

REFERENCE

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
David B. Struhs, *Secretary*

DIVISION OF RESOURCE ASSESSMENT AND MANAGEMENT
Edwin J. Conklin, *Division Director*

FLORIDA GEOLOGICAL SURVEY
Walter Schmidt, *State Geologist and Chief*

OPEN FILE REPORT 83

**FLORIDA AQUIFER STORAGE AND RECOVERY GEOCHEMICAL STUDY:
YEAR THREE PROGRESS REPORT**

By

Jonathan D. Arthur, P.G. #1149, James B. Cowart and Adel A. Dabous

FLORIDA GEOLOGICAL SURVEY
Tallahassee

A report submitted to the Underground Injection Control Program, Bureau of Water
Facilities Regulation, Division of Water Resource Management, Florida Department of
Environmental Protection
2001

ISSN 1058-1391

CONTENTS

INTRODUCTION.....	1
PURPOSE OF INVESTIGATION.....	2
METHODS	
Whole rock chemistry.....	4
Water chemistry.....	6
ARSENIC GEOCHEMISTRY.....	6
Arsenic in the hydrogeologic environment.....	11
RESULTS AND DISCUSSION	
WHOLE ROCK CHEMISTRY.....	12
Rare-earth elements.....	15
WATER CHEMISTRY	
Uranium.....	18
Rome Avenue.....	23
Punta Gorda.....	24
Other trace metals	
Rome Avenue.....	27
Punta Gorda.....	32
Origin of the mobilized metals.....	32
PLANNED RESEARCH.....	38
REFERENCES.....	40

LIST OF TABLES

1. Major-element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida.....	5
2. Trace-element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida.....	7
3. Rare earth element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida.....	10
4. Uranium analyses for Cycle Test samples from Punta Gorda ASR.....	21
5. Trace metal analyses for Rome Avenue ASR samples.....	29
6. Trace metal analyses of water samples from Cycles 1 and 2 (Upper Zone) and Cycles 1A and 2A (Lower Zone), Punta Gorda ASR.....	35

LIST OF FIGURES

1. Location of study areas.....	3
2. Iron oxide (Fe_2O_3) - As variation in Suwannee Limestone, Hillsborough County, Florida.....	14
3. Zinc - As variation in Suwannee Limestone, Hillsborough County, Florida.....	14
4. Normalized rare earth element distribution in Suwannee Limestone samples from W-16618, Hillsborough County, Florida.....	16
5. Normalized rare earth element distribution in Suwannee Limestone samples from W-17687, Hillsborough County, Florida.....	16
6. Normalized rare earth element distribution in Suwannee Limestone samples from W-16574, Hillsborough County, Florida.....	17

7. Normalized rare earth element ratios showing Suwannee Limestone samples relative to fields of enrichment and depletion (LREE - light REE, MREE - middle REE, and HREE - heavy REE)	17
8. Total rare earth element (estimated, see text) distribution in Suwannee Limestone samples versus loss on ignition (LOI)	19
9. Uranium mobilization models for single carbonate grains (coated and uncoated) exposed to flowing and non-flowing groundwater	22
10. Uranium activity ratios through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida	25
11. Uranium concentration through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida	25
12. Uranium activity ratio through time for Cycle 1 (Upper Zone), Punta Gorda ASR, Charlotte County, Florida	26
13. Uranium activity ratio through time for Cycles 1A and 2A, Punta Gorda ASR, Charlotte County, Florida	26
14. Uranium concentration through time for Cycles 1A and 2A, Punta Gorda ASR, Charlotte County, Florida	28
15. Arsenic concentration through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida	30
16. Arsenic concentration through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999	30
17. Arsenic concentration through time for Cycles 1 and 2 (Upper Zone), Punta Gorda ASR, Charlotte County, Florida	33
18. Arsenic concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	33
19. Iron concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	34
20. Calcium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	34
21. Manganese concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	36
22. Sodium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	36
23. Strontium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida	37
24. Sulfate concentration through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999	37
25. Iron and Mn concentrations through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999	38

APPENDICES

1. Lithologic descriptions of samples analyzed for whole rock chemistry. Wells include SWFWMD ROMP TR9-2 (W-16618), NW Hillsborough Reclaimed ASR TPW-1 (W-17687), and SWFWMD WRAP 2D (W-16574)	43
2. Cycle test and drilling activities at the Punta Gorda ASR, Charlotte County, Florida	46

EXECUTIVE SUMMARY

Aquifer storage and recovery (ASR) is a cost-effective, viable solution to address drinking-water shortages in Florida. ASR wells are Class 5 injection wells regulated by the Underground Injection Control Program of the Florida Department of Environmental Protection. Six ASR facilities are in operation in Florida and more than 25 additional sites are under development. Some of the sites include reclaimed water ASR facilities, which are also cost-effective solutions to local water shortages. ASR is a proposed major component of the Everglades restoration plan, which calls for the installation of approximately 300 ASR wells in the Lake Okeechobee region within the next 20 years.

The Florida Aquifer Storage and Recovery Geochemical Study is an ongoing investigation by the Florida Geological Survey, in cooperation with the Florida State University Department of Geological Sciences, to examine water-rock geochemical interactions that take place during ASR cycles. This report includes results from Year Three of the study. Results from Years One and Two are presented in Williams and others (in review). Year Four of the project is underway. Water-quality variations and aquifer system characteristics (including three injection zones) at two ASR facilities, the Rome Avenue ASR (Hillsborough County) and the Punta Gorda ASR (Charlotte County), are the focus of the current study.

Research presented herein confirms that understanding water-rock geochemical interactions is important to the continued success of ASR in Florida. Results of this investigation indicate the following: 1) chemical (including isotopic) variability exists within groundwaters and carbonates of the Floridan aquifer system; 2) this variability may result in site-specific geochemical processes affecting ASR well performance (e.g., plugging) and water quality; and 3) as oxygen-rich surface waters are injected into the Floridan aquifer system, trace metals such as arsenic (As), iron (Fe), manganese (Mn) and uranium (U) are mobilized (chemically leached) from the carbonate rocks and withdrawn during recovery. With regard to the third item, some of the periods of higher metals concentrations in recovered waters are short-lived, depending on the duration of the injection-storage-recovery cycle. It is significant that mobilization of U and As into recovered ASR waters has occurred within all three of the aquifer-storage zones investigated in this study. On the other hand, it is important to emphasize that only Fe and Mn concentrations (for relatively few samples) have exceeded secondary drinking water standards (i.e., maximum contaminant levels – MCL). With the exception of one sample, As is not observed to have exceeded the MCL.

