chloroform, bromoform, bromodichloromethane, and dibromochloromethane. Chloroform and bromodichloromethane are classified as probable human carcinogens (Toxnet 2003). Regulation of TTHMs in drinking water is specified by the Stage I disinfection by-product rule (a revision of the Safe Drinking Water Act; USEPA 2001). The MCL for TTHMs is 80 µg/L. The transport and fate of disinfection by-products in ASR systems is the subject of several investigations to quantify whether TTHM concentrations decrease or increase during storage (Miller et al. 1993; Thomas et al. 2000; Fram et al. 2003). Apparently, TTHMs concentrations in the aquifer are controlled by several physical and geochemical factors, including the following:

a. Residual chlorine and bromine in recharge water.

b. Redox environment in the aquifer.

c. Extent of mixing between recharge and native water during recovery.

Biodegradation does not appear to be a significant mechanism to reduce TTHM concentrations in aquifers studied thus far (Thomas et al. 2000; Fram et al. 2003).

Trends in TTHM concentrations depend on the method of water treatment at each ASR system, rather than on geologic or hydraulic factors. TTHM concentrations typically were greatest in recharge water samples from the ASR well, and declined during the rest of the cycle test (Figure 7). TTHM concentrations exceeded the MCL in recharge water samples at the Marco Lakes, Olga, and North Reservoir sites during cycle tests 1 or 2 (Figure 8), but concentrations declined to levels less than the MCL during recovery at all sites.

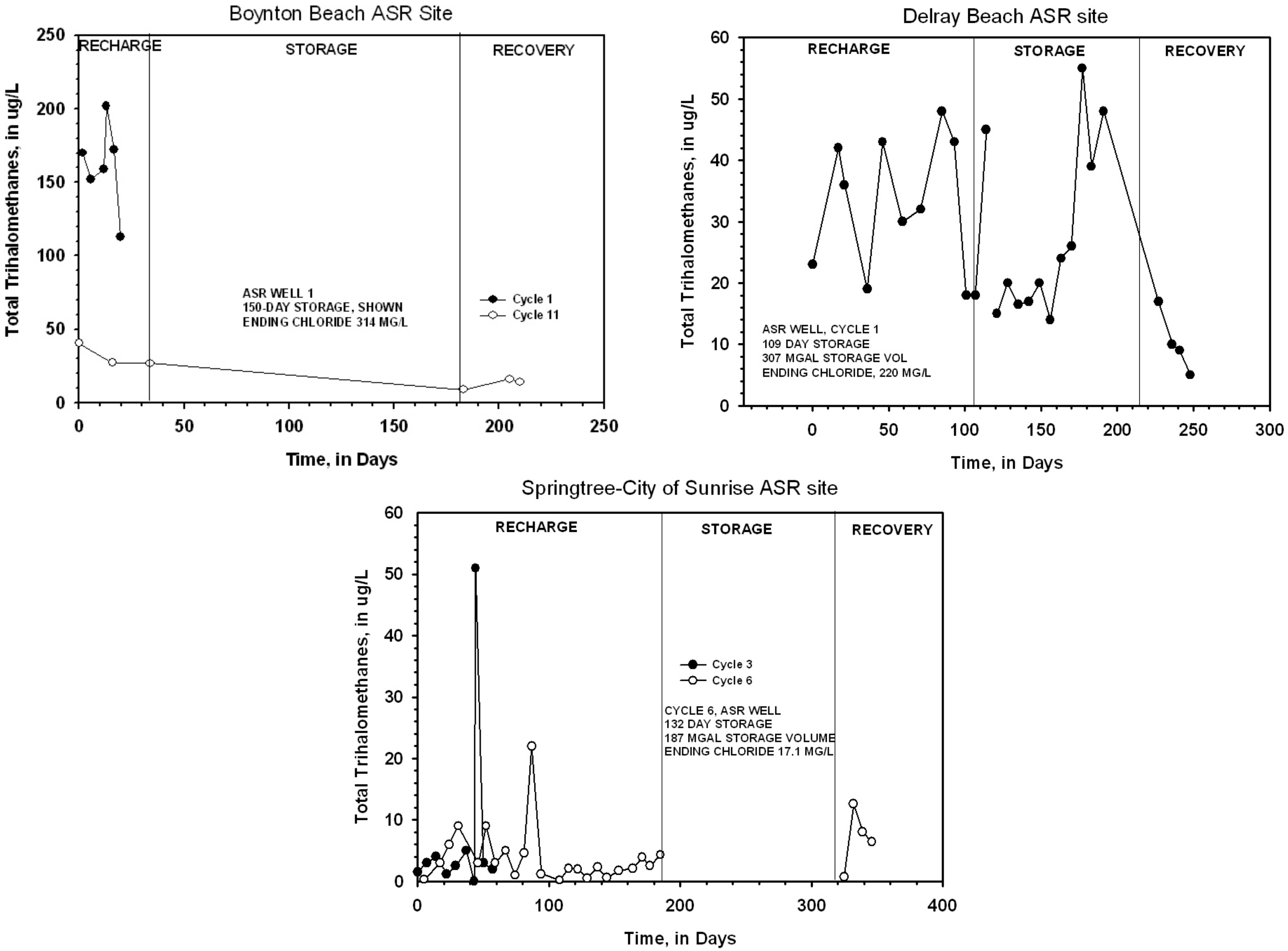

Figure 8. Total trihalomethanes concentrations measured during cycle tests at ASR and monitoring well samples (Sheet 1 of 3)

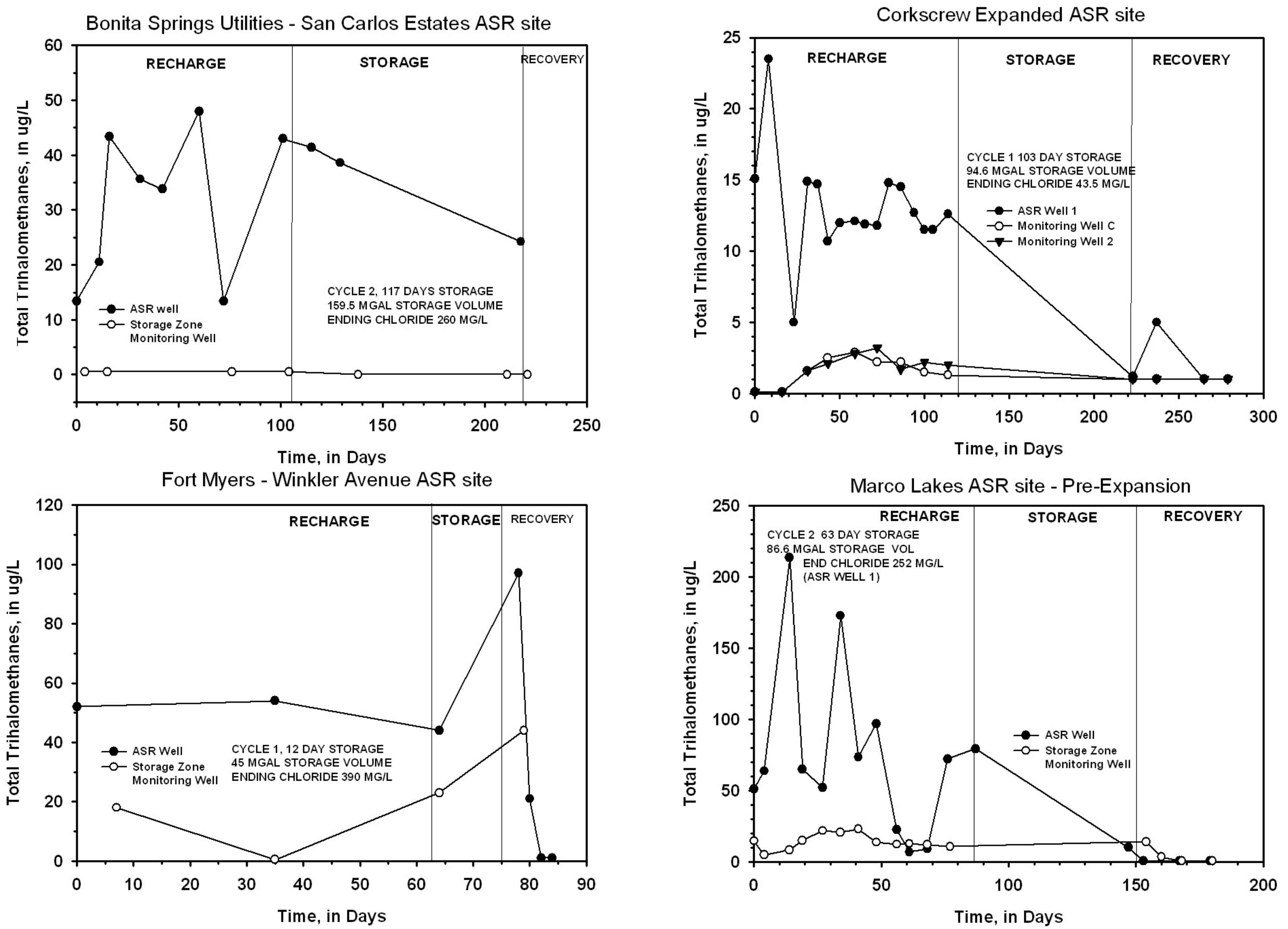

Figure 8. (Sheet 2 of 3)

