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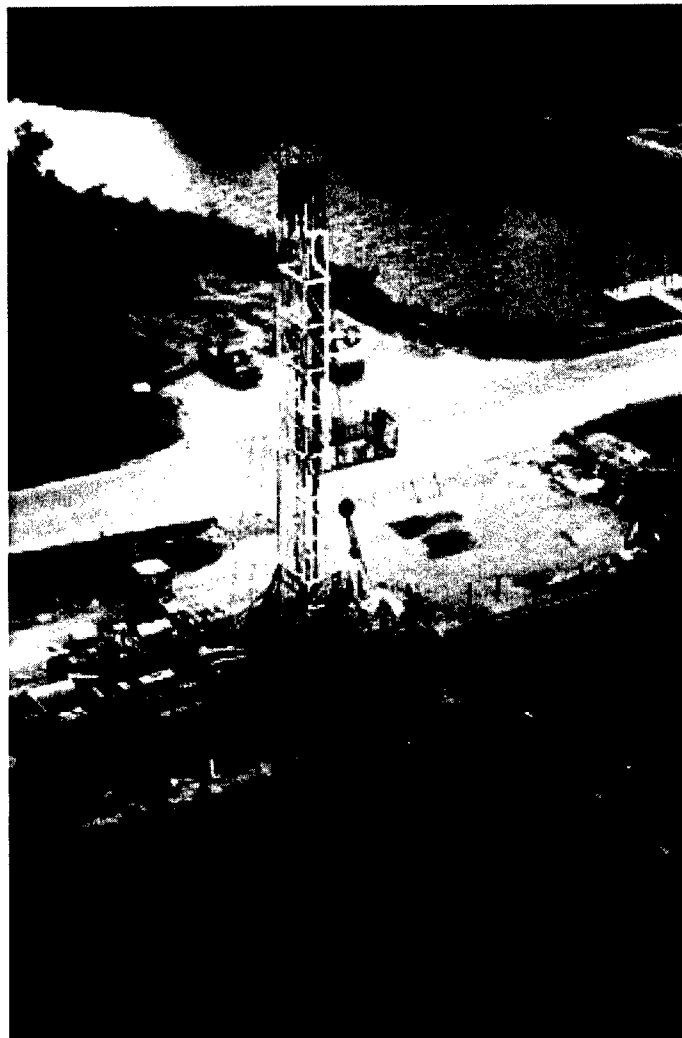


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Water-Quality Changes During Cycle Tests at Aquifer Storage Recovery (ASR) Systems of South Florida

June E. Mirecki

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

Final report

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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 trihalo-methanes. 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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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.

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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 + Nitrate	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	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	X	X	O	(X)	X	O	X	X	O	O	ASR well only	weekly/daily	7	Treated drinking water
Broward	BCOES WTP 2A	X	X	X	X	X	X	X	X	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	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	X	X	X	-	-	O	(X)	X	X	-	-	ASR well only	weekly	6	Potable Biscayne
Dade	MDWASD West	X	X	X	X	X	X	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	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	X	(X)	-	X	-	-	X	X	X	ASR & MW	monthly (limited)	3	Treated drinking water
	Corkscrew - Expanded	X	X	X	X	X	X	X	X	X	X	O	X	X	X	X	(X)	(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)	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	X	X	X	(X)	(X)	X	-	-	X	X	X	ASR & MW	weekly	2	Treated drinking water
Collier	Olga	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	-	-	X	X	X	ASR & MW	weekly	2	Treated drinking water
	Manatee Road	-	X	-	-	-	X	X	X	X	X	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	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	X	X	X	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; O = 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	--	--	--	--
	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
Collier	Corkscrew - Expanded	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
		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
		ASR-1	0.72	455 - 553 ft Lower Hawthorn	MHMMW-1	1: 150 - 200 ft	MW 80 ft S of ASR	Mid-Hawthorn
North Reservoir	Winkler Avenue	ASR-1 LM-6210	0.5	540 - 642 ft UFA Arcadia Fm	SZMW-1 MW-1 LM-6208	1: 455 - 553 ft 1: 537 - 615 ft	MW 200 ft SW of ASR MW 250 ft S of ASR	Lower Hawthorn Upper Floridan
		ASR-1 LM-6086	0.5	859 - 920 ft UFA Suwannee Fm	OBS-1 LM-6209 OBS-3 LM-6615	1: 850 - 895 ft 3: 864 - 945 ft	MW 350 ft W of ASR MW 400 ft SW of ASR	Upper Floridan Upper Floridan
Collier	Marco Lakes	ASR-1 CO-2428	2 - 5 ³	745 - 790 ft UFA	SZ-1 (Shallow) DZ-1 (ASRZMMW1)	1: 293 - 350 ft 1: 745 - 811 ft	750 ft SE of ASR 1 750 ft SE of ASR 1	Mid-Hawthorn Upper Floridan
		ASR-2	1 - 2 ³	735 - 780 ft UFA Arcadia Fm	SZ-2 (MHZ2MMW)	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 (ASRZMMW2)	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.

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 ($k = -0.73 \text{ day}^{-1}$) and Lee County – Olga ($k = -0.03 \text{ day}^{-1}$) data sets are 1 day, and 23 days, respectively.