The current MCL for As is 50 ug/l. The U.S. Environmental Protection Agency (EPA) has proposed to lower the MCL for As to 5 ug/l (Federal Register, 2000). If the As MCL is lowered*, mobilization of metals into injected and recovered waters may become even more of an issue from both a regulatory and human health perspective. For example, more than 50% of the recovery water samples analyzed in this study would exceed the proposed MCL. The EPA proposal is lower than the 10 ug/l MCL established by the World Health Organization.

These results underscore the need for further research on the geochemistry of ASR in Florida. Ongoing research at the Florida Geological Survey will continue to evaluate the geochemical effects of continued ASR cycling and further characterize the lithology and geochemistry of the Floridan aquifer system. Although the observations reported herein concerning water-quality changes during ASR are significant, proper design of ASR facilities (including installation of monitor wells), as well as proper design and monitoring of ASR cycles should be able to overcome any human health concerns.

* Note: During preparation of this document for publication, the EPA published a final rule lowering the MCL for As to 10 ug/l (Federal Register, 2001). This rule is being re-evaluated by the EPA.

Acknowledgements

This study presents results of Year Three of the Florida Department of Environmental Protection (FDEP)/Florida Geological Survey (FGS) Aquifer Storage and Recovery Geochemical study. This research is funded through a cooperative agreement between the FDEP/FGS and the Underground Injection Control (UIC) Program, Bureau of Water Facilities Regulation, Division of Water Resource Management, FDEP. The UIC program administers funds from the U.S. Environmental Protection Agency for this project. The authors thank George Heuler and Richard Deuerling (UIC Program) for their continued support of this research. We are also thankful for administrative support from Joe May and Judy Richtar of the FDEP Southwest District Office in Tampa. Other individuals who have provided valuable administrative support include Mark McNeal (CH2M HILL), Malachi (Mike) C. Bennett and Marjorie F. Guillory (City of Tampa Water Department), A. Ed Fox (Hillsborough County), and Mark Abbott and Rob Dennis (Montgomery Watson Harza). We thank Ed Fox and CH2M HILL for core collected from the NW Hillsborough reclaimed water ASR in support of this project.

Collection of ASR cycle-test samples by cooperators has allowed fund reallocation in support of additional laboratory analyses. We are especially grateful to the following people who collected samples for this project: Brian Fuller (City of Punta Gorda Water Treatment Plant), Pete Larkin and Marty Clasen (CH2M HILL).

Laboratory analyses for this study were completed at Activation Analytical Labs (Ontario, Canada), the Florida State University Isotope Geochemistry Laboratory, and the FDEP Bureau of Laboratories. Conversion of this manuscript to a digital (.pdf file) format was difficult and time-consuming, and we are indebted to Holly Tulpin and Charlie Steed for their work in bringing this aspect of the project to completion. We are also grateful for review of this report by the following FGS staff: Carol Armstrong, Paulette Bond, Jackie Lloyd, Guy Means, Deborah Mekeel, Frank Rupert, Dr. Walt Schmidt, and Dr. Tom Scott.

INTRODUCTION

This annual report summarizes activities and results of Year Three of the Florida Aquifer Storage and Recovery (ASR) Geochemical Study. The reader is referred to the Year One and Two progress report by Williams and others (in review) for background and initial results of the project, including an introduction to ASR, the geological setting of the study area, an introduction to relevant geochemical systems, initial research activities, data and interpretations.

Although the first two years of this investigation significantly improved our understanding of ASR geochemical processes and has resulted in modification of ASR wellfield design and monitoring, many questions remain unresolved. Summarized below are major highlights of the initial study (Williams and others, in review) as well as more recent observations based on their data.

- Uranium isotopes are useful tools in modeling the geochemical history and mixing of the injected surface waters and aquifer system matrix waters (i.e. native water). Groundwater U-isotopic ratios are the result of a dual porosity aquifer system, which may consist of three “end-member” waters: flowing intergranular, relatively non-flowing pore and conduit flow groundwaters. The type and degree of mixing of these waters during ASR cycling, however, is site specific and varies as a function of the hydrogeologic characteristics of the area (Cowart and others, 1998).
- In the Hillsborough County study area, the use of Sr isotopic ratios to determine the degree of limestone dissolution in the aquifer system during ASR is inconclusive (Williams and others, in review). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the injected waters (from the Hillsborough River) contain approximately the same ratios as that of the native groundwater, and both waters indicate equilibrium with Oligocene rocks (~37 to 24 million years old). According to data from the U.S. Geological Survey National Water Information System, the Hillsborough River was flowing at base flow levels during March, 1997, when the sample was collected and analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$. Base flow in the upper reaches of the Hillsborough River in Hillsborough County comes from the Oligocene Suwannee Limestone (Campbell and Arthur, 1993). This suggests that the observed Oligocene $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the injection water sample (pre-treated river water, collected 3/14/97) represents waters that have equilibrated with aquifer system carbonates exposed in the upper river basin. Had there been more surface water runoff in March, 1997, perhaps the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of input waters would have been more useful in modeling dissolution in the aquifer system due to cycle testing.

- Trace metals are leached from the aquifer system matrix during the ASR cycle testing. Of the metals analyzed during the first two years of this study (As, Ba, Cd, Ca, Pb, Mn, Na, Sr, U and Zn), results indicate that As and U are leached by injected, oxygen-rich surface waters. Other metals may be mobilized during ASR cycle testing, however, the data presented in Williams and others (in review) are inconclusive. Although short-term As and U increases are observed, U and As concentrations did not exceed maximum contaminant levels (MCL) (Williams and others, in review). Additional data reported herein, however, suggests that leaching of metals during ASR yield concentrations higher than previously observed and thus warrants further study, monitoring and site specific analysis.

PURPOSE OF INVESTIGATION

The purpose of this investigation is to evaluate the hydrochemical changes that occur during the ASR process within injected and native waters of the Floridan aquifer system at these selected sites. Specific goals for Year Three of the study include:

- Continue to investigate the nature of water-rock interaction as it affects ground-water chemistry.
- Identify the source and mechanism for mobility of trace metals into the injected waters.
- Determine the effect of repeated cycle testing on dissolved metal concentrations.
- Continue to examine uranium concentrations and isotopic ratios ($^{234}\text{U}/^{238}\text{U}$) in native aquifer water (when available), recharge water, recovered water, and water in surrounding wells; explore use of U geochemistry to further understand mixing of pore, native and injected waters.
- Determine the relation between gamma-ray log response and trace metal concentrations in the aquifer system carbonates.
- Provide the Florida Department of Environmental Protection (FDEP) with additional scientific knowledge on which to base protective criteria for future ASR projects.