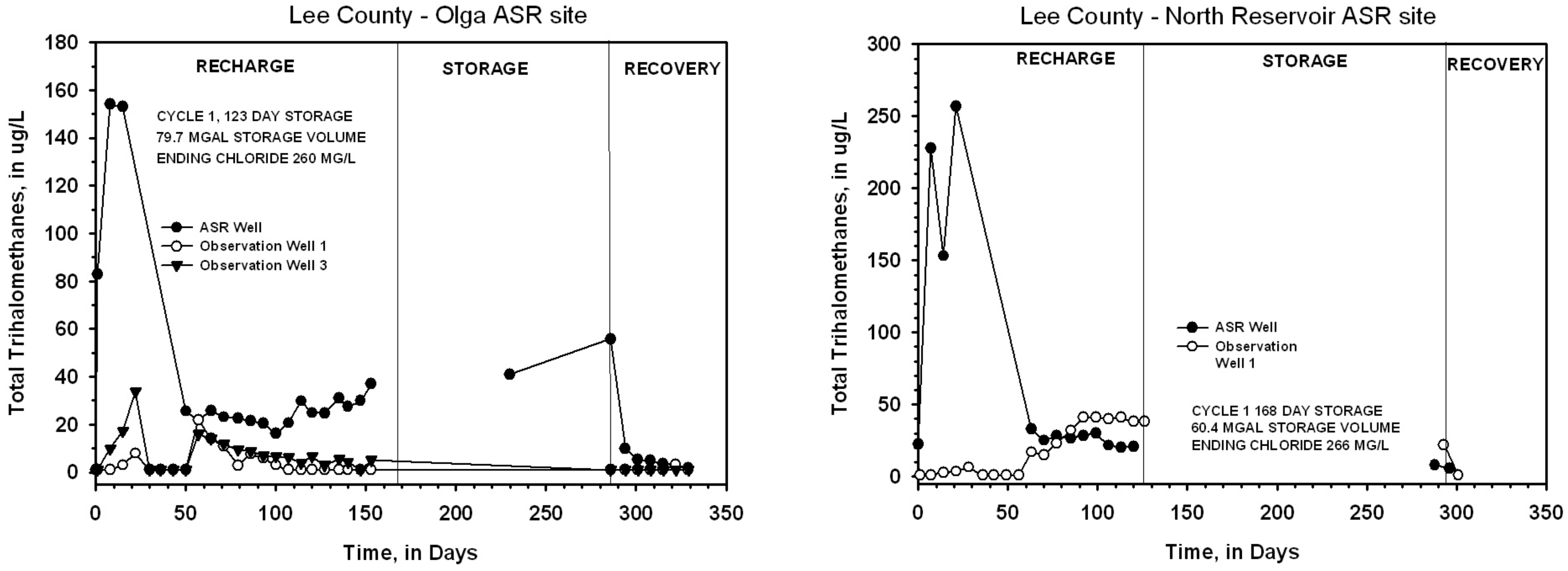

Figure 8. (Sheet 3 of 3)

Existing cycle test data suggest that TTHMs are not produced during storage in South Florida ASR systems. The best data to show changing TTHM concentrations would be obtained from proximal monitoring wells sampled frequently during storage, or at least at the beginning and end of storage. Monitoring well samples from Springtree – City of Sunrise, Bonita Springs, Corkscrew – Expanded, Marco Lakes, Olga, and North Reservoir ASR systems show TTHM concentrations less than 50 μg/L throughout the cycle test (Figure 8). TTHM concentrations in these samples do not increase or remain constant during storage. Monitoring wells are located between 66 and 229 m (217 and 750 ft) from the ASR well at theses sites. TTHM formation during storage may be suggested at the Delray Beach and Fort Myers – Winkler Avenue ASR systems; however, TTHM concentration trends are defined by fewer data points, or data were measured in ASR well samples and may not be representative of aquifer conditions. Because South Florida ASR systems indicate that TTHM formation in storage zones is not significant, no temporal trends could be defined.

3 Conclusions

Water-quality changes were interpreted from existing cycle test data obtained from 11 treated surface-water ASR systems located in South Florida. Six ASR systems are located along the lower east coast (Palm Beach and Broward Counties); five ASR systems are located in Lee and Collier Counties. These diverse data sets were the basis for interpretations of water-quality changes during ASR cycles in different regions. Quantification of temporal changes in water-quality was limited because data were not sufficient. Temporal changes consist of reaction rates for a few major geochemical reactions. Analytes that are reactants or products in major geochemical reactions are: dissolved oxygen, nitrate and ammonia, sulfate and hydrogen sulfide, gross alpha radioactivity and radium isotopes, and total trihalomethanes.

Ideally, major geochemical reactions and reaction rates are interpreted from analyses of samples collected during storage from monitoring wells. These samples provide a more quantitative record of reaction between water, aquifer material, and microbial activity in the aquifer environment than do samples from the ASR well. Degassing of volatiles and well-bore mixing during recovery in the ASR well will obscure ground-water concentrations that characterize the aquifer environment. For these reasons, ASR and monitoring well data were interpreted for trends in water-quality changes. Estimates of reaction rates or half-lives are based only on data obtained from monitoring wells during storage.

Dissolved oxygen (DO) is reduced during cycle testing at ASR systems in Lee and Collier Counties. DO concentration is reduced from 4- to 8-mg/L saturation to approximately 2 mg/L, as measured throughout cycle tests in ASR well samples. DO concentrations do not vary significantly in samples from monitoring wells located 200 to 750 ft from the ASR well. Apparently, DO is consumed along the flowpath prior to reaching the ASR well during recharge and storage. Half-lives calculated for DO are 1 day (Fort Myers – Winkler Avenue) and 23 days (Lee County – Olga). Concentrations of 1 to 2 mg/L DO in samples collected during storage and recovery suggest that oxygen diffusion during sample measurement and collection may have occurred.

Nitrate reduction to ammonia (denitrification) is suggested from increasing ammonia concentrations measured at three sites: Boynton Beach, Fiveash, and Springtree – City of Sunrise. Ammonia concentrations in recovered water samples from the ASR wells at these sites exceed the Florida Classes I and III surface water-quality criterion (0.020 mg/L), although concentrations of volatile ammonia will likely decline by degassing during postrecovery water treatment.

Where measured, nitrate concentrations in all samples are well below the Federal MCL of 10 mg/L.

Sulfate concentrations vary during cycle testing at all ASR systems. However, the processes that control sulfate concentration probably differ among all sites considered. Sulfate concentration increases during cycle testing as the result of dissolution of gypsum ($CaSO_4$) in aquifer material, and/or mixing of recharged water with seawater or brackish native ground water. Although sulfate concentration increases through the cycle test, concentrations of recovered water in ASR well samples do not exceed the Federal MCL of 250 mg/L.

Limited hydrogen sulfide data suggest that microbe-mediated sulfate reduction occurs during storage. Hydrogen sulfide concentrations measured at Fiveash (432-day storage) and Corkscrew (103-day storage) monitoring wells increase during storage, although statistical support for an increasing trend is weak. It may be necessary to use laboratory methods rather than a field test kit for hydrogen sulfide data, because concentrations are likely to be near or below the detection limit (0.10 mg/L) for the field test method.

Gross alpha radioactivity and radium isotope activities show pronounced regional trends. Elevated gross alpha radiation and radium isotope activity occurs at those ASR systems in Southwest Florida that use permeable zones within the phosphate-rich Lower Hawthorn Group as the storage zone, and to a lesser extent the Suwannee Limestone. Gross alpha activity in recovered water samples from ASR wells exceed the Federal MCL (15 picocuries/L) at all ASR systems in Lee and Collier Counties except Corkscrew and North Reservoir. No gross alpha data were available for ASR systems located in Palm Beach and Broward Counties.

Radium isotope ($Ra^{226} + Ra^{228}$) activity data are rare compared to gross alpha data. Because radium isotope activity is a significant proportion of gross alpha activity, similar trends are observed with both constituents. Radium isotope activities as measured in ASR well samples exceed the Federal MCL at Bonita Springs Utilities and Fort Myers – Winkler Avenue ASR systems. Limited data from one site (Delray Beach) suggests that radium isotope activities do not exceed the MCL in ASR systems of the lower east coast.

Few ASR systems surveyed here show increasing arsenic concentration during cycle testing. Seven (7) ASR systems (of eleven (11) surveyed) analyzed arsenic using the graphite furnace atomic absorption method, for quantifying concentrations below the arsenic MCL (10 µg/L). Of these seven ASR systems, two (Olga and Marco Lakes – Expanded) show arsenic concentrations in recovered water that exceeded the arsenic MCL. The storage zones of these two sites are in the Suwannee Limestone (Olga) and the Arcadia Formation (Marco Lakes), at depths of approximately 224 to 280 m (735 to 920 ft).

Trends in TTHM concentrations reflect water treatment strategies applied at each ASR system. The highest TTHM concentrations are measured during recharge in ASR well samples. Generally, TTHM concentrations decline through the cycle test, so that concentrations are below the Federal MCL (80 µg/L) in recovered water from both ASR and monitoring wells. Increased TTHM concentrations during storage were observed only in ASR well samples at the

Delray Beach and Fort Myers – Winkler Avenue ASR systems, but these data probably do not represent aquifer conditions.

Data and interpretations presented here provide qualitative guidance for sampling design and analysis during CERP ASR pilot cycle tests. However, there are some limitations to these data sets, identified as follows:

a. Major dissolved anions and cations are not analyzed consistently in each sample of a cycle test so that charge balance errors cannot be calculated for quality assurance

b. Qualitative trends in regional water-quality changes can be inferred from these data but only for particular analytes (radium isotopes and gross alpha radioactivity). Examination of sulfate and hydrogen sulfide cycles will require sulfur isotope analyses of specific phases in water and rock samples.

c. Few data sets comprise samples from both ASR and monitoring wells through a complete cycle test. Ideally, reaction rates of major geochemical reactions can be calculated from data obtained during storage from monitoring wells. Reaction rates could only be estimated for dissolved oxygen reduction at a few sites, owing to insufficient data for quantitative analysis.

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Appendix A
Cycle Test Schedules

Table A1
Marco Lakes, Collier County

Cycle/Phase	Begin	End	Duration Days	Volume (Mgal)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
1/Recharge	6/26/1997	8/4/1997	54	19.7				ViroGroup, Inc. (1998)[1]
1/Storage	--	--	0					
1/Recovery	8/4/1997	8/14/1997	10		4.41	22.4	252	
		8/19/1997	15		6.045	30.7	384	
2/Recharge	8/21/1997	11/17/1997	87	86.6				ViroGroup, Inc. (1998)
2/Storage	11/17/1997	1/19/1998	63					
2/Recovery	1/19/1998	2/10/1998	22		3.801	4.4	252	
					14.81	17.1	356	
3/Recharge	3/5/1998	3/31/1998	26	21.045				ViroGroup, Inc. (1998)
3/Storage	3/31/1998	4/2/1998	2					
3/Recovery	4/2/1998	4/3/1998	1		6.992	33.2	250	
		4/27/1998	25		15.808	75.1	385	
4/Recharge	9/1/1998	1/13/1999		110.9				Water Resource Solutions (1999)
4/Storage	1/13/1998	4/8/1999	83					
4/Recovery	4/8/1999	6/21/1999	68		38.9	35.1	250	
					55	49.6	350	
5/Recharge	8/19/1999	1/6/2000	139	132				Water Resource Solutions (2000)
5/Storage	1/6/2000	4/17/2000	101					
5/Recovery	4/17/2000	7/10/2000	84		67	50.8	350	
1E/Recharge	8/24/2001	12/11/2001	109	100 (ASR-1) 130 (ASR-2) 95 (ASR-3)				3 ASR wells (ASR-1,-2,-3). ASR-2,-3 recharge began 8/24/2001. ASR-1 recharge began 10/4/2001
1E/Storage	12/11/2001	4/2/2002	112					
1E/Recovery	4/2/2002	6/24/2002	83		55 (ASR1)	55	250	Water Resource Solutions (2002c)
					49 (ASR-2)	37.7	350	
					38.5 (ASR-3)	40.5	350	

Note: Cycle test schedule and performance characteristics for the Marco Lakes ASR system, Collier County. Cycles 1 through 5 were conducted prior to expansion of production facilities. Cycle 1E was conducted after site expansion from one to three ASR wells.