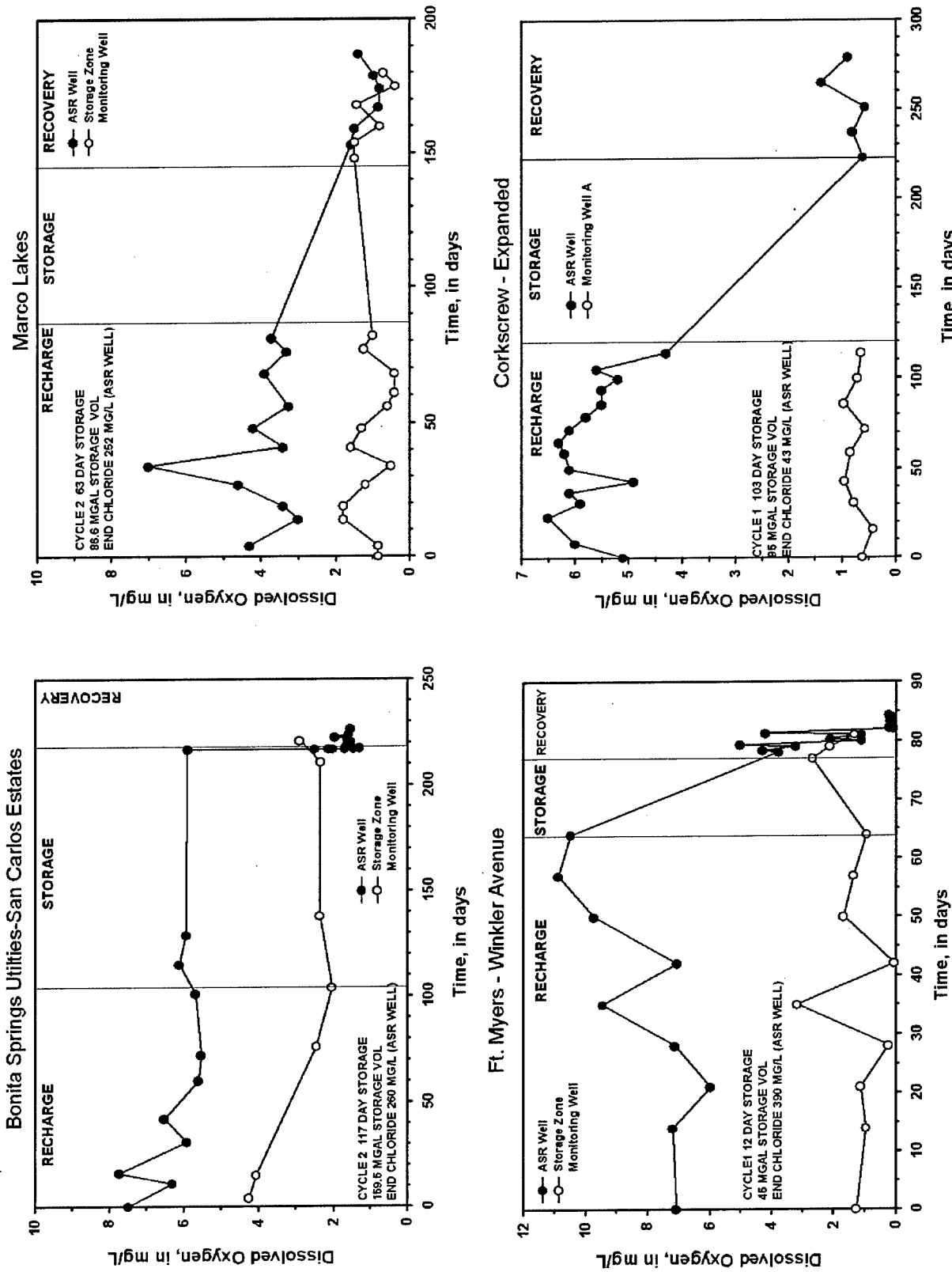


Figure 1. Dissolved oxygen concentrations measured during cycle tests in ASR and monitoring well samples (Continued)

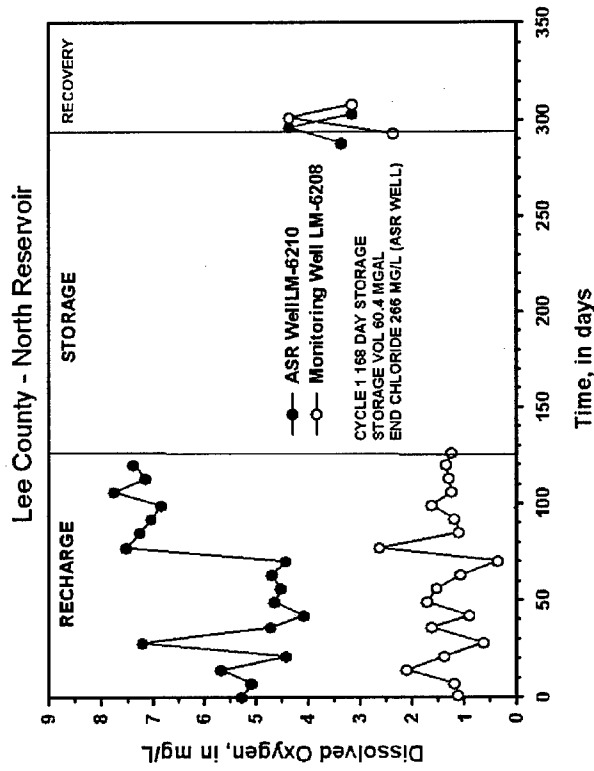
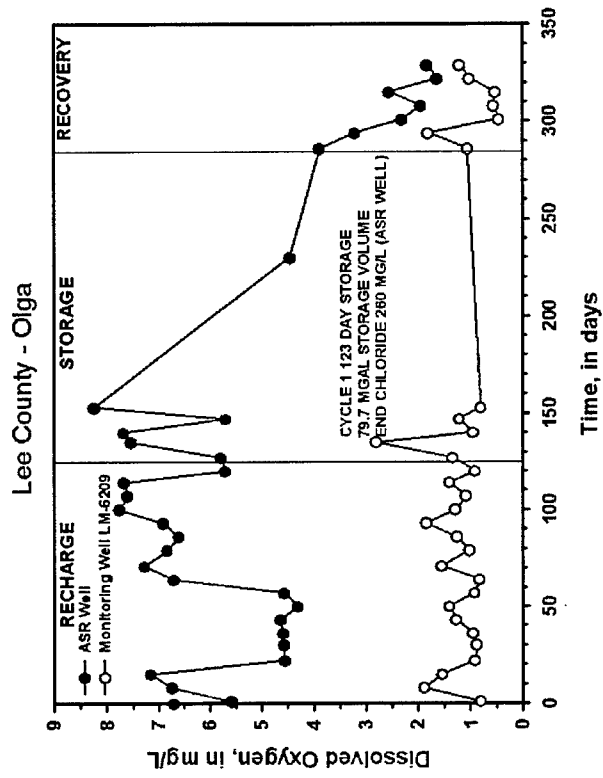


Figure 1. (Concluded)

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 O₂ 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 (Fe²⁺) 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 N₂ or ammonia (NH₃). 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 (Figure 2). Ammonia concentrations increase to nearly 1.0 mg/L throughout cycle test 6 at Boynton Beach