The two ASR facilities in southwestern Florida that were initially included in this multi-year study remain the focus of this investigation: the Rome Avenue ASR facility in Hillsborough County, and the Punta Gorda ASR facility in Charlotte County (Figure 1). Additional ASR facilities did not perform cycle testing during Year Three (1999). Analyses of rock samples from the NW Hillsborough Reclaimed Water ASR facility are included in this report. Cycle testing is anticipated to begin in the near future at the NW Hillsborough facility.

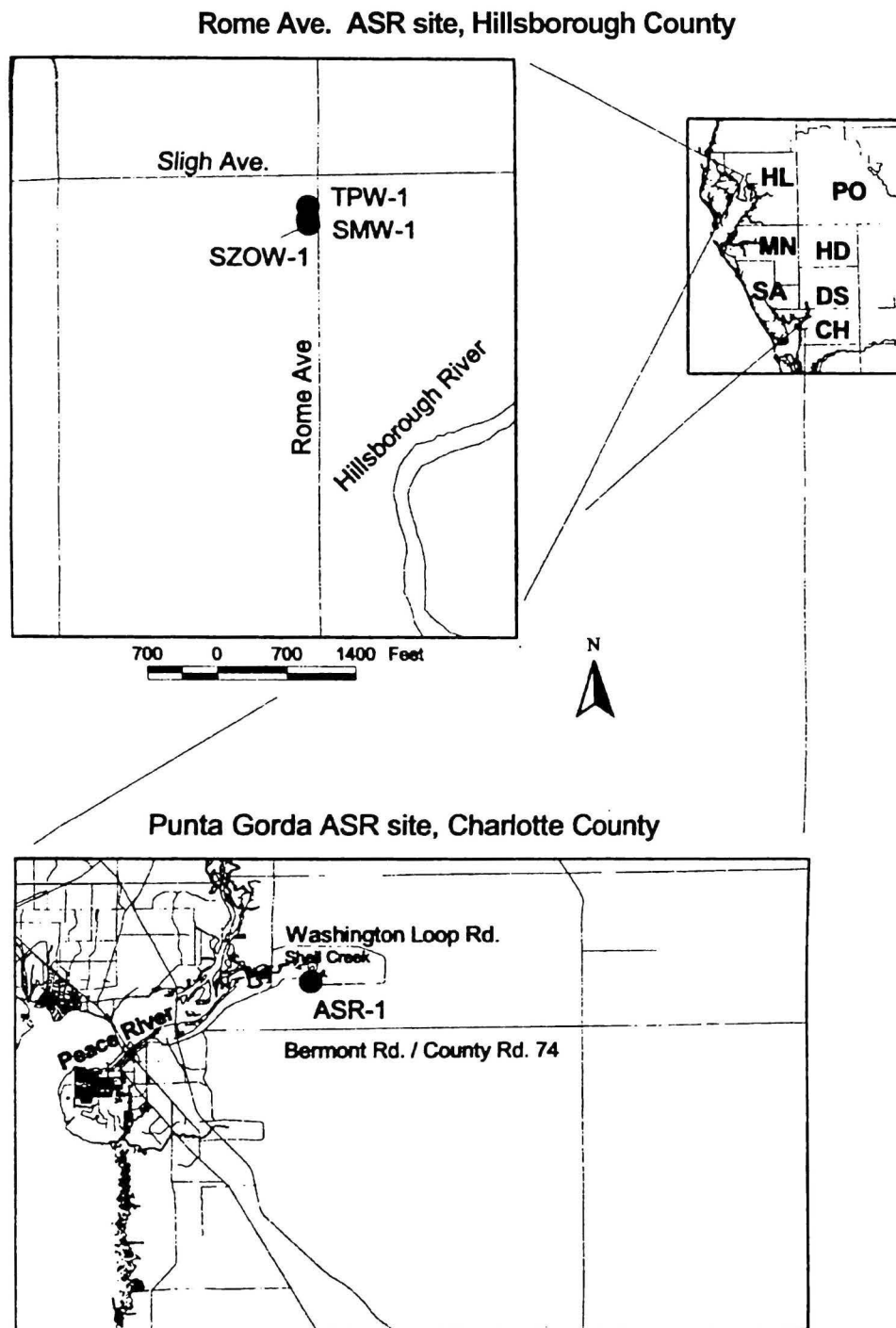


Figure 1. Location of study areas.

In a scientific investigation under optimum experimental conditions, data collection is designed to support the goals of the study. This investigation, however, is appended to existing activities at relatively new ASR facilities. As such, data collection is not driven by this research, but rather by the need to place the facilities in full production while meeting all water quality standards. Limiting factors in this study include gaps in time series data, lack of control over cycle test parameters (e.g., input/output rates and volumes) and types of borehole samples collected. Despite these limitations, significant progress has been made toward addressing the goals of this multi-year investigation.

METHODS

Whole rock chemistry

Whole rock analyses of 67 major, trace and rare-earth elements (REE's) were completed on 21 samples. These samples were collected from three wells at or near the ASR sites in the present study. Samples from the Rome Avenue injection well were not available for analysis. However, a nearby monitor well, WRAP 2D, (W-16574) provided cuttings at five-foot intervals. At the NW Hillsborough site, samples from the injection well TPW-1 (W-17687) were available as core segments and cuttings. Samples from another well in Hillsborough County, W-16618, were also included for regional comparison. W-16618 is located approximately 17 miles south-southeast of the study area. Uranium leaching experiments were completed on rock samples from this well (Green and others, 1995). Four of these samples are included in the present investigation to compare high-U samples (and high leaching potential) with variations in other trace metals in the carbonate matrix.

Rock samples were collected and analyzed based on the following criteria: lithology, gamma-ray activity and stratigraphic unit. Representative samples of limestones and two dolostone samples were collected for chemical comparison. The presence/absence of organic material in the samples was also noted. Using gamma-ray logs, samples were selected "on peak" and "off peak." This qualitative data is denoted on Table 1 as "HI" and "LO," respectively, in the column labeled "Gamma." Although higher concentrations of U, Th, and K are expected with increasing gamma-ray activity, the relation between other metals (and organic content) and gamma-ray response is not well understood for these rocks. All samples were collected from the Suwannee Limestone, which is utilized as the ASR storage zone in the region.