[1] References cited in Appendix A can be found in the References section following the main text.

Table A2
Fort Myers – Winkler Avenue ASR Site, Lee County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
1/Recharge	11/15/2000	1/17/2001	63	45				CH2M HILL (2002b)
1/Storage	1/17/2001	1/29/2001	12					
1/Recovery	1/29/2001	2/4/2001	6		4.5	10	390	

Table A3
North Reservoir ASR Site, Lee County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
Recharge	2/25/2000	3/10/2000	14	6.179				FDEP monthly operating reports
Storage	3/11/2000	3/17/2000	7					
Recovery	3/17/2000	3/18/2000	1		0.6	9.7	250	
1/Recharge	7/12/2001	11/13/2001	125	60.4				Water Resource Solutions (2002a) and monthly operating reports
1/Storage	11/13/2001	4/29/2002	168					
1/Recovery	4/29/2002	5/14/2002	15		6.6	11	266	
2/Recharge	6/24/2002	2/25/20031	209	127.04				D. Acquaviva, written comm. (8 Jul 2003)
2/Storage	2/25/2003	4/16/2003	50					
2/Recovery	4/16/2003	7/31/2003	103		23.73	18.6[1]	272 (7/1/2003)	

[1] Plugged ASR well reduced performance during July 2003.

Table A4
Olga Water Treatment Plant, Lee County ASR System

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
1/Recharge	7/17/2001	12/27/2001	162	79.7				Water Resource Solutions (2002c) plus monthly operating reports
1/Storage	12/27/2001	4/29/2002	123					
1/Recovery	4/29/2002	6/12/2002	44		18.9	24	260	
2/Recharge	6/24/2002	1/28/2003	215	129.02				D. Acquaviva, written comm. (8 Jul 2003)
2/Storage	1/29/2003	5/7/2003	98					
2/Recovery	5/7/2003	7/28/2003	82		35.09	29.2	202 (7/22/2003)	

Table A5
Bonita Springs Utilities – San Carlos Estates ASR System

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
1/Recharge	12/30/1999	5/23/2000	144	138.149				CH2M HILL (2000c)
1/Storage	--	--	0					
1/Recovery	5/23/2000	6/28/2000	36		4.375	3.17	254	
2/Recharge	9/14/2000	(12/27/2000)[1]	104	159.5				M. McNeal, written comm. (2 Jul 2003)
2/Storage	(12/27/2000)	(4/23/2001)	117					
2/Recovery	4/23/2001	5/4/2001	10		9.7	6.1	260	

[1] Cycle 2 recharge rate reduced from 1-2 MGD to 0.216 MGD from Dec 2000 to April 23, 2001.

Table A6
Corkscrew ASR System, Lee County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
1/Recharge	10/25/1995	11/1/1995	7	2.001				Reese (2002); Viro Group, Inc. (1997)
1/Storage	11/2/1995	11/3/1995	1					
1/Recovery	11/4/1995	11/14/1995	10		2.963	148	Not reported	
2/Recharge	2/14/1996	4/30/1996	76	31.3				Reese (2002); Viro Group, Inc. (1997)
2/Storage	5/1/1996	6/3/1996	35					
2/Recovery	6/4/1996	10/4/1996	72		22.8	72.8	Not reported	
3/Recharge	10/7/1996	12/10/1996	63	26.1				Reese (2002); Viro Group, Inc. (1997)
3/Storage	12/10/1996	1/8/1997	30					
3/Recovery	1/9/1997	2/12/1997	34		19.8	75.8	Not reported	
Postexpansion Cycle Tests								
1/Recharge	8/7/2000	12/5/2000	120	94.617				Water Resource Solutions (2001)
1/Storage	12/6/2000	3/19/2001	103					
1/Recovery	3/19/2001	5/18/2001	60		82.219	86.9	43.5 [1]	
2/Recharge	7/24/2001	11/15/2001	114	107.463				Water Resource Solutions (2002d)
2/Storage	11/15/2001	3/20/2002	115					
2/Recovery	3/20/2002	5/17/2002	58		106.747	99	43 [2]	

Note: Postexpansion tests were conducted after site expansion from two to five ASR wells.

[1] Chloride measured on 14 May 01, 4 days prior to the end of recovery.

[2] Chloride measured on 16 May 02, 1 day prior to the end of recovery.

Table A7
Broward County Office of Environmental Services 2A (BCOES2A) Water Treatment Plant ASR System

Cycle/Phase	Begin	End	Duration days	Volume (Mgal) Recharge	Volume (Mgal) Recovery	Recovery Efficiency %	Recovery Chloride mg/L	Reference
1/Recharge	7/9/1998	7/19/1998	10	22.13				CH2M HILL (1999); Hazen and Sawyer (2002a)
1/Storage	--	--	0					
1/Recovery	7/20/1998	7/21/1998	1		1.5	6.8	168	
2/Recharge	7/27/1998	10/26/1998	91	195.835				CH2M HILL (1999); Hazen and Sawyer (2002a)
2/Storage	--	--	0					
2/Recovery	10/26/1998	11/12/1998	17		36.646	18.7	240	
3/Recharge	11/13/1998	2/8/1999	88	185.94				CH2M HILL (1999); Hazen and Sawyer (2002a)
3/Storage	2/9/1999	2/17/1999	9					
3/Recovery	2/18/1999	3/11/1999	21		62.625	33.7	227	

Table A8
Fiveash Water Treatment Plant ASR System, Broward County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
1/Recharge	10/12/1999	10/22/1999	11	19.499				Reese (2002); Hazen and Sawyer (2002b)
1/Storage	--	--	0					
1/Recovery	10/23/1999	10/23/1999	1		1.04	5.3	212	
2/Recharge	10/25/1999	12/3/1999	40	75.036				Reese (2002); Hazen and Sawyer (2002b)
2/Storage	--	--	0					
2/Recovery	12/3/1999	12/6/1999	2		4.7	6.2	160	
3a/Recharge	12/7/1999	3/29/2000	112	224.445				Reese (2002); Hazen and Sawyer (2002b)
3a/Storage	3/30/2000	6/5/2001	443					
3a/Recovery	--	--	0		0	--	--	
3b/Recharge	6/6/2001	2/1/2002	229	413.534				Reese (2002); Hazen and Sawyer (2002b)
3b/Storage [1]	--	--	0					
3b/Recovery	2/2/2002	3/21/2002	48		54.2	13.1	244	
4/Recharge	6/19/2002	7/18/2002	30	56.097				Hazen and Sawyer (2003); monthly operating reports (2002)
4/Storage	--	--	0					
4/Recovery	7/19/2002	10/2/2002	75		34.3	61	260	
5/Recharge	10/4/2002	11/4/2002	30	61.803				Hazen and Sawyer (2003); monthly operating reports (2002)
5/Storage	--	--	0					
5/Recovery	11/5/2002	1/2/2003	59		37.2	60	242 (1/31/02)	
6/Recharge	5/28/2003	9/24/2003	119	240.6				J. Cargill; written comm. (3 Feb 2004); monthly operating reports (2003)
6/Storage	--	--	0					
6/Recovery	9/24/2003	12/28/2003	95		54.8	22.7	260	

[1] Pump out of service 8/17/2001 to 9/10/2001; injection commenced 9/11/2001 through 3/21/2002.

Table A9
Springtree – City of Sunrise ASR System, Broward County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
1/Recharge	7/29/1999	8/17/1999	19	20				Montgomery Watson Harza (2002)
1/Storage			0					
1/Recovery	8/18/1999	8/21/1999	3		4	28	61	
2/Recharge	8/22/1999	9/30/1999	39	40				Montgomery Watson Harza (2002)
2/Storage	9/30/1999	10/2/1999	2					
2/Recovery	10/2/1999	10/12/1999	10		11	30	213	
3/Recharge	10/13/1999	11/24/1999	39 (intermittent)	41				Montgomery Watson Harza (2002)
3/Storage			0					
3/Recovery	11/25/1999	12/9/1999	14		15	40	220	
4/Recharge	12/10/1999	2/10/2000	62 (intermittent)	40				Montgomery Watson Harza (2002)
4/Storage	2/11/2000	3/12/2000	29					
4/Recovery	3/13/2000	3/27/2000	14		15	42	222	
5/Recharge	3/28/2000	9/23/2000	107 (intermittent)	103				Montgomery Watson Harza (2002)
5/Storage	9/24/2000	10/23/2000	29					
5/Recovery	10/23/2000	11/23/2000	31		32	30	218	
6/Recharge	11/24/2000	5/31/2001	188	187				Montgomery Watson Harza (2002) and monthly operating reports
6/Storage	6/1/2001	10/9/2001	130					
6/Recovery	10/9/2001	10/31/2001	130		23	22	171	