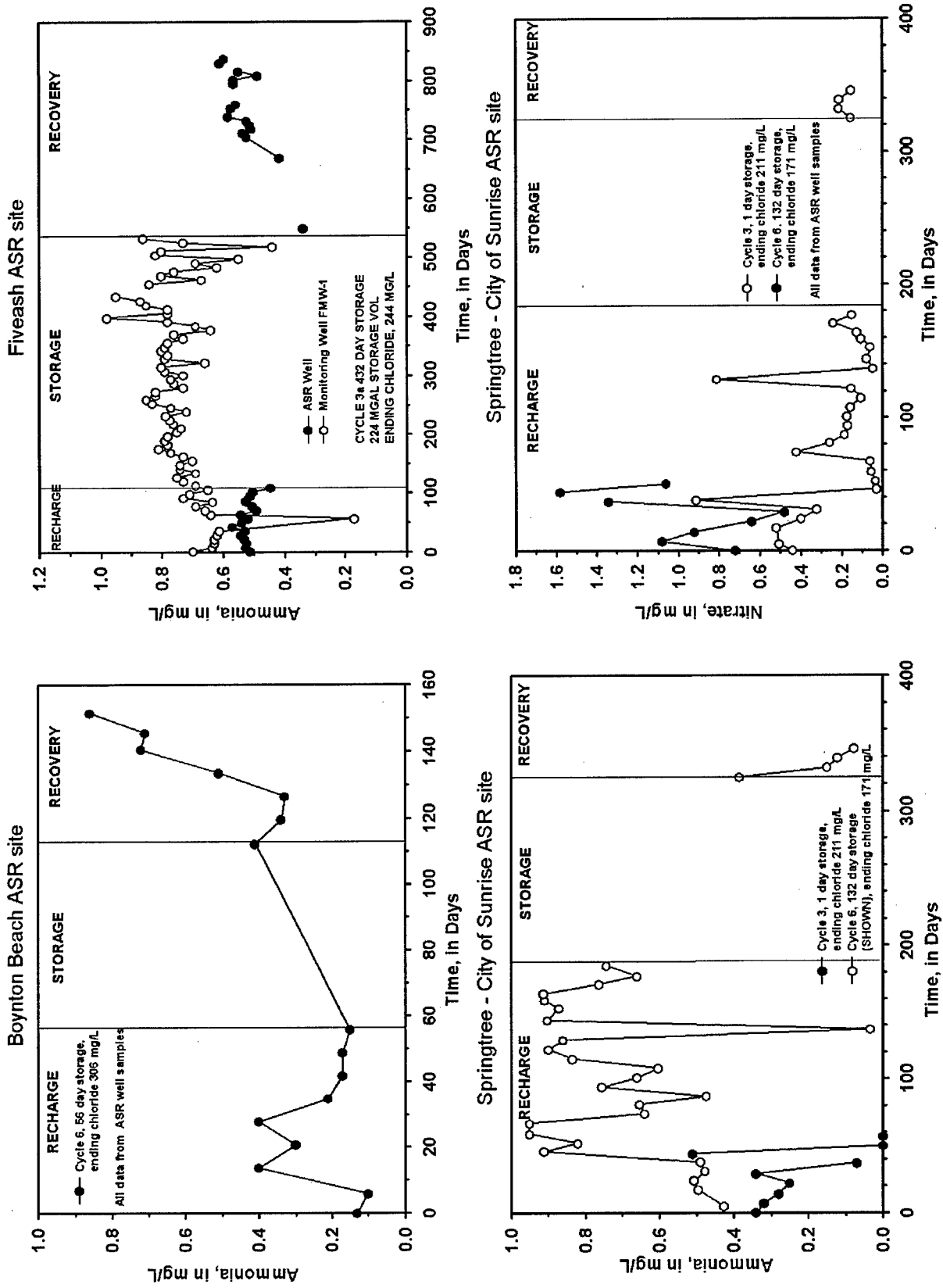


Figure 2. Dissolved ammonia and nitrate (Springtree only) concentrations measured during cycle tests in ASR and monitoring well samples

(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 between 100 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

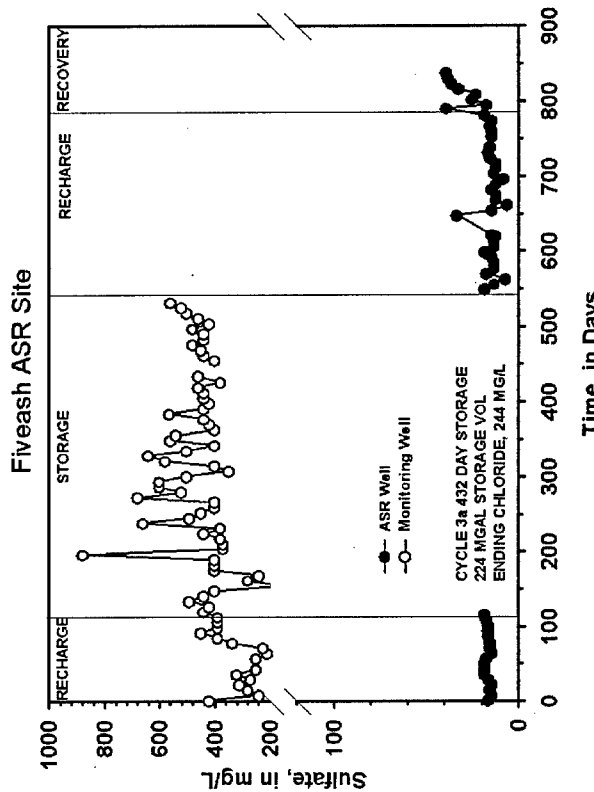
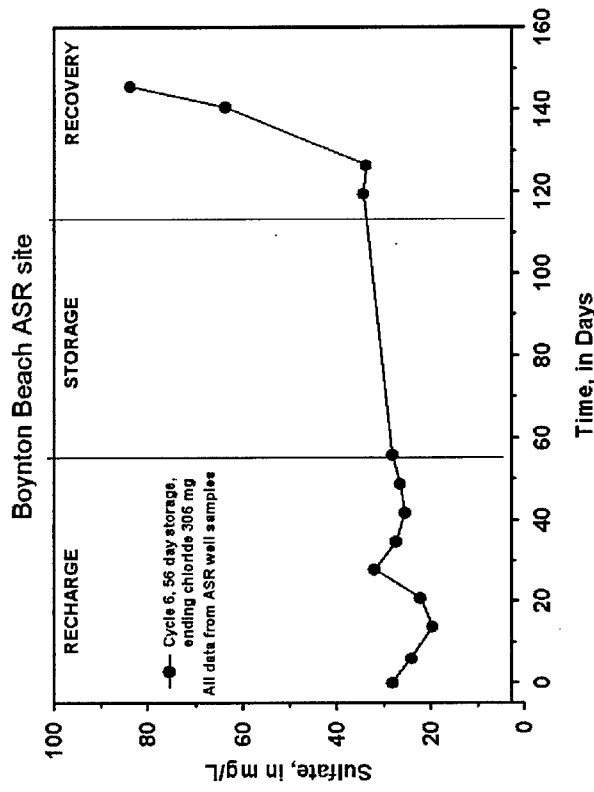
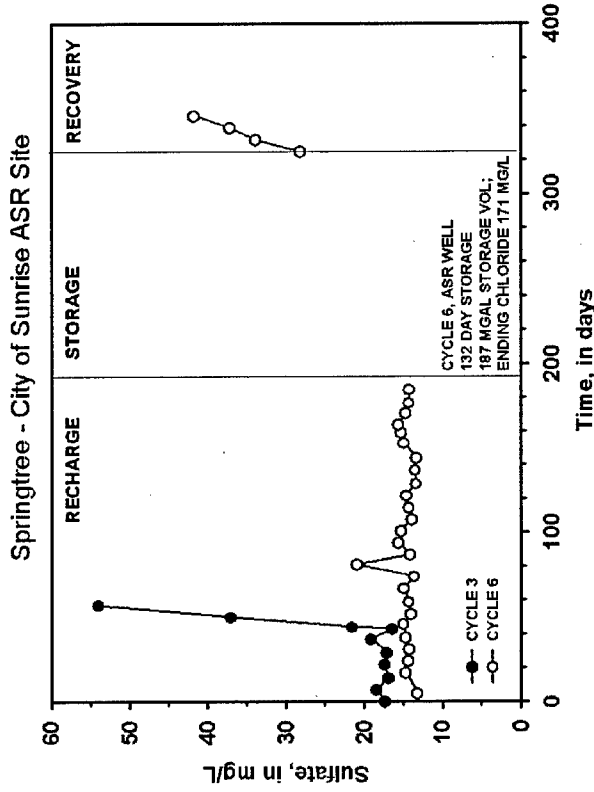
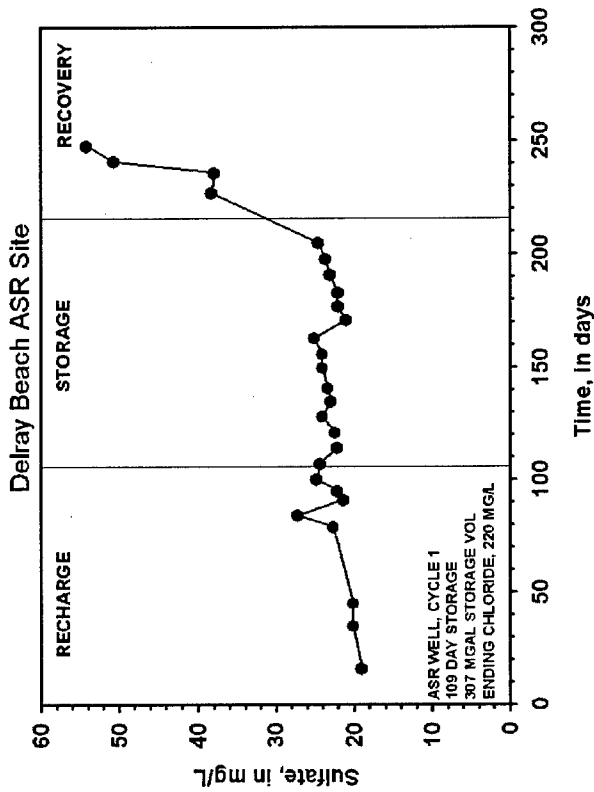