XRAL Laboratories (Toronto, Canada) completed all whole rock chemical analyses,

Table 1. Major-element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida

Well Number	Depth (ft. *)	Gamma HI/LO	Coatings Or Organics Y/N	Sample Ident Scheme Code Analysis Unit Detection Limit	Na2O ME3XRF % 0.01	MgO ME3XRF % 0.01	Al2O3 ME3XRF % 0.01	SiO2 ME3XRF % 0.01	P2O5 ME3XRF % 0.01	K2O ME3XRF % 0.01	CaO ME3XRF % 0.01	TiO2 ME3XRF % 0.001	MnO ME3XRF % 0.01	Fe2O3 ME3XRF % 0.01	LOI ME3XRF % 0.01
16618	368	LO	N	FGS-1	n.d.	0.8	0.15	1.21	0.03	0.02	54.6	0.017	n.d.	0.15	43
16618	382.5	HI	N	FGS-2	n.d.	0.61	0.11	1.07	n.d.	0.03	54.1	0.02	n.d.	0.11	43.1
16618	392	HI	Y	FGS-3	n.d.	0.84	1.15	10.6	0.05	0.2	47.3	0.143	n.d.	0.38	39.4
16618	425	LO	N	FGS-4	n.d.	0.68	0.32	6.94	0.11	0.07	51.9	0.065	n.d.	0.15	40.3
17687	310-315	LO	Y	FGS-5	n.d.	0.81	0.16	1.95	0.03	0.03	54.6	0.026	n.d.	0.17	42.6
17687	320-325	HI	Y	FGS-6	n.d.	0.71	0.08	1.11	0.02	0.02	55	0.015	n.d.	0.2	43.1
17687	325-330	HI	Y	FGS-7	n.d.	0.74	0.09	1.15	0.03	0.02	55	0.019	n.d.	0.2	43.1
17687	330-335	HI	Y	FGS-8	n.d.	0.65	0.45	2.11	0.03	0.03	54.4	0.033	n.d.	0.27	42.5
17687	340-345	LO	N	FGS-9	n.d.	0.8	0.09	1.43	0.02	0.02	54.7	0.017	n.d.	0.19	42.9
17687	360-365	LO	Y	FGS-10	n.d.	0.86	0.16	1.43	0.02	0.02	54.6	0.024	n.d.	0.31	42.9
17687	420-421	HI	Y	FGS-11	n.d.	0.91	0.09	0.86	0.03	0.02	55	0.016	n.d.	0.13	43.3
17687	429	HI	Y	FGS-12	0.04	18.2	0.35	1.6	0.1	0.06	33.3	0.025	0.02	0.18	45.4
17687	431	HI	Y	FGS-13	0.04	19	0.11	0.67	0.03	0.03	33.8	0.015	n.d.	0.16	46.4
17687	432	LO	Y	FGS-14	n.d.	0.77	0.06	0.6	0.02	0.02	55.2	0.01	n.d.	0.13	43.4
16574	295-300	LO	N	FGS-15	n.d.	0.79	0.1	1	0.03	0.03	54.2	0.015	n.d.	0.18	42.8
16574	325-330	LO	N	FGS-16	n.d.	0.78	0.11	1.41	0.03	0.02	54.8	0.015	n.d.	0.15	43.1
16574	330-335	HI	N	FGS-17	n.d.	0.81	0.11	1.19	0.03	0.02	55.1	0.021	n.d.	0.18	42.9
16574	335-340	HI	N	FGS-18	n.d.	0.79	0.13	1.73	0.03	0.03	54.1	0.023	n.d.	0.17	42.6
16574	370-375	LO	N	FGS-19	n.d.	0.75	0.14	4.12	0.03	0.02	53.5	0.016	n.d.	0.22	41.5
16574	459	LO	N	FGS-20	n.d.	0.82	0.1	0.29	0.04	0.02	55	0.017	n.d.	0.39	43.4
16574	459.5	LO	N	FGS-21	n.d.	0.77	0.09	0.43	0.04	0.02	55.3	0.014	n.d.	0.14	43.4
16574	459	LO	N	FGS-22	n.d.	0.79	0.11	0.41	0.04	0.03	55.4	0.013	n.d.	0.17	43.3
AVERAGE					0.04	2.4	0.19	2.0	0.04	0.04	52.3	0.03	0.02	0.20	42.9
Minimum					n.d.	0.6	0.06	0.29	0.02	0.02	33.3	0.01	n.d.	0.11	39.4
Maximum					0.04	19.0	1.15	10.6	0.11	0.20	55.4	0.14	0.02	0.39	46.4

Explanation

n.d. = not detected (below detection limit)

FGS 22 is blind duplicate of FGS 20

* = below land surface

Scheme Code:

MERXRF - x-ray fluorescence spectrometry (pellet)

ME3XRF - x-ray fluorescence spectrometry (fused disk)

ME3ICP - inductively coupled plasma/mass spectrometer

MEXNA - neutron activation

MERLEC - LECO/combustion

MERWET - specific ion (Cl), cold vapor (Hg)

MERMS - mass spectrometer

utilizing a high precision, multi-method technique. Analytical methods for each element are listed in Tables 1 through 3. Due to limited sample availability, borehole cuttings were analyzed in addition to core chips. Cuttings were handpicked under binocular microscope to minimize contaminants and maximize lithologic homogeneity. All drill-bit contact surfaces were removed from core samples taken from W-16574 and W-17687.

Water chemistry

Uranium analyses were performed at the Florida State University Geochemistry Laboratory in Tallahassee, Florida. This laboratory, under Comprehensive Quality Assurance Plan #960078-5, is approved by the FDEP. Thirty-four 5-gallon (18.9 liters) water samples were collected during cycle testing and delivered to the laboratory, where samples were then split for uranium analyses. Detailed sample preparation is described in Williams and others (in review). The $^{234}\text{U}/^{238}\text{U}$ activity ratio and uranium concentration in each sample was determined with alpha pulse-height spectrometry.

Seventy-five trace metal samples were collected in 250 ml amber-colored glass jars, preserved with 5% HNO_3 per FDEP groundwater sampling protocol. Unless otherwise noted, all water samples were unfiltered. The samples were first transported to the Florida Geological Survey, and then to the FDEP Central Laboratory. All samples were analyzed for trace metals by inductively coupled plasma emission spectroscopy at the FDEP Central Laboratory. Some samples did not meet FDEP sample preparation protocol because they were splits taken from the five gallon uranium samples. Interpretation limitations for these particular samples are addressed in a later section.

ARSENIC GEOCHEMISTRY

This section on As geochemistry is included herein based on the results of the Williams and others' (in review) report to the FDEP Underground Injection Control Program, as well as subsequent events such as maximum contaminant level (MCL) exceedences and changes in ASR facility design and testing. This information is provided as an overview to describe the natural occurrence of As in the hydrogeochemical environment.

Arsenic contamination in groundwater and As-associated illness in humans has been observed around the globe since the late 1950's (Das and others, 1996). Perhaps the most recent and notable occurrence of As contamination during the last decade has been the health crisis in

Table-2. Trace-element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida.