Table A10
Delray Beach ASR System, Palm Beach County

Cycle/Phase	Begin	End	Duration days	Sum Duration days	Volume (Mgal)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
					Recharge	Recovery			
Target Storage Volume Develop.	5/23/2000	8/24/2000	83	83	250				
1/Recharge	8/25/2000	9/15/2000	21		63				CH2M HILL (2002a)
1/Storage	9/16/2000	1/2/2001	110						
1/Recovery	1/11/2001	1/29/2001	18	149		50	79	225	
2/Recharge	1/30/2001	2/17/2001	18		50				CH2M HILL (2002a)
2/Storage	2/17/2001	2/21/2001	4						
2/Recovery	2/21/2001	3/10/2001	17	39		47	94	225	
3/Recharge	3/13/2001	4/1/2001	18		48				CH2M HILL (2002a)
3/Storage	4/1/3001	4/2/2001	1						
3/Recovery	4/2/2001	4/16/2001	14	33		38	71	200	
Target Storage Volume Develop.	4/18/2001	5/7/2001	19	19	50				
4/Recharge	5/7/2001	5/29/2001	22		52				CH2M HILL (2002a)
4/Storage	--	--	--						
4/Recovery	5/29/2001	6/19/2001	22	44		54	104	170	
Target Storage Volume Develop.	6/19/2001	7/4/2001	15	15	20				
5/Recharge	7/4/2001	7/24/2001	20		49				CH2M HILL (2002a)
5/Storage	--	--							
5/Recovery	7/24/2001	8/15/2001	24	44		52	106	170	
6/Recharge	8/22/2001	9/17/2001	26		70.567				D. Stryjek, oral comm. (31 Mar 2003)
6/Storage	9/18/2001	9/20/2001	2						
6/Recovery	9/21/2001	10/15/2001	22	50		55.36	78.4	225	
7/Recharge	10/16/2001	11/19/2001	34		73.065				Cycle incomplete-pump failed (D. Stryjek, oral comm. 31 Mar 2003)
7/Storage	--	--	0						
7/Recovery	11/20/2001	11/30/2001	11	45		20.632	--	62	

Table A11
Boynton Beach ASR System, Palm Beach County

Cycle/Phase	Begin	End	Duration days	Volume (Mgal)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
1/Recharge	10/21/1992	11/3/1992	13	12.52				Peter Mazzella, written comm. (9 Apr 2003); CH2M HILL (1993)
1/Storage	--	--	0					
1/Recovery	11/3/1992	11/10/1992	7		9.58	76.5	756	
6/Recharge	2/24/1994	4/21/1994	57	61.19				Monthly operating reports
6/Storage	4/21/1994	6/16/1994	56					
6/Recovery	6/16/1994	7/25/1994	39		47.71	77.9	306	
7/Recharge	7/25/1994	9/7/1994	44	60.06				Monthly operating reports
7/Storage	9/7/1994	19/9/1995	124					
7/Recovery	1/7/1995	2/13/1995	35		20.05	33.3	302	

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14. ABSTRACT

Water-quality changes were interpreted from existing cycle test data obtained from 11 treated surface-water Aquifer Storage Recovery (ASR) systems located in South Florida. Six ASR systems are located along the lower east coast (Palm Beach and Broward Counties), and five ASR systems are located in Lee and Collier Counties. These diverse data sets were the basis for interpretations of water-quality changes during ASR cycles in different regions. These data sets were interpreted to provide guidance for cycle test performance at Comprehensive Everglades Restoration Plan (CERP) ASR pilot sites. ASR and monitoring well data were interpreted for trends in water-quality changes. Estimates of reaction rates or half-lives are based only on data obtained from monitoring wells during storage. Analytes that are reactants or products in major geochemical reactions are: dissolved oxygen, nitrate and ammonia, sulfate and hydrogen sulfide, gross alpha radioactivity and radium isotopes, and total trihalomethanes. Concentrations of these solutes in recovered water samples from recharge/recovery wells were compared to state and Federal water quality regulations to identify regulatory exceedences. Concentrations of arsenic and gross alpha in recovered water sometimes exceeded regulatory criteria at ASR sites in Southwest Florida.

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Arsenic
ASR
Comprehensive Everglades Restoration Plan
CERP
Dissolved oxygen
Everglades
Florida
Floridan Aquifer
Gross alpha
Ground-water quality
Hydrogen sulfide
Nitrate
Radium
Total trihalomethanes
Water quality

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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

Environmental Laboratory

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Final report

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. Specifcially, 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.

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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.

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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 pε, 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 possible 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.

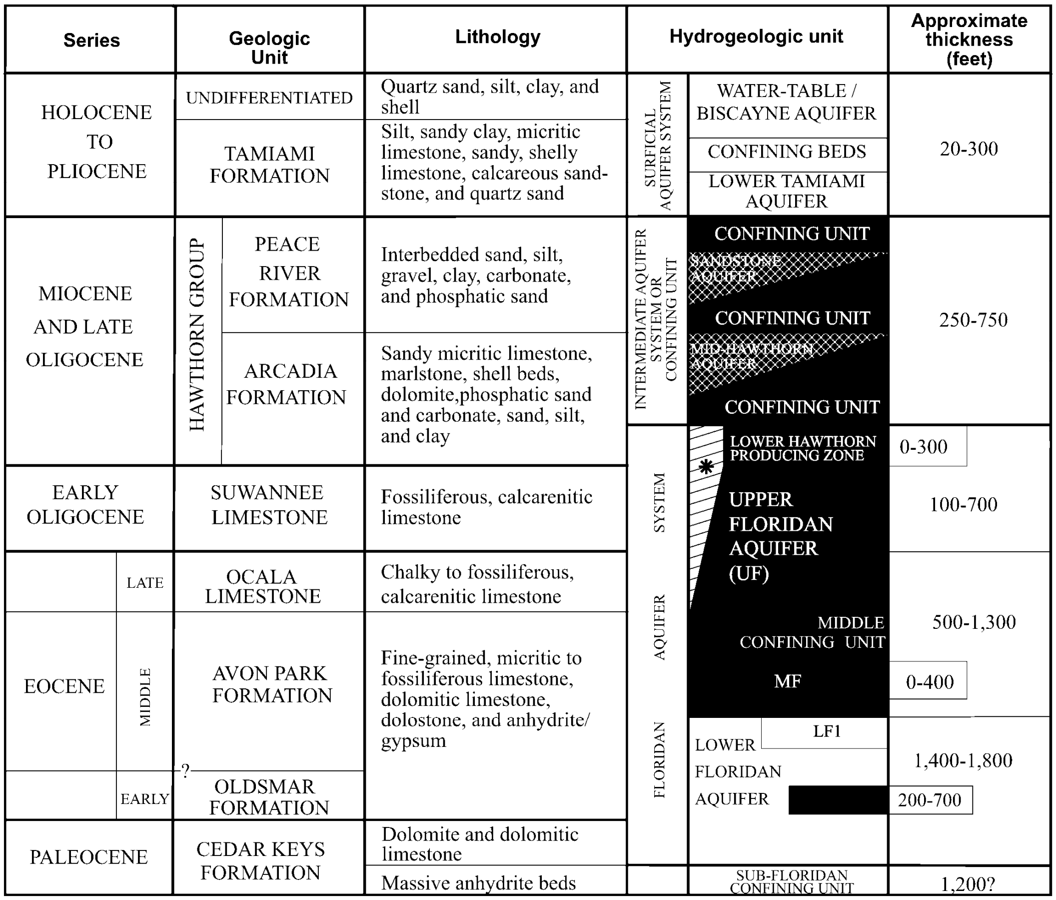
2 Hydrogeologic Setting

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 Memberg 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 Memberg 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 PLIOCENE		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 SANDSTONE AQUIFER CONFINING UNIT	250-750
		HAWTHORN GROUP: ARCADIA FORMATION	Sandy micritic limestone, marlstone, shell beds, dolomite,phosphatic sand and carbonate, sand, silt, and clay		MID-HAWTHORN AQUIFER CONFINING UNIT	
EARLY OLIGOCENE		SUWANNEE LIMESTONE	Fossiliferous, calcarenitic limestone	FLORIDAN AQUIFER SYSTEM	LOWER HAWTHORN PRODUCING ZONE UPPER FLORIDAN AQUIFER (UF)	0-300 100-700
	LATE	OCALA LIMESTONE	Chalky to fossiliferous, calcarenitic limestone		MIDDLE CONFINING UNIT	500-1,300
EOCENE	MIDDLE	AVON PARK FORMATION	Fine-grained, micritic to fossiliferous limestone, dolomitic limestone, dolostone, and anhydrite/ gypsum		MF LOWER FLORIDAN AQUIFER LF1	0-400 1,400-1,800
	EARLY	-?- OLDSMAR FORMATION				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

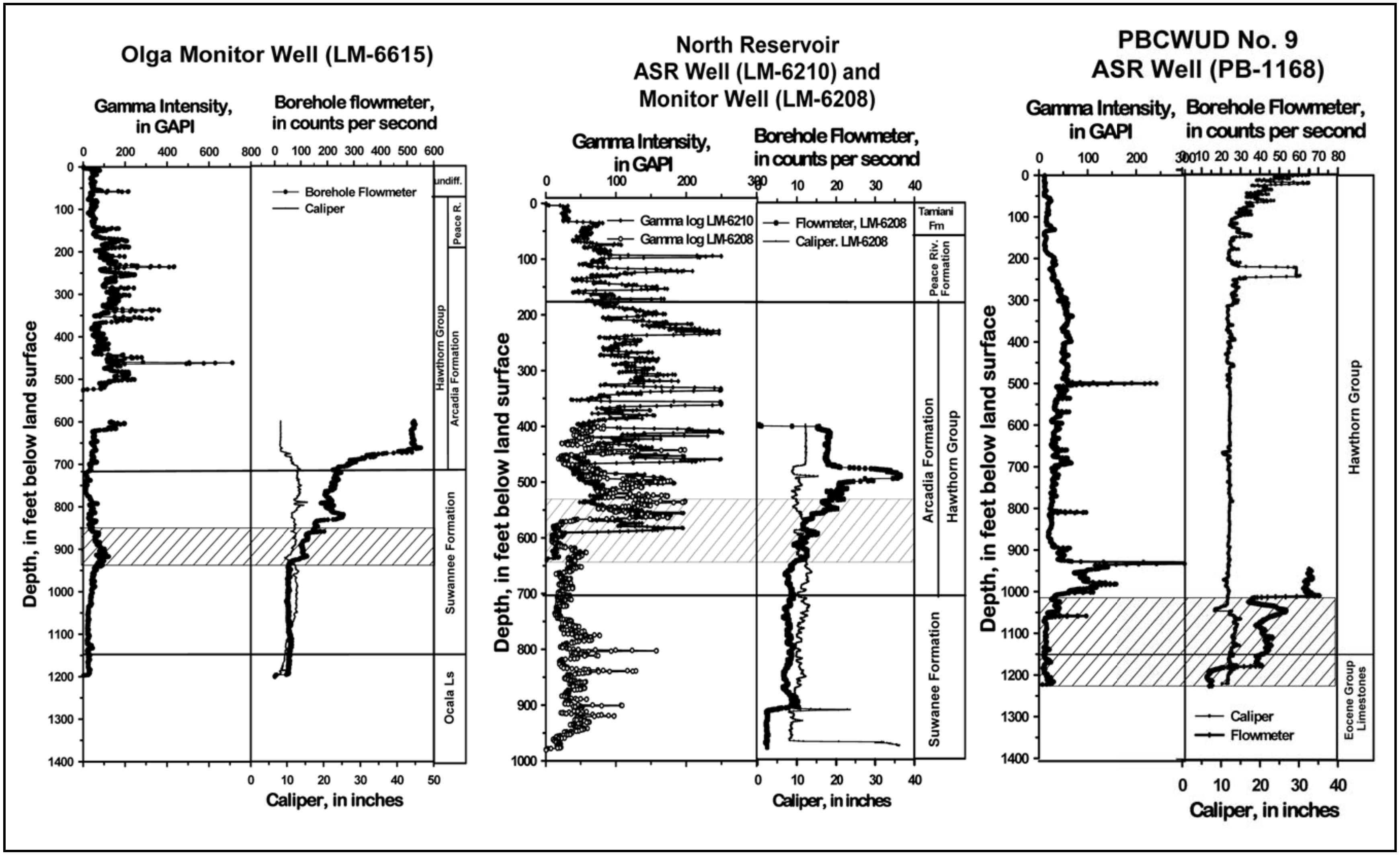


Figure 2. Selected geophysical logs from Olga, North Reservoir, and East Hillsboro (PBCWUD) ASR systems. Stratigraphic picks at Olga and North Reservoir from Water Resource Solutions (2002a,,2002b); East Hillsboro from Reese and Memberg (2000). Geophysical logs from DBHydro database (SFWMD 2004). Gamma 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 occuring 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.