Figure 3. Dissolved sulfate concentrations measured during cycle tests in ASR and monitoring well samples (Sheet 1 of 3)

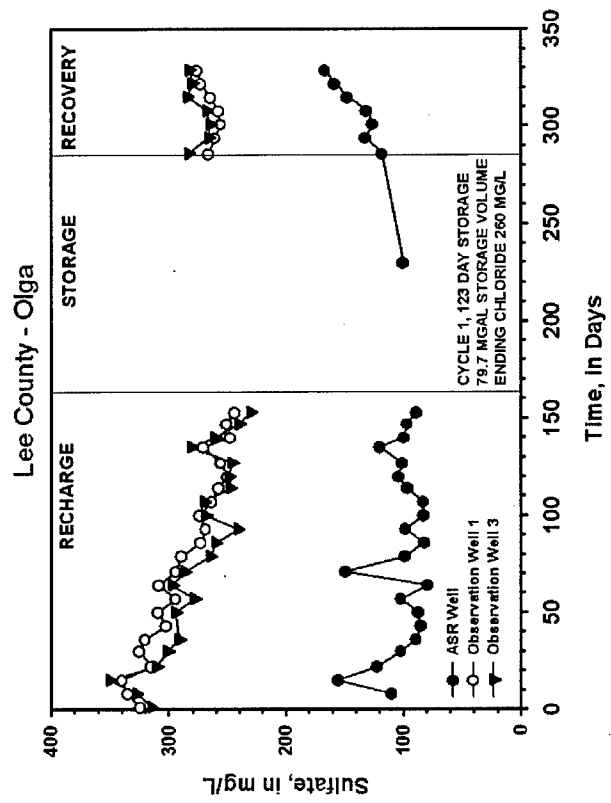
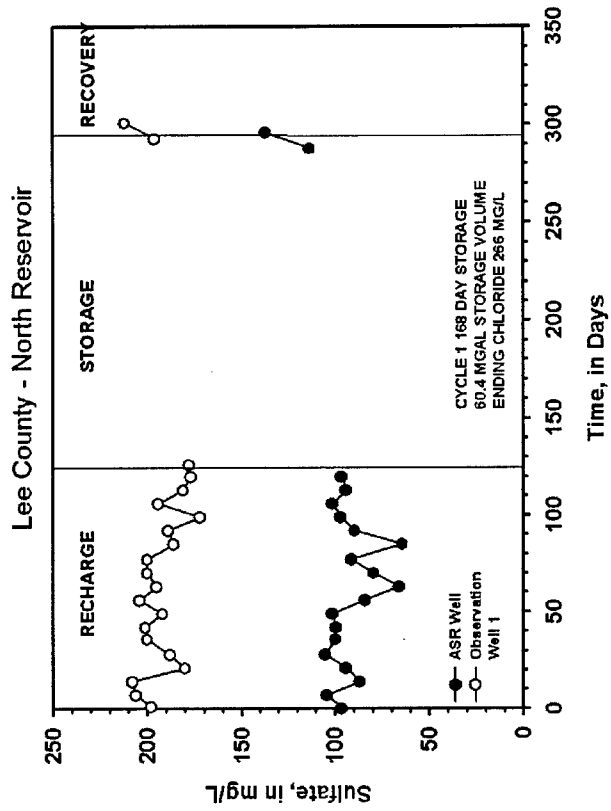


Figure 3. (Sheet 3 of 3)

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 ($\delta^{34}\text{S}$) 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 $\delta^{34}\text{S}$. 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.

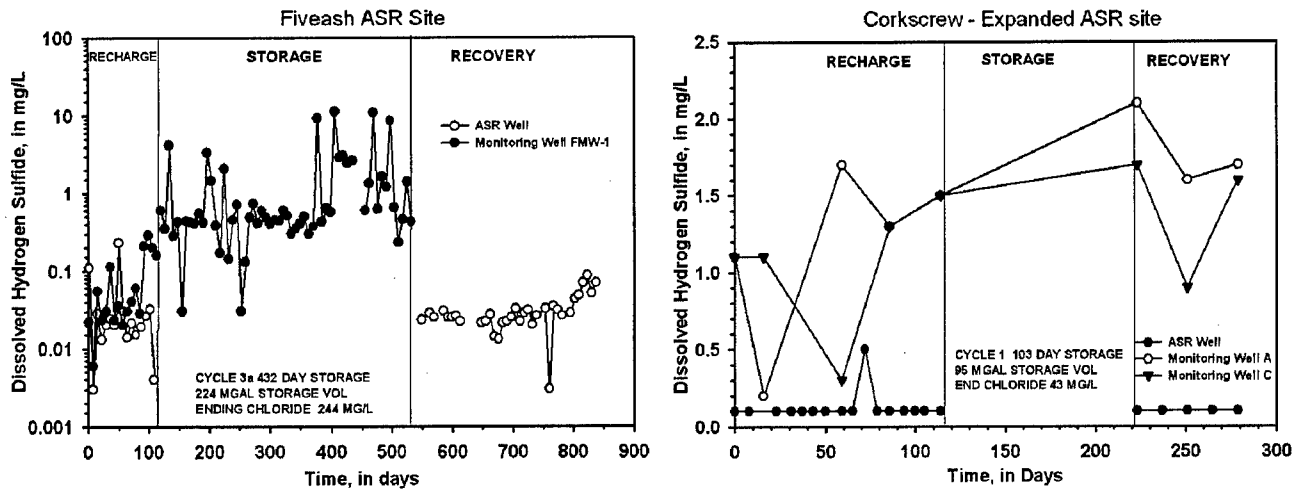


Figure 4. Dissolved hydrogen sulfide concentrations measured during cycle tests in ASR and monitoring well samples

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 $<1.0 \pm 0.5$ 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 ($\text{Ra}^{226} + \text{Ra}^{228}$) 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.