Well Number	Depth (ft.)	Gamma HI/LO	Coatings or Organics Y/N	Sample Ident Scheme Code	Rb ME3XRF ppm 2	Sr ME3XRF ppm 2	Zr ME3XRF ppm 2	Nb ME3XRF ppm 2	Ba ME3XRF ppm 20	B ME3ICP ppm 10	V ME3ICP ppm 2	Ni ME3ICP ppm 1	Cu ME3ICP ppm 0.5	Zn ME3ICP ppm 0.5
Detection Limit														
16618	368	LO	N	FGS-1	5	398	5	n.d.	60	25	23	4	4.1	5.7
16618	382.5	HI	N	FGS-2	n.d.	685	6	n.d.	68	n.d.	18	4	0.6	1.7
16618	392	HI	Y	FGS-3	9	2150	41	4	63	29	108	17	11.5	11.6
16618	425	LO	N	FGS-4	4	566	17	n.d.	64	n.d.	6	n.d.	0.7	3.7
17687	310-315	LO	Y	FGS-5	10	439	6	n.d.	56	n.d.	7	n.d.	1	2.7
17687	320-325	HI	Y	FGS-6	6	773	6	n.d.	43	n.d.	8	3	n.d.	2.1
17687	325-330	HI	Y	FGS-7	8	798	5	2	78	n.d.	4	1	0.6	5.2
17687	330-335	HI	Y	FGS-8	15	614	5	n.d.	72	n.d.	8	4	1.3	3.9
17687	340-345	LO	N	FGS-9	4	745	5	n.d.	61	n.d.	3	n.d.	n.d.	3.4
17687	360-365	LO	Y	FGS-10	10	576	5	n.d.	63	n.d.	10	1	n.d.	2
17687	420-421	HI	Y	FGS-11	9	441	4	n.d.	77	n.d.	21	4	n.d.	3.4
17687	429	HI	Y	FGS-12	n.d.	254	19	3	n.d.	n.d.	9	n.d.	n.d.	8.7
17687	431	HI	Y	FGS-13	3	228	13	2	27	n.d.	7	n.d.	n.d.	2
17687	432	LO	Y	FGS-14	11	429	3	2	56	n.d.	5	n.d.	n.d.	1.5
16574	295-300	LO	N	FGS-15	5	480	5	n.d.	49	n.d.	5	n.d.	0.7	6.3
16574	325-330	LO	N	FGS-16	17	453	4	n.d.	50	n.d.	4	n.d.	0.6	4.7
16574	330-335	HI	N	FGS-17	11	432	4	n.d.	46	n.d.	6	4	n.d.	6
16574	335-340	HI	N	FGS-18	n.d.	425	5	n.d.	37	n.d.	9	2	n.d.	4.5
16574	370-375	LO	N	FGS-19	15	436	5	n.d.	43	n.d.	6	2	n.d.	4.5
16574	459	LO	N	FGS-20	13	388	3	36	38	n.d.	6	2	n.d.	4.8
16574	459.5	LO	N	FGS-21	3	408	4	n.d.	54	n.d.	6	3	n.d.	4.9
16574	459	LO	N	FGS-22	15	382	3	3	54	n.d.	6	2	n.d.	2.1
AVERAGE					9	568	8	7	55	27	13	4	2	4
MINIMUM					n.d.	228	3	n.d.	27	n.d.	3	n.d.	n.d.	2
MAXIMUM					17	2150	41	36	78	29	108	17	12	12

Explanation

n.d. = not detected (below detection limit)

FGS 22 is blind duplicate of FGS 20

* = below land surface

Scheme Code:

MERXRF - x-ray fluorescence spectrometry (pellet)

ME3XRF - x-ray fluorescence spectrometry (fused disk)

ME3ICP - inductively coupled plasma/mass spectrometer

MEXNA - neutron activation

MERLEC - LECO/combustion

MERWET - specific ion (Cl), cold vapor (Hg)

MERMS - mass spectrometer

Table 2. (Continued)

Well Number	Depth (ft.)	Gamma HI/LO	Coatings or Organics Y/N	Sample Ident Scheme Code	Pb ME3ICP ppm 2	Au MEXNA ppb 2	Cr MEXNA ppm 2	Co MEXNA ppm 0.5	As MEXNA ppm 1	Se MEXNA ppm 1	Br MEXNA ppm 1	Mo MEXNA ppm 2	Sb MEXNA ppm 0.1	Hf MEXNA ppm 0.2
Detection Limit														
16618	368	LO	N	FGS-1	4	3	20	n.d.	n.d.	n.d.	1	4	n.d.	0.3
16618	382.5	HI	N	FGS-2	5	n.d.	15	n.d.	1	2	2	6	0.2	0.2
16618	392	HI	Y	FGS-3	n.d.	n.d.	53	0.9	10	57	5	67	1.9	2.2
16618	425	LO	N	FGS-4	n.d.	n.d.	17	n.d.	2	n.d.	2	8	n.d.	1.4
17687	310-315	LO	Y	FGS-5	7	n.d.	24	n.d.	3	n.d.	1	n.d.	0.3	n.d.
17687	320-325	HI	Y	FGS-6	n.d.	n.d.	25	n.d.	2	n.d.	2	n.d.	n.d.	n.d.
17687	325-330	HI	Y	FGS-7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
17687	330-335	HI	Y	FGS-8	n.d.	n.d.	17	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.
17687	340-345	LO	N	FGS-9	n.d.	n.d.	14	n.d.	n.d.	n.d.	1	n.d.	n.d.	n.d.
17687	360-365	LO	Y	FGS-10	4	n.d.	15	n.d.	n.d.	n.d.	1	n.d.	n.d.	n.d.
17687	420-421	HI	Y	FGS-11	n.d.	n.d.	8	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.
17687	429	HI	Y	FGS-12	n.d.	n.d.	18	n.d.	3	n.d.	n.d.	n.d.	0.3	n.d.
17687	431	HI	Y	FGS-13	n.d.	n.d.	14	n.d.	n.d.	n.d.	1	n.d.	n.d.	n.d.
17687	432	LO	Y	FGS-14	n.d.	n.d.	7	n.d.	n.d.	n.d.	2	n.d.	n.d.	n.d.
16574	295-300	LO	N	FGS-15	4	n.d.	16	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.
16574	325-330	LO	N	FGS-16	3	n.d.	16	n.d.	3	n.d.	1	n.d.	n.d.	n.d.
16574	330-335	HI	N	FGS-17	3	n.d.	14	n.d.	3	n.d.	2	n.d.	n.d.	n.d.
16574	335-340	HI	N	FGS-18	9	n.d.	14	n.d.	3	n.d.	1	n.d.	n.d.	n.d.
16574	370-375	LO	N	FGS-19	4	n.d.	11	n.d.	2	n.d.	1	n.d.	n.d.	n.d.
16574	459	LO	N	FGS-20	n.d.	n.d.	8	n.d.	n.d.	n.d.	8	n.d.	n.d.	n.d.
16574	459.5	LO	N	FGS-21	n.d.	n.d.	10	n.d.	n.d.	n.d.	8	n.d.	n.d.	n.d.
16574	459	LO	N	FGS-22	4	n.d.	9	n.d.	n.d.	n.d.	7	n.d.	n.d.	n.d.