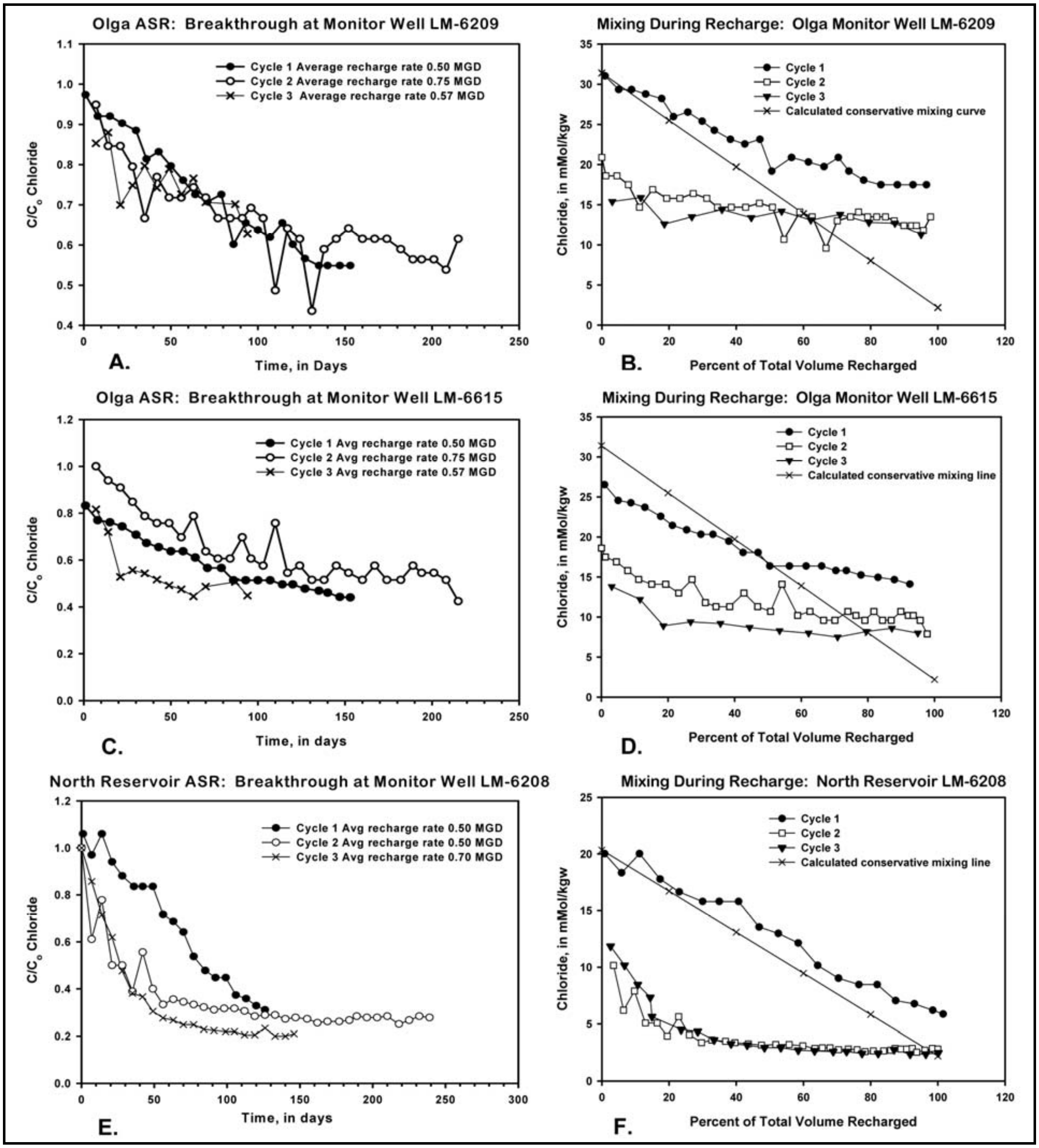


Figure 3. Breakthrough curves and mixing curves during recharge at Olga and North Reservoir ASR systems. Breakthrough curves (A, C, E) are plotted using chloride concentrations measured in monitor wells at Olga (A, 350 ft from ASR well; C, 400 ft from ASR well) and North Reservoir (E, 250 ft from ASR 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.

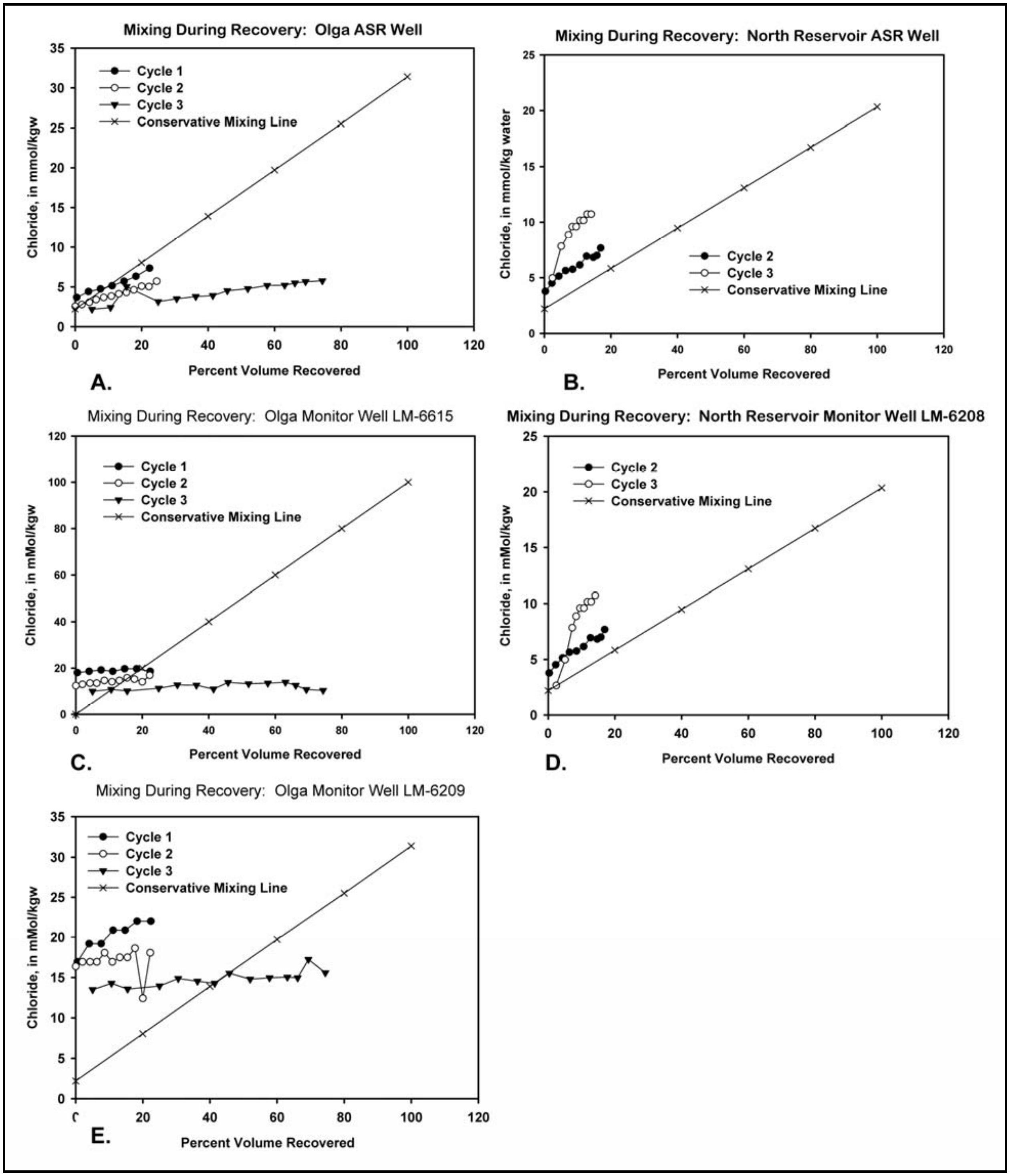


Figure 4. Mixing models during recovery at Olga and North Reservoir ASR systems. Measured chloride concentrations from the Olga ASR well (A) and monitor wells (C, E) are compared to conservative mixing lines for Cycle Tests 1 through 3. Measured chloride concentrations from the North Reservoir ASR (B) 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 CO_2 (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 CO_2 degasses. In this simulation, dissolved CO_2 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 Limestone 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.