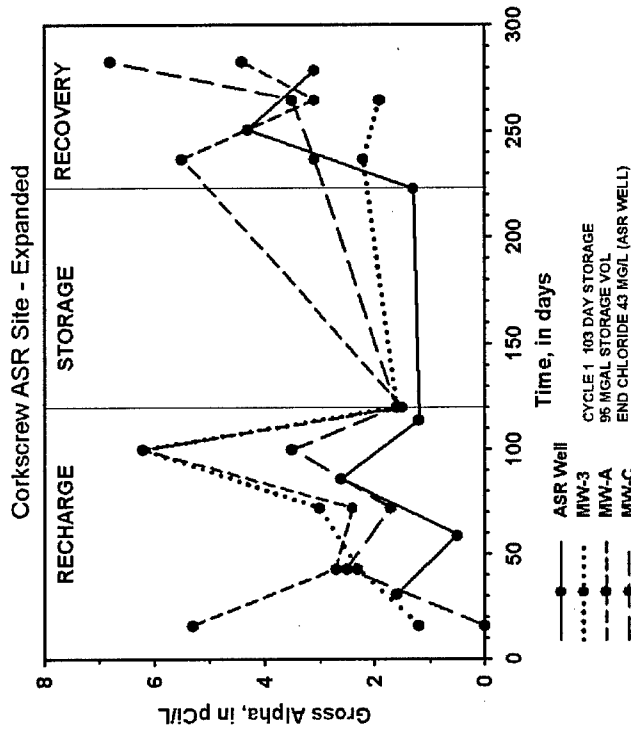
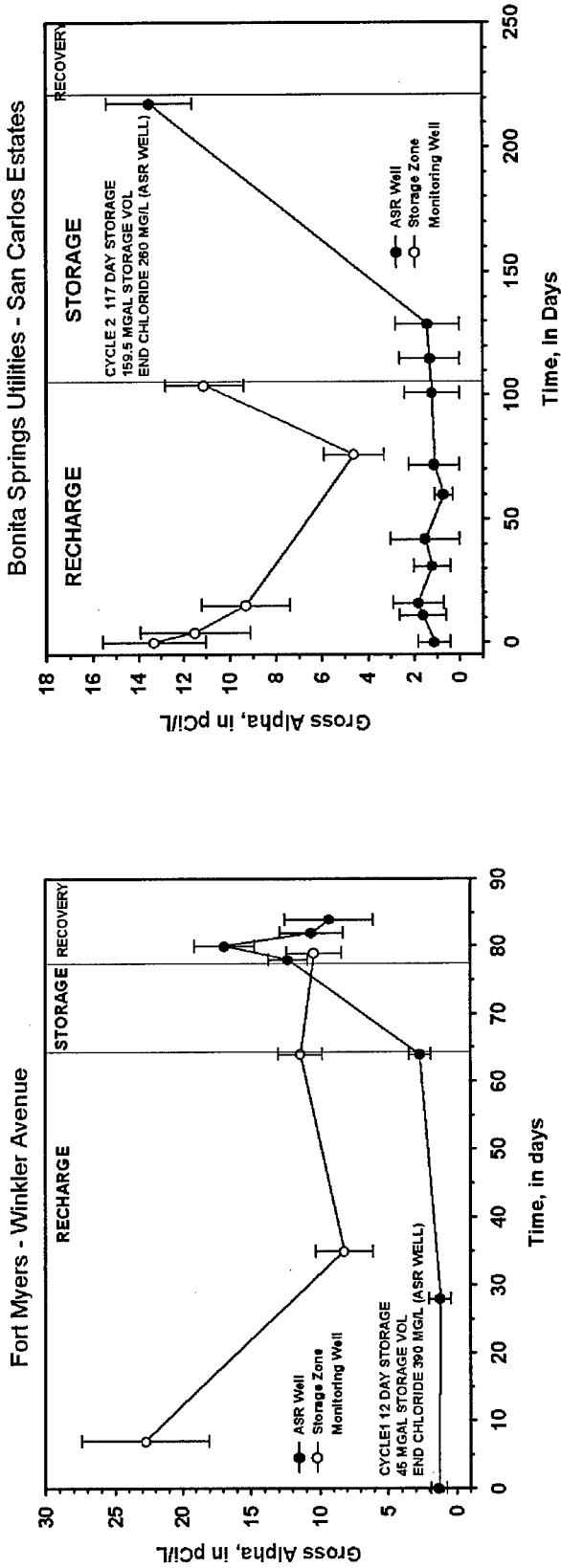


Figure 5. Gross alpha activities measured during cycle testing in ASR and monitoring well samples from sites in Lee and Collier Counties, Florida. Some ASR systems report standard deviations about gross alpha values. If reported, standard deviation about the measured gross alpha value is shown (Continued)

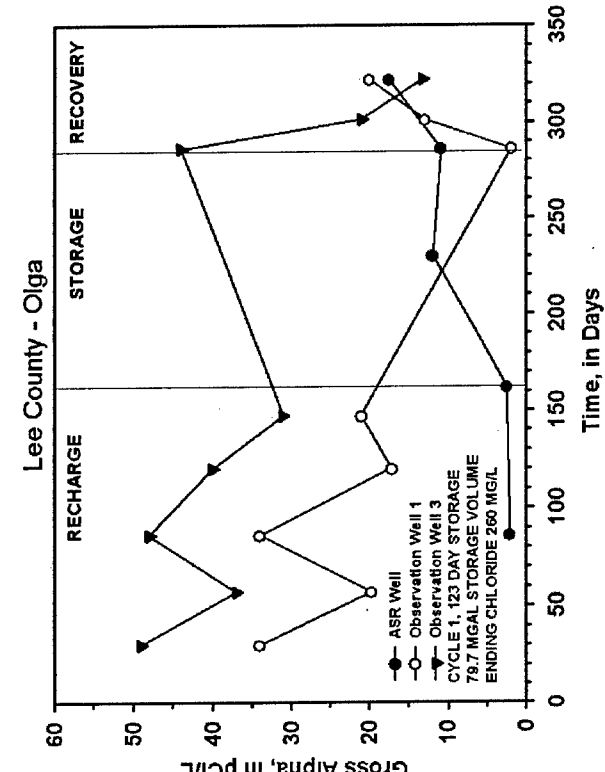
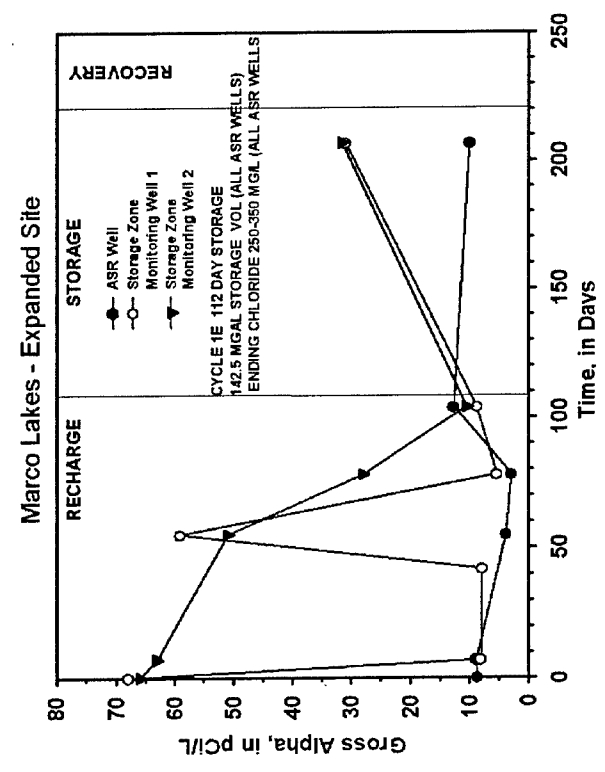
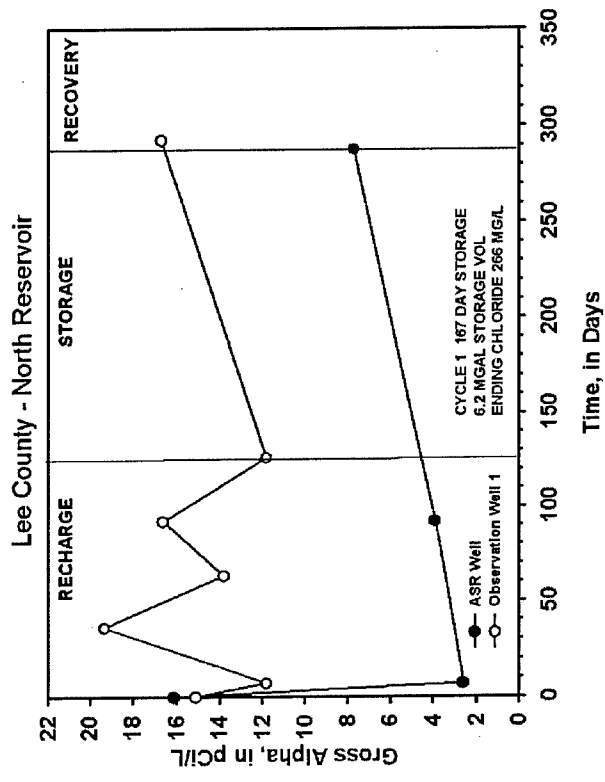
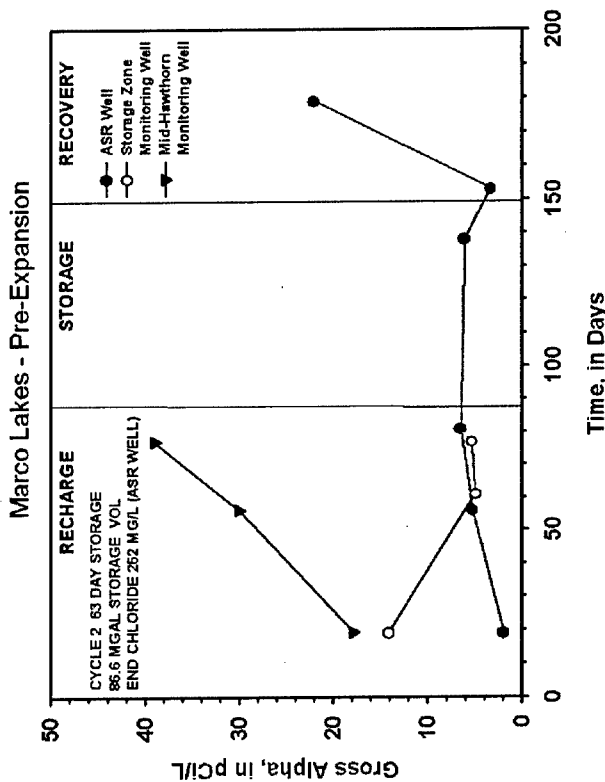