AVERAGE		5	3	16	1	3	30	3	21	0.7	1.0
MINIMUM		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MAXIMUM		9	3	53	1	10	57	8	67	1.9	2.2

Explanation

n.d. = not detected (below detection limit)

FGS 22 is blind duplicate of FGS 20

* = below land surface

Table 2. (Continued)

Well Number	Depth (ft.')	Gamma HI/LO	Coatings or Organics Y/N	Sample Ident Scheme Code	W MEXNA ppm 1	Th MEXNA ppm 0.2	U MEXNA ppm 0.1	Sn MERXRP ppm 2	S MERLEC % 0.01	Cl MERWET ppm 50	Hg MERWET ppb 5	Cd MERMS ppm 0.2	Y ME3XRF ppm 2
				Detection Limit									
16618	368	LO	N	FGS-1	7	0.3	10	n.d.	n.d.	n.d.	n.d.	n.d.	12
16618	382.5	HI	N	FGS-2	n.d.	0.2	7.9	n.d.	n.d.	n.d.	n.d.	n.d.	3
16618	392	HI	Y	FGS-3	1	1.4	28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
16618	425	LO	N	FGS-4	n.d.	0.6	3.4	n.d.	n.d.	n.d.	n.d.	n.d.	8
17687	310-315	LO	Y	FGS-5	n.d.	0.6	3.4	2	0.08	63	44	n.d.	9
17687	320-325	HI	Y	FGS-6	n.d.	0.7	5.9	n.d.	0.11	72	10	0.6	12
17687	325-330	HI	Y	FGS-7	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	18	n.d.	8
17687	330-335	HI	Y	FGS-8	n.d.	0.8	3.4	n.d.	0.08	89	105	n.d.	5
17687	340-345	LO	N	FGS-9	n.d.	n.d.	2.8	2	0.06	61	8	0.3	4
17687	360-365	LO	Y	FGS-10	n.d.	n.d.	5.7	n.d.	0.07	75	8	n.d.	3
17687	420-421	HI	Y	FGS-11	n.d.	n.d.	8.2	n.d.	0.07	130	26	0.3	n.d.
17687	429	HI	Y	FGS-12	n.d.	n.d.	4.9	n.d.	0.08	108	6	n.d.	2
17687	431	HI	Y	FGS-13	n.d.	n.d.	5.3	n.d.	0.05	116	n.d.	n.d.	n.d.
17687	432	LO	Y	FGS-14	n.d.	n.d.	3.8	2	0.06	n.d.	56	n.d.	n.d.
16574	295-300	LO	N	FGS-15	n.d.	n.d.	3.7	7	0.08	65	26	0.4	3
16574	325-330	LO	N	FGS-16	n.d.	n.d.	3	n.d.	0.07	n.d.	20	n.d.	3
16574	330-335	HI	N	FGS-17	n.d.	n.d.	4.6	5	0.08	n.d.	81	n.d.	2
16574	335-340	HI	N	FGS-18	n.d.	n.d.	5.7	n.d.	0.08	59	158	0.2	3
16574	370-375	LO	N	FGS-19	n.d.	n.d.	3.1	7	0.08	52	23	0.5	4
16574	459	LO	N	FGS-20	n.d.	n.d.	1.8	3	0.05	n.d.	36	n.d.	4
16574	459.5	LO	N	FGS-21	n.d.	n.d.	2	2	0.05	n.d.	49	0.2	4
16574	459	LO	N	FGS-22	n.d.	n.d.	1.9	7	0.05	n.d.	23	n.d.	4

AVERAGE		4	0.7	5.6	4	0.07	81	41	0.4	5.2
MINIMUM		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MAXIMUM		7	1.4	28.0	7	0.11	130	158	0.6	12.0

Explanation

n.d. = not detected (below detection limit)

FGS 22 is blind duplicate of FGS 20

* = below land surface

Table 3. Rare earth element concentrations; Floridan aquifer system carbonates; Hillsborough County, Florida.