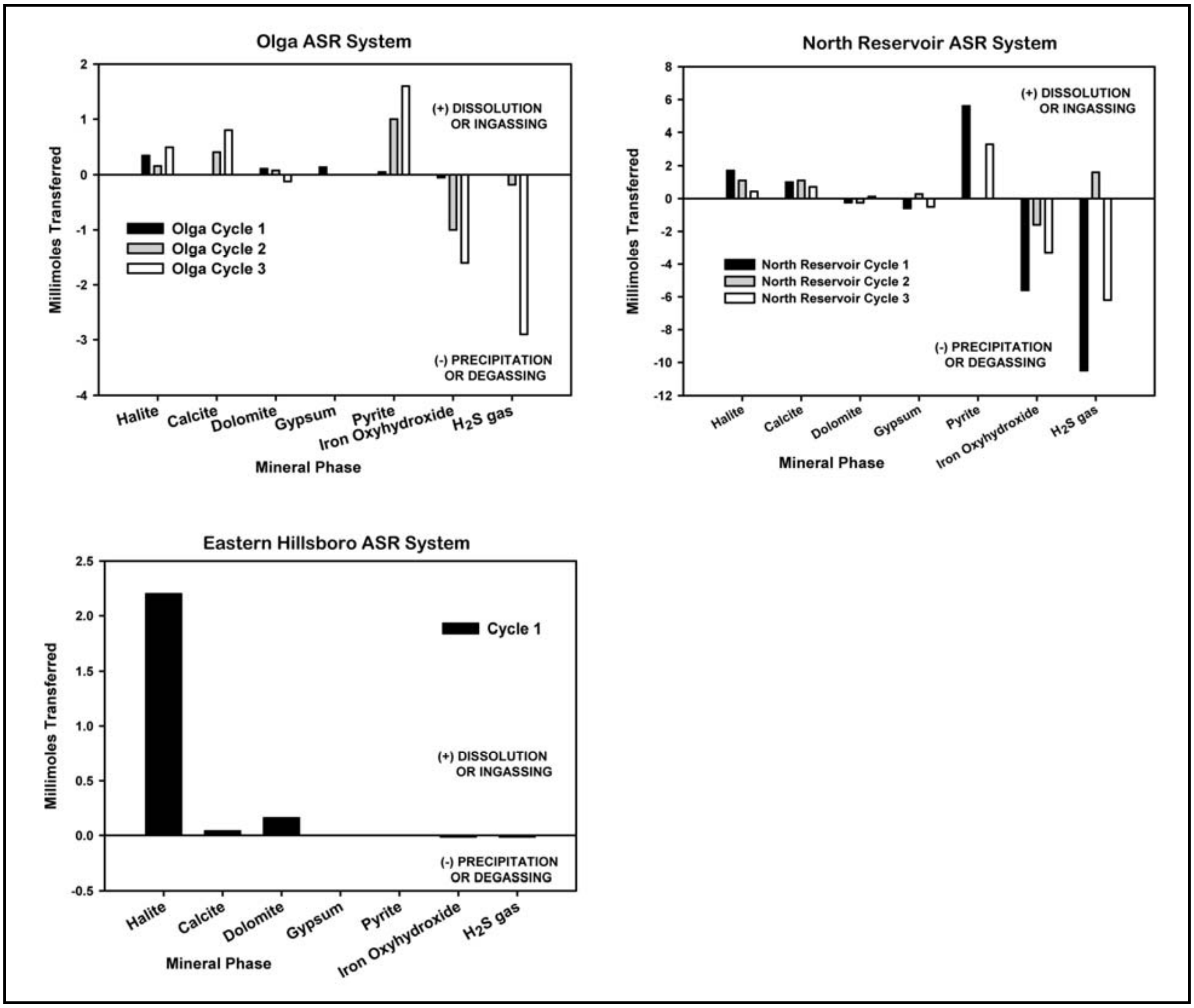


Figure 5. Bar graphs showing phase mole- transfer values calculated by PHREEQC inverse models (Table B1). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga, North Reservoir, and Eastern Hillsboro ASR systems.

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.

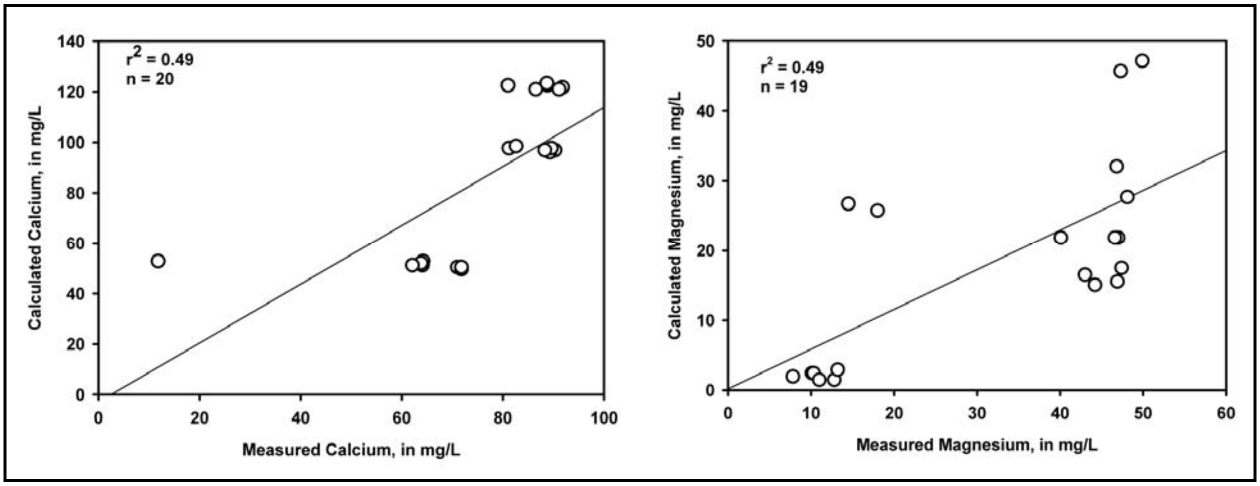


Figure 6. Linear regression plots that compare measured versus calculated concentrations of calcium and magnesium in Cycle 4 recovered water samples (ASR and monitor wells) at the Olga ASR system.

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 contact 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 alkalinity, 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 µg/L in recharge water; less than 40 µg/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 (Manning 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 µg/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.

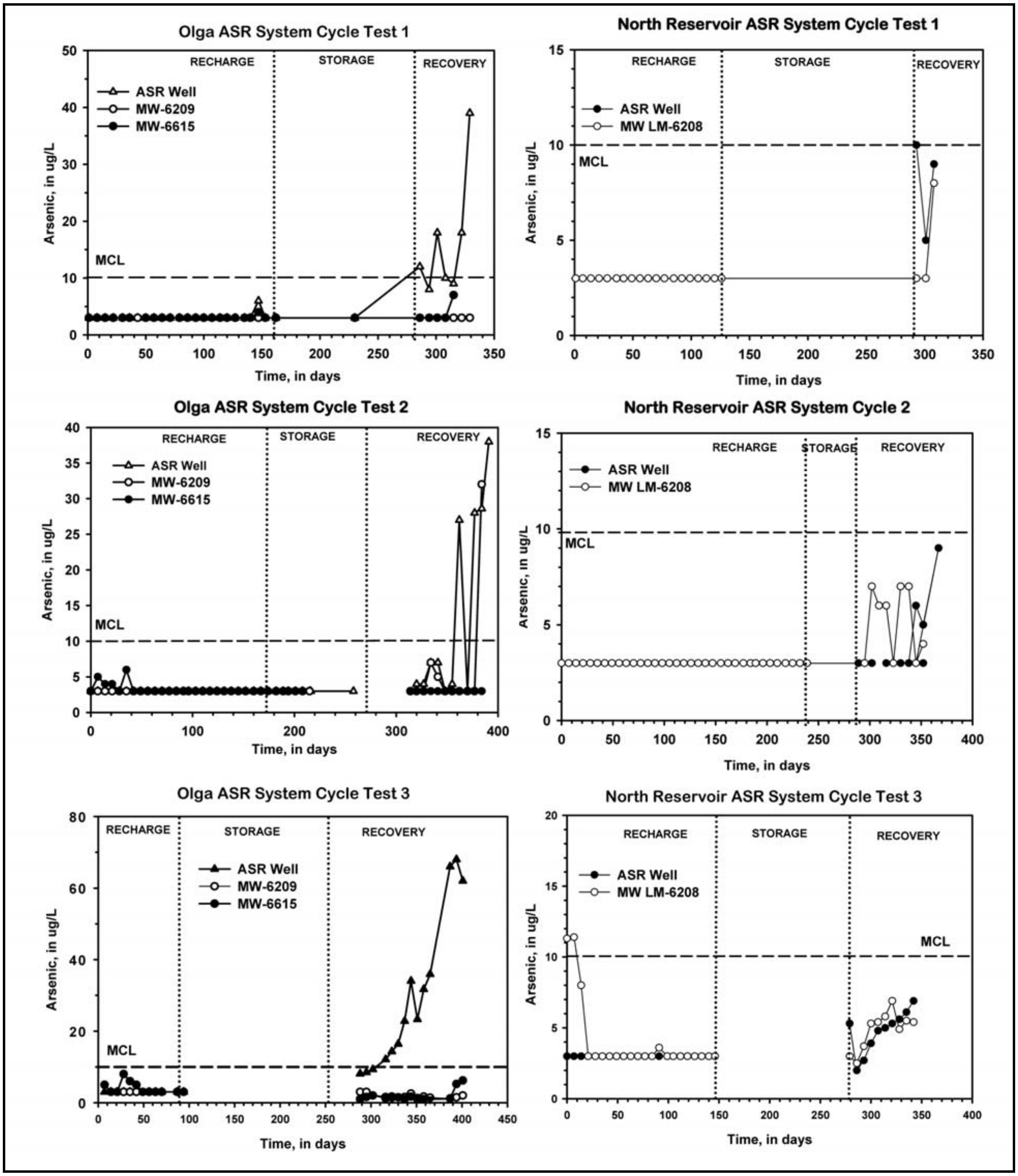


Figure 7. Trends in total dissolved arsenic concentrations measured in ASR and monitor wells at the Olga and North Reservoir ASR systems during Cycle Tests 1 through 3. Concentrations plotted here as 3 µg/L actually were below the detection limit for the ICP-MS method. Data are tabulated in Appendix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

At the North Reservoir ASR system, arsenic concentrations remain low (approximately 3 µg/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 ($p\varepsilon$ -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 amphorphous iron oxyhydroxides is the only surface that can effectively immobilize dissolved arsenite.