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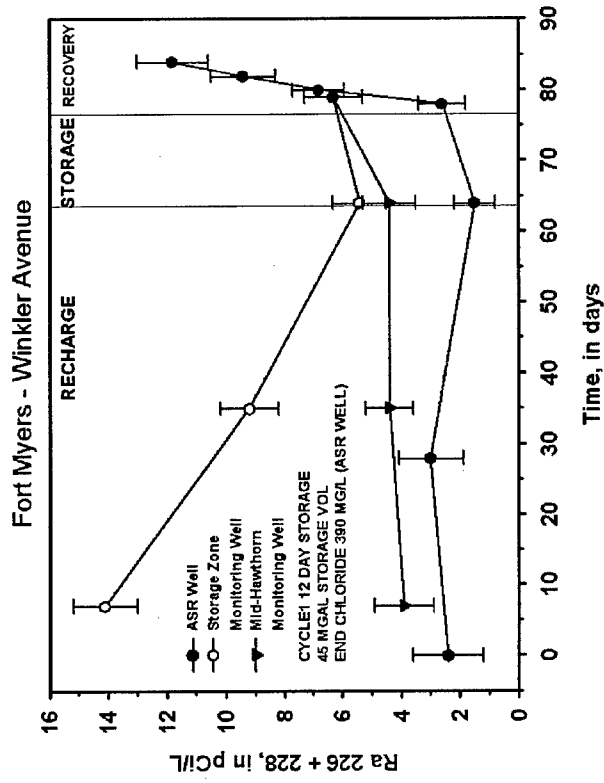
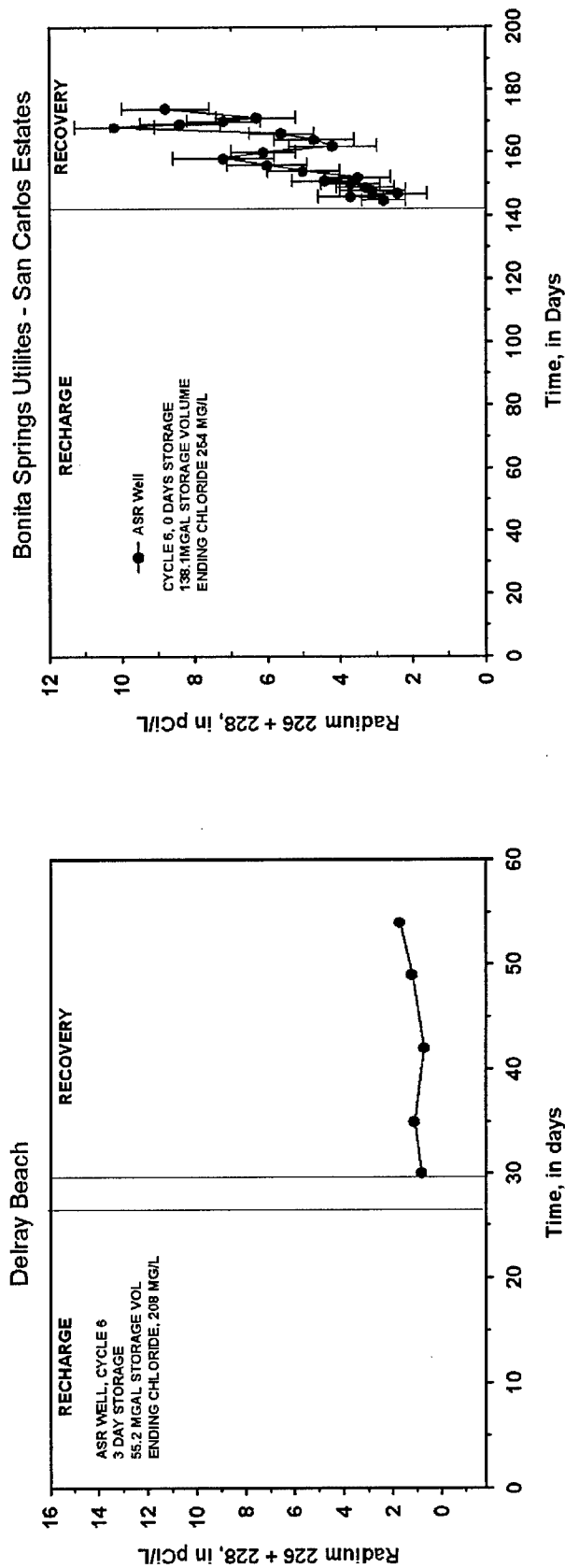


Figure 6. Radium isotope activity measured during cycle tests in ASR and monitoring well samples

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.

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.

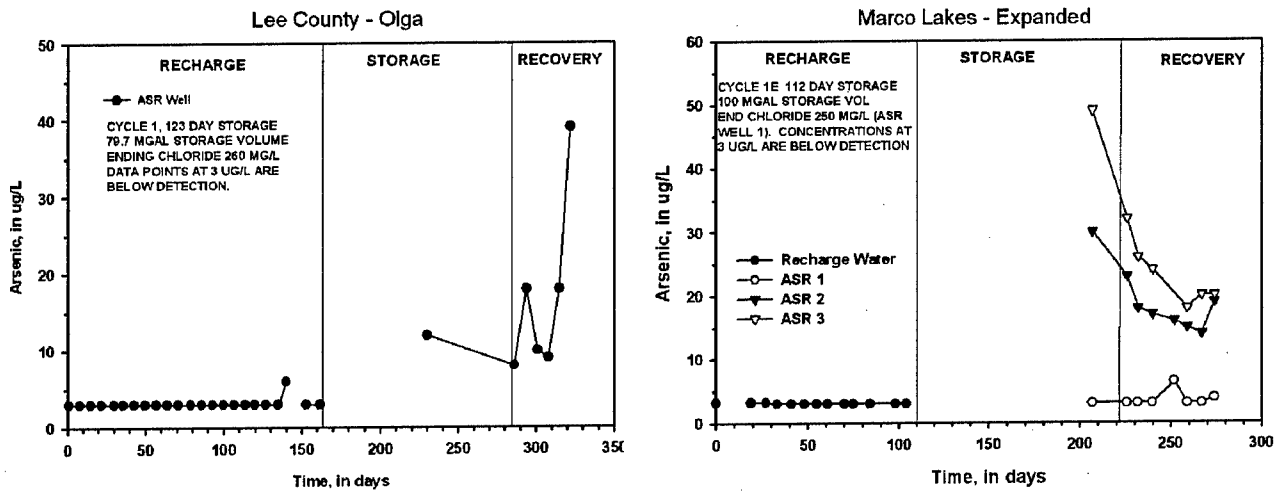


Figure 7. Arsenic concentrations measured during cycle tests in ASR well samples

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.