Well Number	Depth (ft.)	Gamma HI/LO	Coatings Or Organics Y/N	Sample Ident Scheme Code Analysis Unit Detection Limit	La MEXNA ppm 0.1	Ce MEXNA ppm 1	Pr MERMS ppm 0.2	Nd MEXNA ppm 3	Sm MEXNA ppm 0.01	Eu MEXNA ppm 0.05	Gd MERMS ppm 0.1	Tb MEXNA ppm 0.1	Dy MERMS ppm 0.1	Er MERMS ppm 0.1	Yb MEXNA ppm 0.05	Lu MEXNA ppm 0.01	Total REE (estimate)
16618	368	LO	N	FGS-1	2	2	n.d.	5	0.5	0.09	n.d.	n.d.	n.d.	n.d.	0.24	0.03	10.46
16618	382.5	HI	N	FGS-2	0.9	1	n.d.	4	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	0.01	6.95
16618	392	HI	Y	FGS-3	6.3	8	n.d.	7	1.5	0.2	n.d.	n.d.	n.d.	n.d.	0.28	0.08	23.96
16618	425	LO	N	FGS-4	2.8	4	n.d.	5	0.52	0.13	n.d.	0.1	n.d.	n.d.	0.29	0.05	13.39
17687	310-315	LO	Y	FGS-5	5.4	5.8	1.3	4.8	1	0.2	1.4	0.2	1.1	0.8	0.6	0.11	22.71
17687	320-325	HI	Y	FGS-6	5.2	3.8	1.2	4.5	1.3	0.21	1.4	0.2	1.3	0.9	0.7	0.12	20.83
17687	325-330	HI	Y	FGS-7	2.9	2.6	0.6	2.3	0.6	0.13	1	0.2	0.9	0.6	0.5	0.07	12.4
17687	330-335	HI	Y	FGS-8	2.9	3.2	0.7	2.5	0.7	0.13	0.9	0.1	0.7	0.4	0.4	0.08	12.71
17687	340-345	LO	N	FGS-9	2.2	2.2	0.4	1.6	0.5	0.09	0.6	n.d.	0.5	0.3	0.3	n.d.	8.8
17687	360-365	LO	Y	FGS-10	1.9	2.4	0.4	1.6	0.5	0.08	0.5	n.d.	0.4	0.2	0.3	n.d.	8.39
17687	420-421	HI	Y	FGS-11	0.6	0.8	n.d.	0.6	0.2	n.d.	0.2	n.d.	0.2	n.d.	n.d.	n.d.	3.1
17687	429	HI	Y	FGS-12	1.8	2.5	0.4	1.6	0.3	0.08	0.3	n.d.	0.3	0.1	0.1	n.d.	7.63
17687	431	HI	Y	FGS-13	1.4	1.3	0.2	0.8	0.3	n.d.	0.2	n.d.	0.2	0.1	0.1	n.d.	4.76
17687	432	LO	Y	FGS-14	0.5	0.7	n.d.	0.4	0.2	n.d.	0.1	n.d.	0.1	n.d.	n.d.	n.d.	0.51
16574	295-300	LO	N	FGS-15	1.2	1.2	0.2	0.9	0.3	0.06	0.4	n.d.	0.3	0.2	0.2	n.d.	5.07
16574	325-330	LO	N	FGS-16	1.5	1.7	0.3	1.1	0.4	0.1	0.3	n.d.	0.5	0.2	0.3	n.d.	6.51
16574	330-335	HI	N	FGS-17	7.1	9.5	1.3	3.9	0.3	0.07	0.4	n.d.	0.3	0.2	0.1	n.d.	23.28
16574	335-340	HI	N	FGS-18	1.9	2.6	0.4	1.5	0.4	0.08	0.4	n.d.	0.4	0.2	0.2	n.d.	8.19
16574	370-375	LO	N	FGS-19	2.7	2.3	0.5	1.9	0.6	0.13	0.6	n.d.	0.6	0.3	0.2	0.06	9.99
16574	459	LO	N	FGS-20	2.4	1.7	0.5	1.7	0.5	0.09	0.6	0.1	0.5	0.3	0.3	n.d.	8.7
16574	459.5	LO	N	FGS-21	4.2	2.6	0.9	2.8	0.5	0.14	0.6	0.1	0.5	0.3	0.2	n.d.	12.85
16574	459	LO	N	FGS-22	2.4	1.7	0.5	1.7	0.6	0.11	0.6	0.1	0.6	0.3	0.3	0.05	8.96
AVERAGE					2.7	2.9	0.6	2.6	0.5	0.12	0.6	0.1	0.5	0.3	0.3	0.07	10.92
MINIMUM					0.5	0.7	n.d.	0.4	0.2	0.06	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
MAXIMUM					7.1	9.5	1.3	7.0	1.5	0.21	1.4	0.2	1.3	0.9	0.7	0.12	23.96

Explanation

n.d. = not detected (below detection limit)

FGS 22 is blind duplicate of FGS 20

* = below land surface

Scheme Code:

MERXRP - x-ray fluorescence spectrometry (pellet)

ME3XRF - x-ray fluorescence spectrometry (fused disk)

ME3ICP - inductively coupled plasma/mass spectrometer

MEXNA - neutron activation

MERLEC - LECO/combustion

MERWET - specific ion (Cl), cold vapor (Hg)

MERMS - mass spectrometer

West Bengal, India, and in adjacent Bangladesh. Approximately one-third of the 50 million people in Bangladesh are feared to be at risk from chronic exposure to As (Bhattacharya and others, 1999a). Along with other incidents, the India crisis has led to an increased awareness and response in the scientific community. Since 1998, organizations in the United States (e.g., Geological Society of America and the American Geophysical Union) and other countries have held special sessions on the subject of As in groundwater. In 1999, the National Research Council released their report, *Arsenic in Drinking Water*.

As part of the Safe Drinking Water Act, the U.S. Environmental Protection Agency has set an MCL of 50 ug/l (ppb) for As. A proposal to revise this standard to 5 ug/l, however, is under review (Federal Register, 2000). For comparison, the World Health Organization MCL for As is 10 ug/l.

Arsenic in the hydrogeologic environment

In groundwater, two oxidation states of arsenic are arsenate (As^{5+}) and arsenite (As^{3+} ; Hemm, 1985). In most natural waters, As^{3+} exists as arsenite hydroxide ($\text{As}(\text{OH})_3$) and arsenous acid (H_3AsO_3), whereas the less mobile As^{5+} occurs as arsenic acid (H_3AsO_4). Several methylated acid species exist as well (National Research Council, 1999). Arsenic is present in a variety of solid phases in the hydrogeological environment. Summarized below are examples of these As-mobilization mechanisms and associated mineral phases:

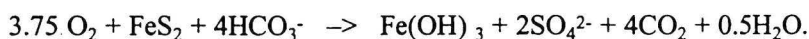
- *Oxidation of sulfide minerals* such as pyrite and arsenopyrite (e.g., White and Scully, 1999; Nickson and others, 2000). Pyrite (FeS_2) contains the following trace elements as impurities or in solid solution: Cu, Pb, As, Zn, and Mn (Deer and others, 1992). Nickel and Co commonly substitute for Fe in the pyrite lattice. Thomas and Saunders (1998) report As concentrations in authigenic pyrite up to 1000 ppm. A variant of this category is oxidation of framboid masses (Kolker and others, 1999), which are microscopic, spheroidal clusters of sulfide minerals associated with organic material.
- *Fe and Mn hydroxide grain coating desorption/dissolution* (e.g., Schlottmann and Breit, 1992; Welch, A.H., 1999). These coatings are reported to contain up to 30 ppm As (Thomas and Saunders, 1998). Nickson and others (2000) report As concentrations in grain coatings (recalculated as pure FeOOH) in excess of 500 ppm.
- *Oxidation-reduction of organic material* (e.g., Welch and Lico, 1998; Bhattacharya and

others, 1999b; Stollenwerk and Colman, 1999). Redox reactions can mobilize organically complexed As.

Arsenic occurrences in groundwater are also related to biological transformations (Maddox and others, 1992; Ahmann, D., 1999; National Research Council, 1999) and anthropogenic activities such as contamination from pesticides (Maddox and others, 1992), tannery waste (Brandon and others, 1999) and landfill leachate (Colman and Lyford, 1999).

Recent studies document As mobility during artificial recharge of aquifers (Stuyfzand, 1998; Ruiter and Stuyfzand, 1998, Brun and others, 1998). In a study of 11 deep well recharge experiments, oxidation of pyrite is reported, resulting in mobilization of As, Co, and Ni (Stuyfzand, 1998). Stuyfzand found that As remains relatively mobile while Ni and Co are less mobile and likely coprecipitate or adsorb on to Fe-hydroxides further away from the injection well. Although Zn is associated with pyrite, it did not mobilize, possibly due to scavenging by Fe-hydroxide (Stuyfzand, 1998).