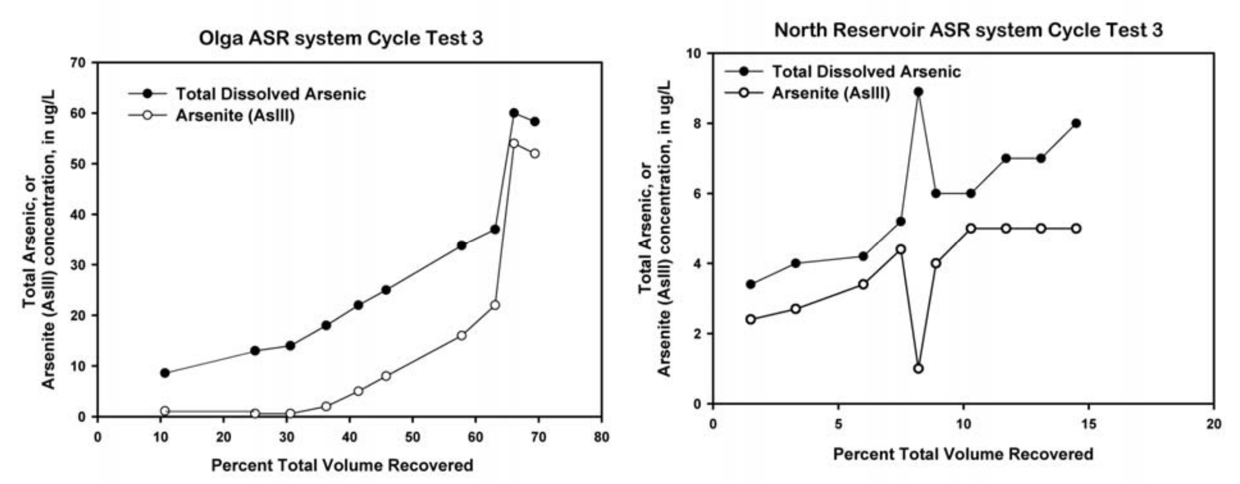


Figure 8. Trends in total dissolved arsenic and arsenite (AsIII) concentrations in ASR well samples from the recovery phase of Cycle Test 3 at Olga and North Reservoir ASR systems. Data are tabulated in Tables C8 and C9.

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 µg/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.

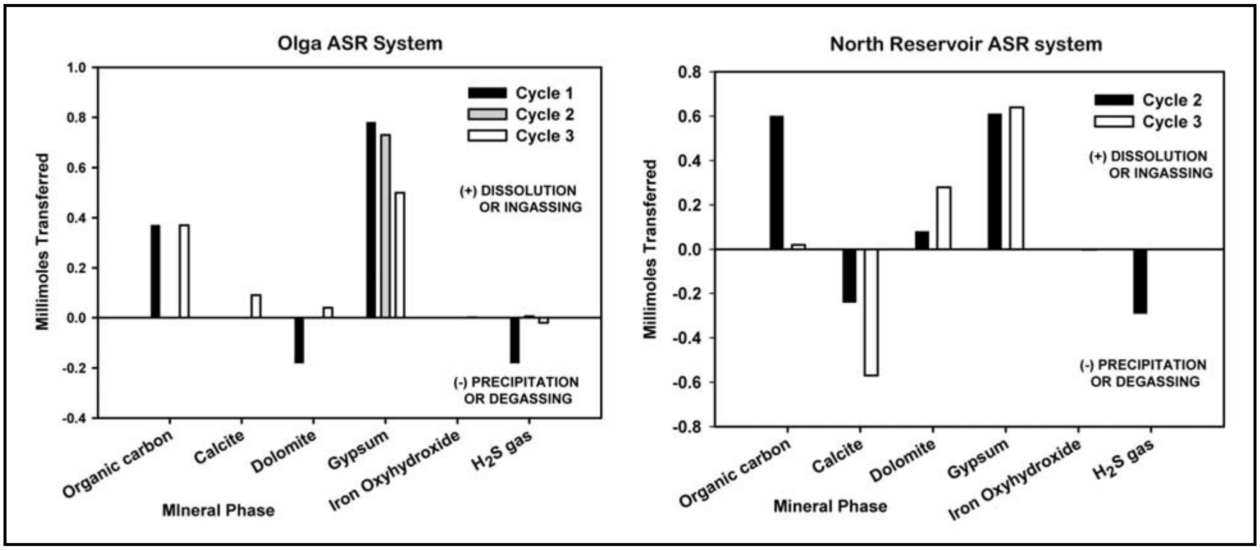


Figure 9. Bar graphs showing phase mole-transfer values calculated by PHREEQC inverse models (Table B2). Bars show mass that is dissolved or ingassed (positive values) versus precipitated or outgassed (negative values) during storage at Olga and North Reservoir ASR systems.

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 $HAsO4^{-}$), and arsenite (AsIII, as $H_3AsO_3^{o}$), 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.

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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.

Table A2. Bulk chemistry of selected samples from the Arcadia Formation and Suwannee Limestone in core CCBRY-1[1]

Sample Interval, ft bls	Lithostrati-graphic Fm	As, mg/kg	CaO, weight percent	SiO_2, weight percent	MgO, weight percent	Fe_2O_3, weight percent	Al_2O_3, weight percent	K_2O, weight percent	Na_2O, weight percent	P_2O_5, weight percent	TiO_2, weight percent
421.5-421.8	Arcadia										
500.5-501.0	Arcadia										
523.5-524.0	Arcadia										
539.5-540.0	Arcadia										
545-547	Arcadia	6	29.04	14.48	14.59	0.39	1.4	0.25	0.23	2.44	0.079
553-554	Arcadia	2	34.25	36.91	0.43	0.16	0.43	0.13	0.08	0.06	0.034
563.0-563.5	Arcadia										
632.0-632.5	Suwannee										
637-638	Suwannee	2	48.19	11.35	0.68	0.16	0.69	0.17	0.12	0.06	0.063
640.0-640.5	Suwannee										
661	Suwannee										
661-662	Suwannee	2	49.47	8.73	0.81	0.14	0.57	0.16	0.08	0.02	0.042
709-710	Suwannee	< 1	34.55	35.79	0.38	0.12	0.3	0.07	0.09	0.26	0.036
728-729	Suwannee	1	39.29	27.15	0.48	0.16	0.54	0.19	0.1	0.17	0.072
757.0-757.5	Suwannee										
761-762	Suwannee	5	28.94	45.21	0.31	0.16	0.58	0.18	0.15	0.64	0.076
782-783	Suwannee	8	38.48	27.41	0.44	0.3	1.13	0.39	0.2	0.74	0.169
798.0-798.2	Suwannee										
827-828	Suwannee	5	51.95	4.79	0.63	0.11	0.23	0.07	0.03	0.29	0.047
829.0-830.0	Suwannee										
847.5-847.7	Suwannee										
849-850	Suwannee	3	53.55	2.45	0.59	0.11	0.21	0.01	0.04	0.16	0.029
860-861	Suwannee	5	50.58	6.94	0.64	0.11	0.28	0.1	0.07	0.33	0.083
915-916	Suwannee	4	54.13	1.68	0.69	0.03	0.09	< 0.01	0.06	0.03	0.009
954-955	Suwannee	2	54.24	0.55	0.85	0.03	0.09	< 0.01	0.03	0.12	0.003
1000-1001	Suwannee	1	33.67	1.08	18.43	0.06	0.15	0.05	0.03	0.15	0.007

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 A3. Bulk chemistry of selected samples from the Arcadia Formation and Suwannee Limestone in core EXBRY-1[1]

Sample Interval, ft bls	Lithostrati-graphic Fm	As, mg/kg	CaO, weight percent	SiO_2, weight percent	MgO, iweight percent	Fe_2O_3, weight percent	Al_2O_3, weight percent	K_2O, weight percent	Na_2O, weight percent	P_2O_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-1[1]

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-1[1]

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" [Ca(Fe, Mg, Mn)$(CO_3)_2$] are interpreted to be ferroan dolomite

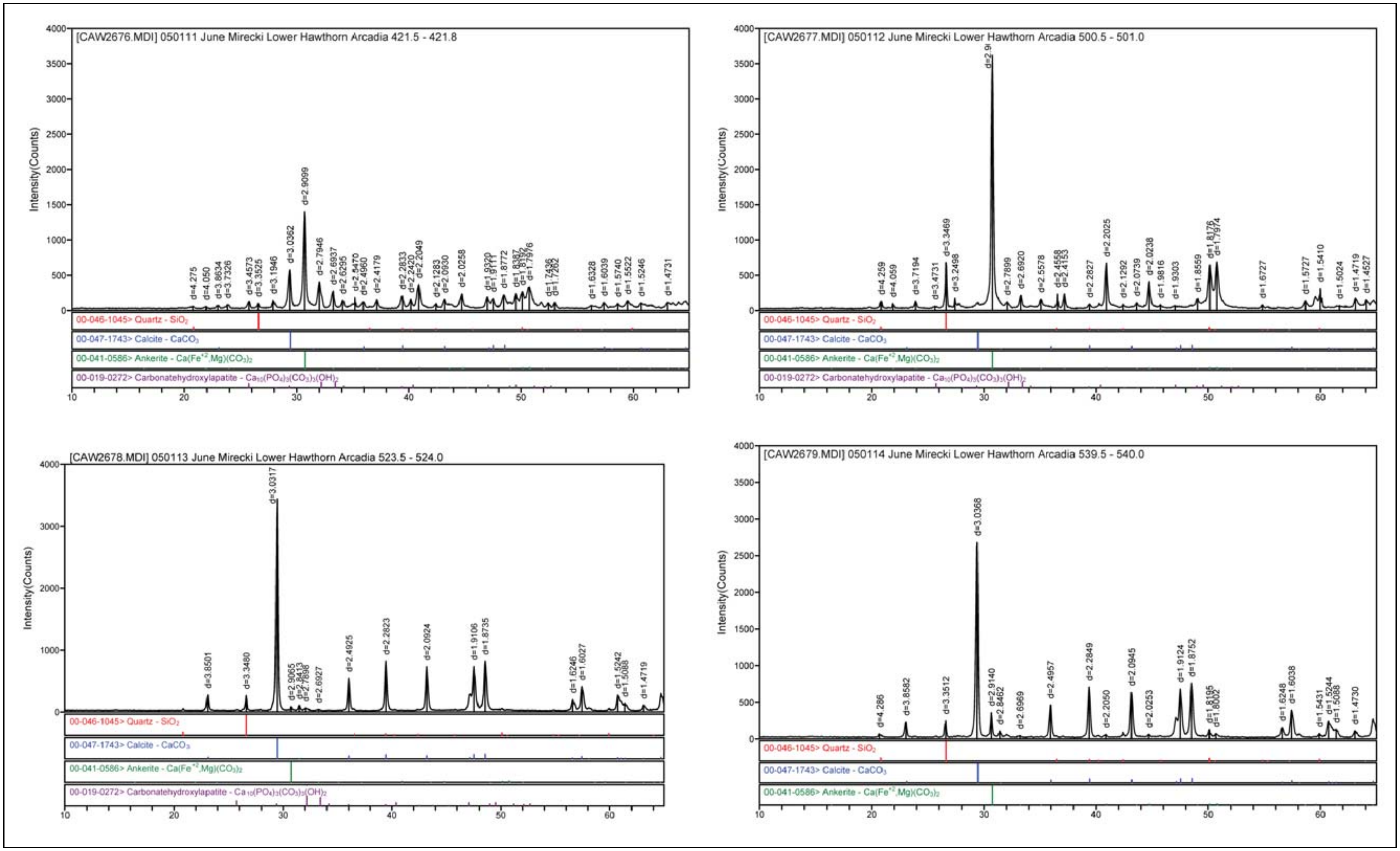


Table A6. (Continued).