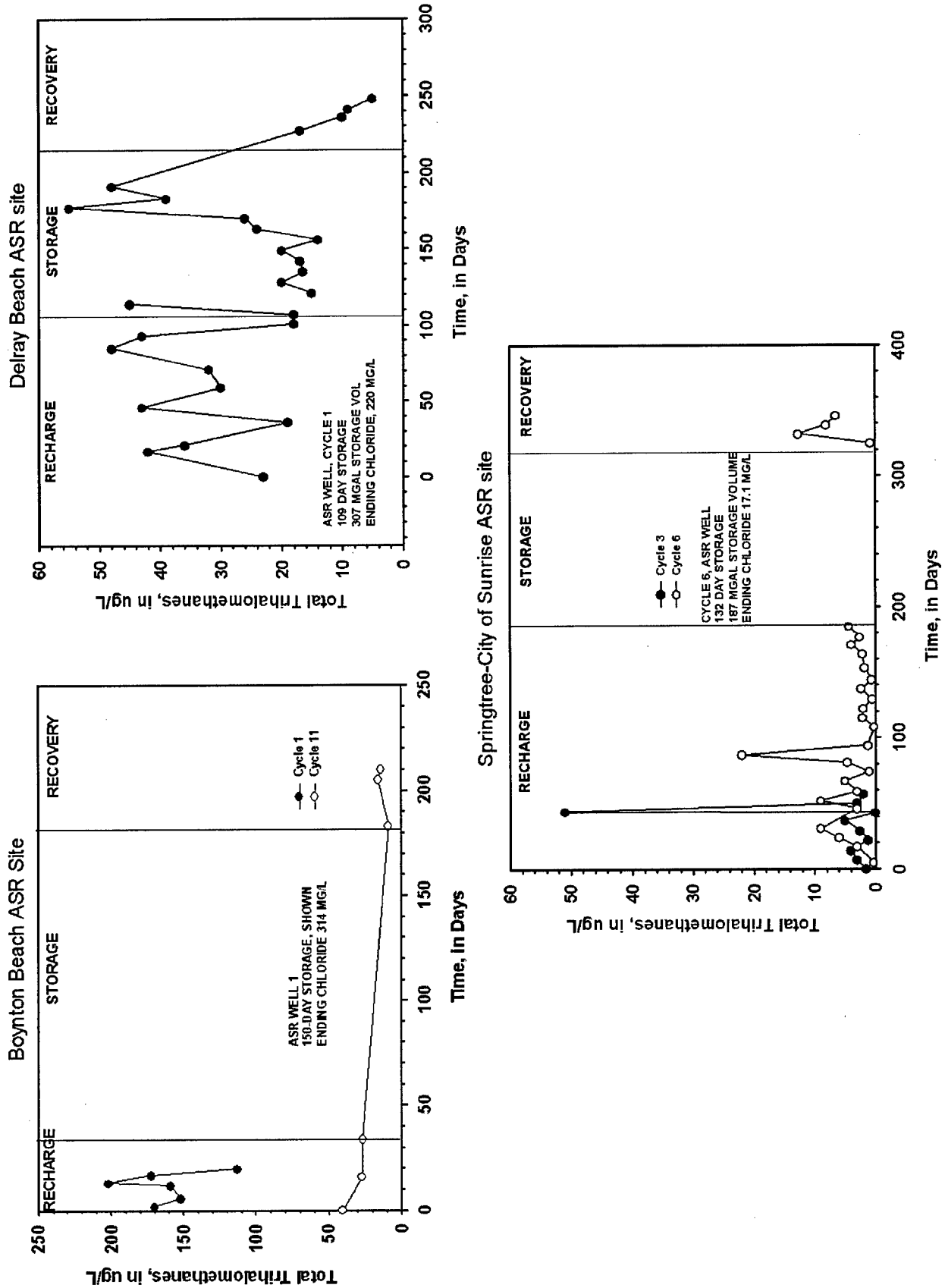


Figure 8. Total trihalomethanes concentrations measured during cycle tests at ASR and monitoring well samples (Sheet 1 of 3)

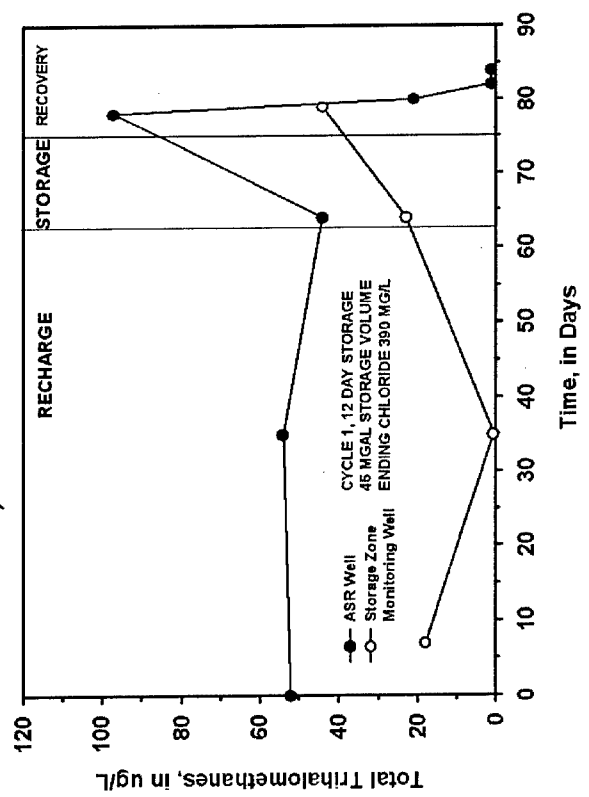
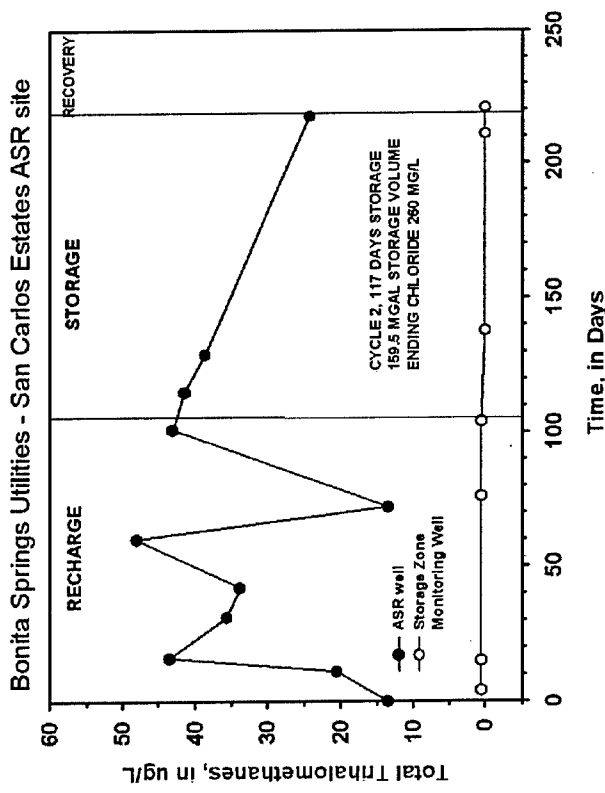
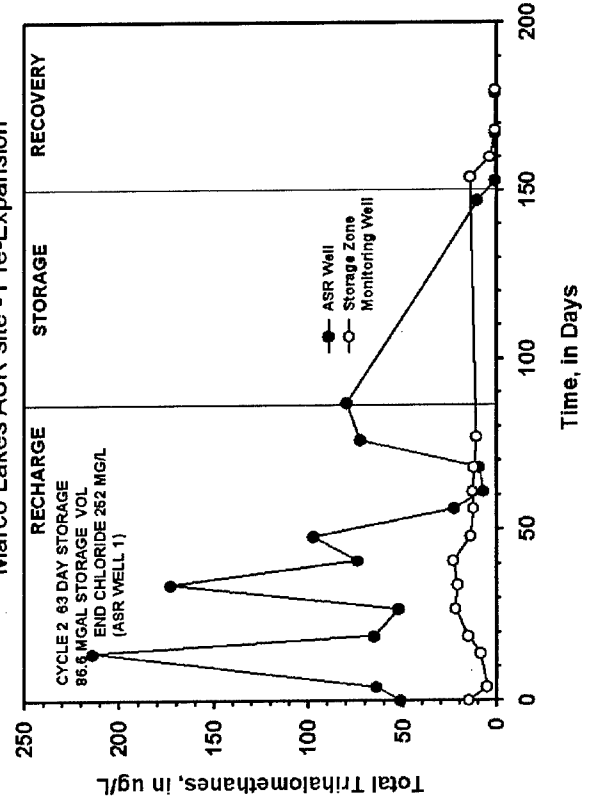
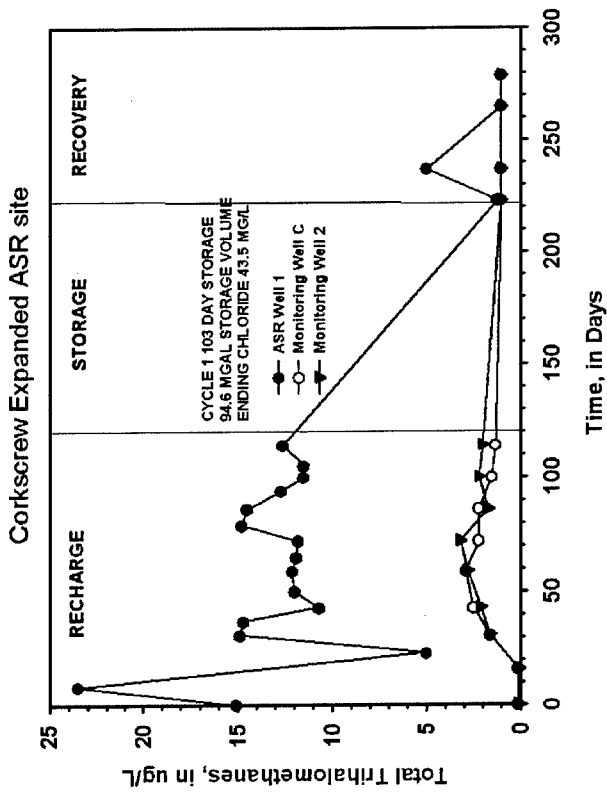


Figure 8. (Sheet 2 of 3)

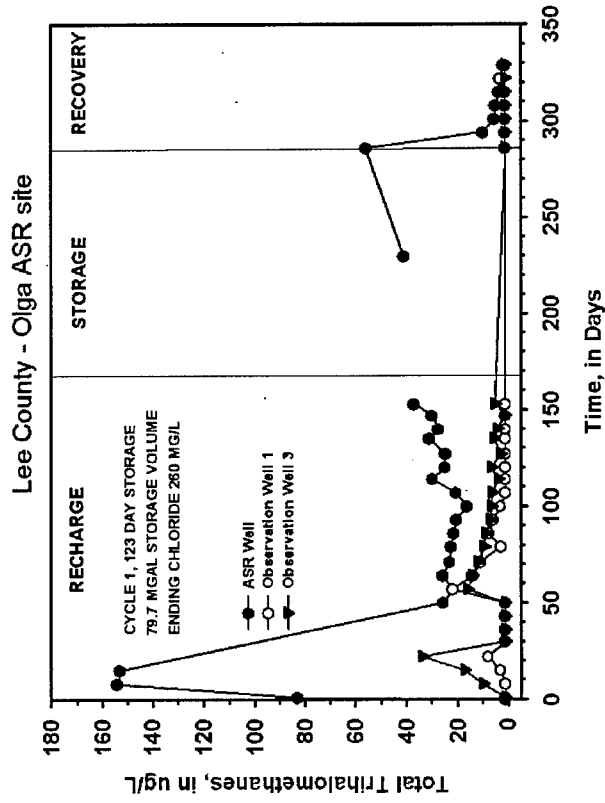
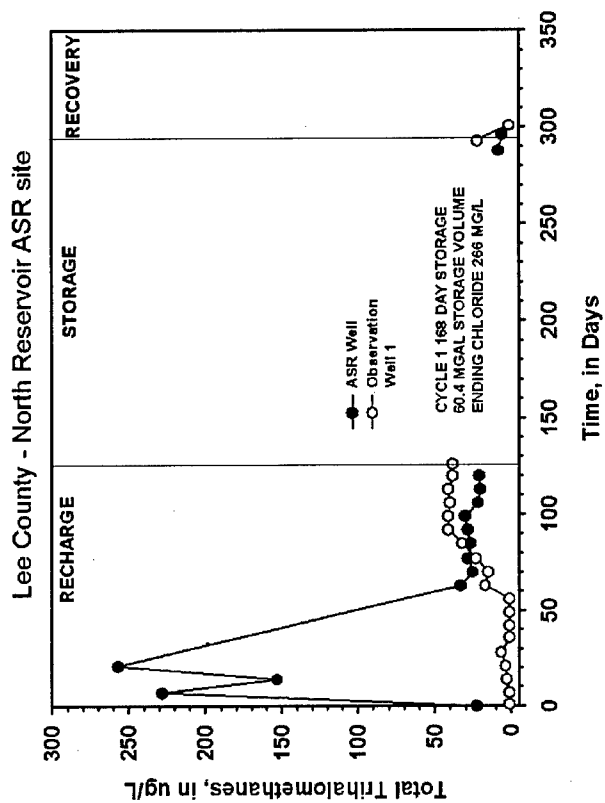


Figure 8. (Sheet 3 of 3)

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 these 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 ($\text{Ra}^{226} + \text{Ra}^{228}$) 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 $\mu\text{g/L}$). 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 $\mu\text{g/L}$) 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 geo-chemical 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

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 Water Resource Solutions (2002c)
1E/Storage	12/11/2001	4/2/2002	112					
1E/Recovery	4/2/2002	6/24/2002	83		55 (ASR1) 49 (ASR-2) 38.5 (ASR-3)	55 37.7 40.5	250 350 350	

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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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	2/25/2003	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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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)		Recovery Efficiency %	Recovery Chloride mg/L	Reference
				Recharge	Recovery			
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	4/1/2001	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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Ammonia
Aquifer Storage Recovery
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