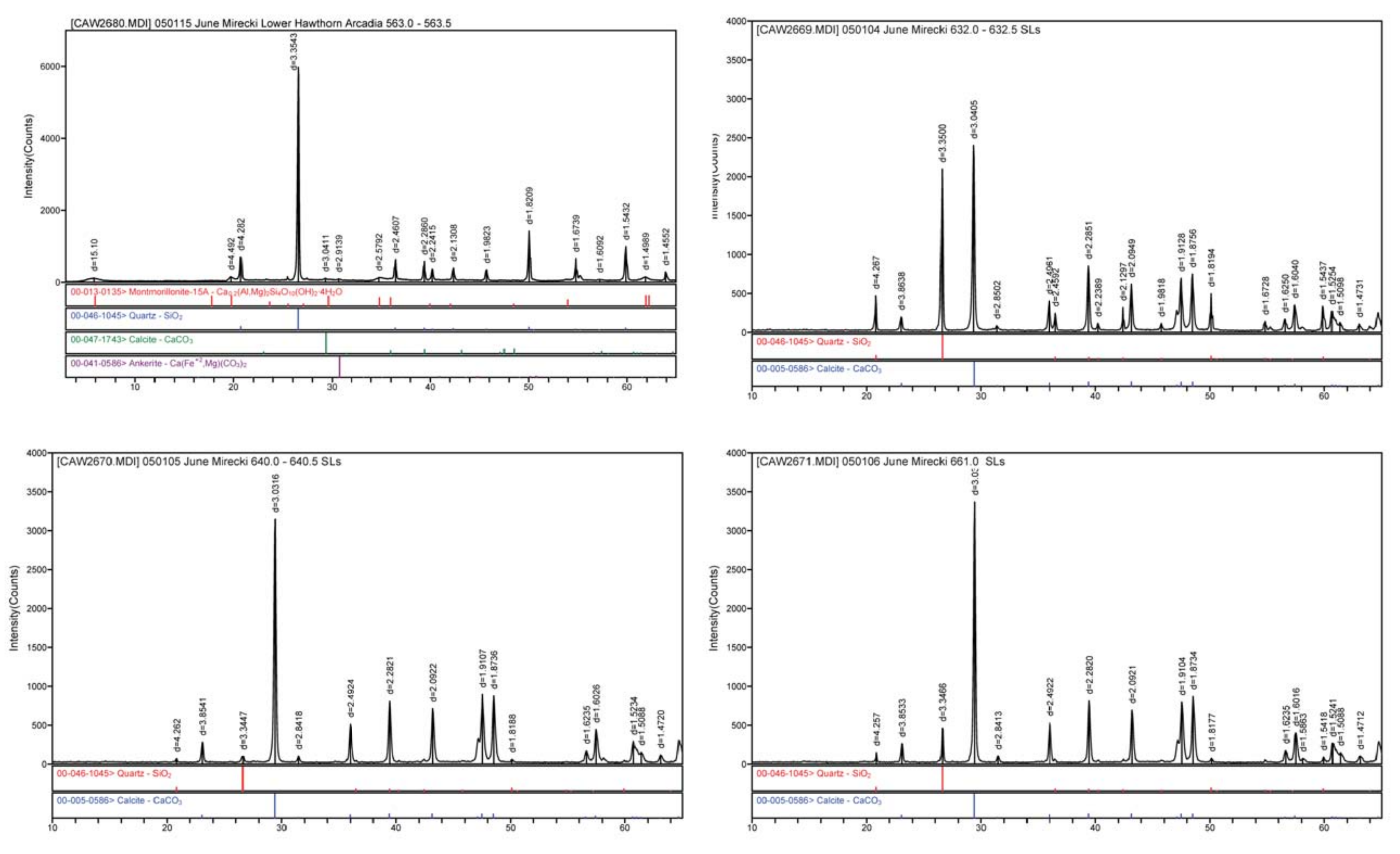
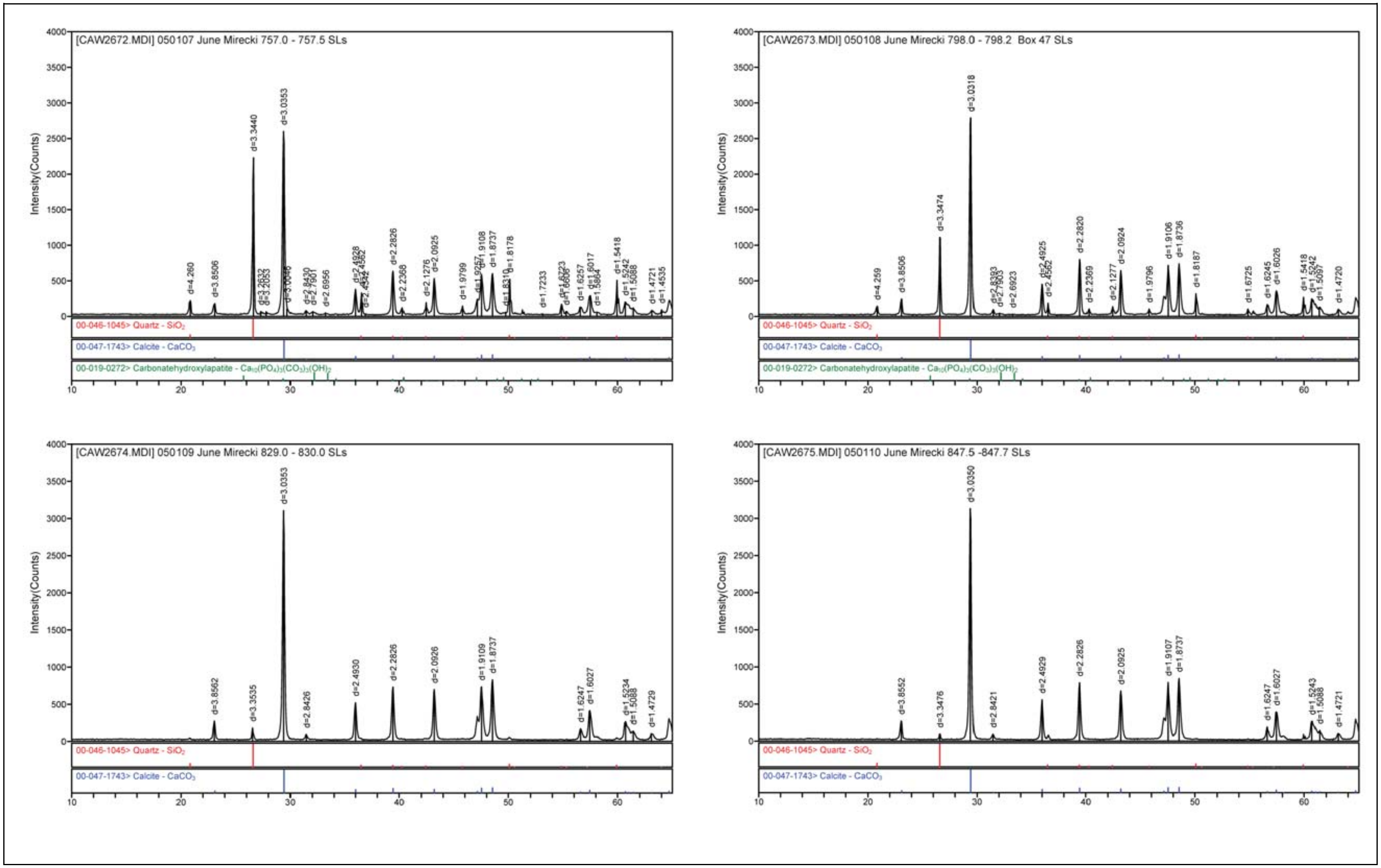


Table A6. (Concluded).



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 Oxyhydroxide	H_2S 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
```

Geochemical model input - continued

```
CH2O
      CH2O + H2O = CO2 + 4H+ + 4e-
      log_k0.0   # No log_k inverse modeling only
Sulfur
    SO4-2 + 8e- + 10H+ = H2S + 4H2O
    log_k 0.0 # real log_k 40.7 sulfate reduction


INVERSE_MODELING 1
-solutions 1 2
-phases
    dolomite
    CH2O
    H2S(g)
    gypsum
    calcite
    Fe(OH)3
-uncertainty    0.07
-range
-minimal
END
```

Table B2. Inverse geochemical models simulating iron oxyhydroxide dissolution during recovery.

ASR System	Recovery, in days	Phase Mole Transfers, millimoles						Model Evaluation Criteria			Input Data Source
		CH2O	Calcite	Dolomite	Gypsum	Iron Oxy-hydroxide	H_2S gas	No. of models	Sum of Resid-uals	Uncer-tainty, %	
Olga Cycle 1	44	0.37	0	(-0.18)	0.79	(-0.002)	(-0.18)	1	4.4	9	WRS, 2002a
Olga Cycle 2	82	0	0	0	0.73	0	0.006	1	2.3	7	WRS, 2003a
Olga Cycle 3	120	0.37	(-0.09)	0.04	0.50	0.001	(-0.02)	1	3.7	9	MORs
North Reservoir Cycle 1		Insufficient data for modeling									
North Reservoir Cycle 2	103	0.6	(-0.24)	0.08	0.61	0.001	(-0.29)	1	5	7	WRS, 2003b
North Reservoir Cycle 3	70	0.02	(-0.57)	0.28	0.64	(-0.001)	0	2	4.7	13	WRS, 2004
Eastern Hillsboro Cycle 1		Insufficient data for modeling									

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.

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 C8and 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

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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)

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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. Specifcially, 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.