In a similar study utilizing separate recharge and recovery wells, Ruiter and Stuyfzand (1998) also report oxidation of pyrite leading to mobilization of As, Co and Ni. In their study, Zn is also reported to be mobile. Of the mobilized metals, only As reached the most distant recovery well (relative to the recharge well) due to its higher mobility (Ruiter and Stuyfzand, 1998). An increase in SO_4^{2-} and diminishing O_2 and NO_3^- is also attributed to pyrite oxidation. Of the several important geochemical reactions that may occur during artificial recharge listed in Stuyfzand (1998), the following reaction represents oxidation of pyrite leading to precipitation of Fe-hydroxides and increases in sulfate in the injected water:



This reaction is one of many listed in Stuyfzand (1998) that may be relevant to geochemical processes taking place in ASR wells utilizing the Floridan aquifer system.

RESULTS AND DISCUSSION

WHOLE ROCK CHEMISTRY

Multi-method, multi-element chemical analyses of Suwannee Limestone samples from Hillsborough County are listed in Tables 1, 2 and 3. The tables also show minimum, maximum and average concentrations for the samples. These samples provide reconnaissance chemistry of a variety of carbonate lithologies (Appendix 1). A statistical evaluation of these and additional data is planned.

Two of the samples (FGS-12 and FGS-13) are dolostones, with MgO concentrations up to 19 weight percent. These two samples have slightly higher loss on ignition (LOI) values than the limestones. Moreover, the samples are depleted in Ca, Sr and REE's and enriched in Zr relative to the limestones. Both samples contain trace amounts of organic material and represent zones of higher gamma-ray activity.

Of the other carbonates analyzed, one sample, FGS-3 contains trace metal concentrations exceeding all other samples in this study. This sample contains the highest reported values for Al, Si, K, Ti, As, Sr, Zr, B, Ni, Cu, Zn, Cr, Co, Se, Mo, Sb, Hf, Th and U and contains the lowest LOI and LREE concentrations. High Si, Al and K concentrations suggest that this sample has a siliciclastic component. Possible heavy mineral content (likely in a fine-sand to silt-sized fraction) in the siliciclastic component of this sample may account for maximum observed concentrations of Ti and Zr, among other metals. The As concentration in this sample is 10 ppm. Of the U content in this sample (FGS-3; U = 28 ppm), approximately one-third of the U is leachable under oxidizing (laboratory) conditions (Green and others, 1995). Sulfur was below detection in this sample. Samples FGS 1-4 were analyzed using an analytical package that could not resolve concentrations of S, Cl, Hg and Cd in these carbonates. The choice of analytical packages will be re-evaluated for subsequent chemical analyses to maximize detection of S, which may reflect, in part, pyrite content. Mineralogical investigation of these samples is planned for Phase 5 of the project.

Trends observed in most bivariate plots tend to be anchored by the high-concentrations in sample FGS-3. Although many of the "trends" are not discussed herein, a few plots indicate a possibly important trend that is not entirely biased by FGS-3. Figure 2 shows the relation between Fe_2O_3 and As, suggesting a possible presence of Fe-sulfides and/or Fe-hydroxides in the samples. Arsenic is present in both of these phases. Zinc is also associated with sulfides. A positive correlation exists between Zn and As as well (Figure 3).

Available data suggest no relation between As and U concentrations, organic content or high gamma-ray activity in these samples. There exists, however, a relation between high gamma-ray activity and organic content within the samples. In general, those samples with high gamma-ray activity contain organic material and those samples with low gamma-ray activity do not contain observable organic material. Of 21 samples, six do not fit this generalization. Additional data and a statistical evaluation may further substantiate this observation.

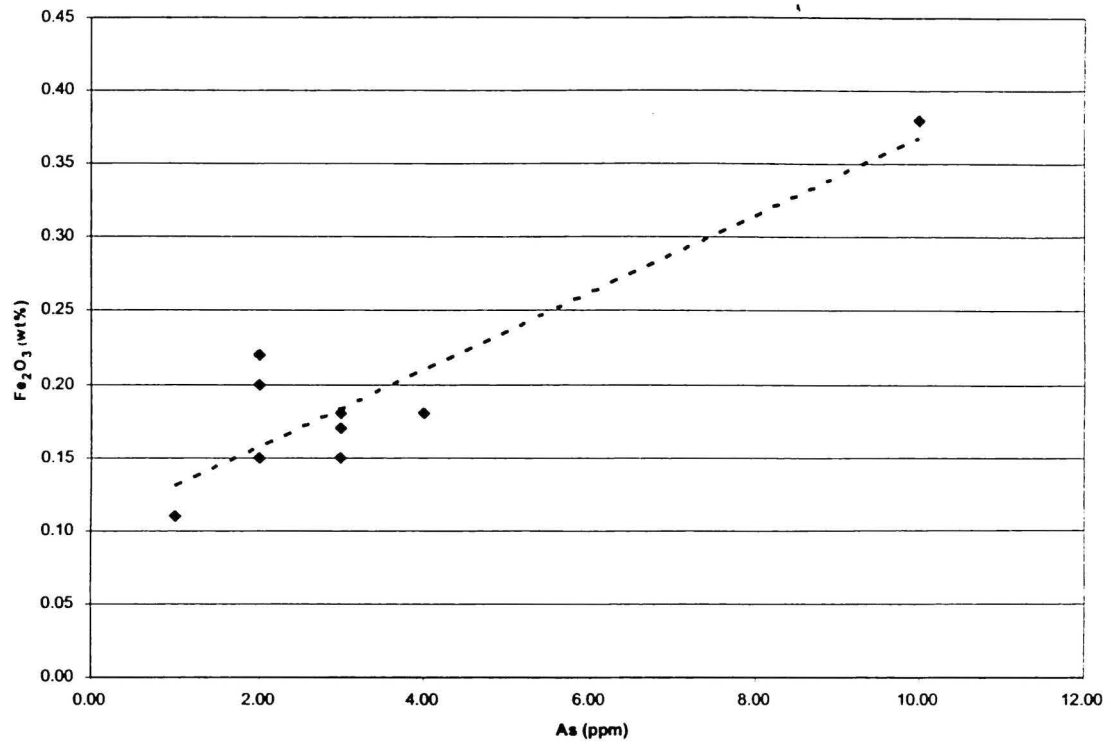


Figure 2. Iron oxide (Fe₂O₃) - As variation in Suwannee Limestone, Hillsborough County, Florida

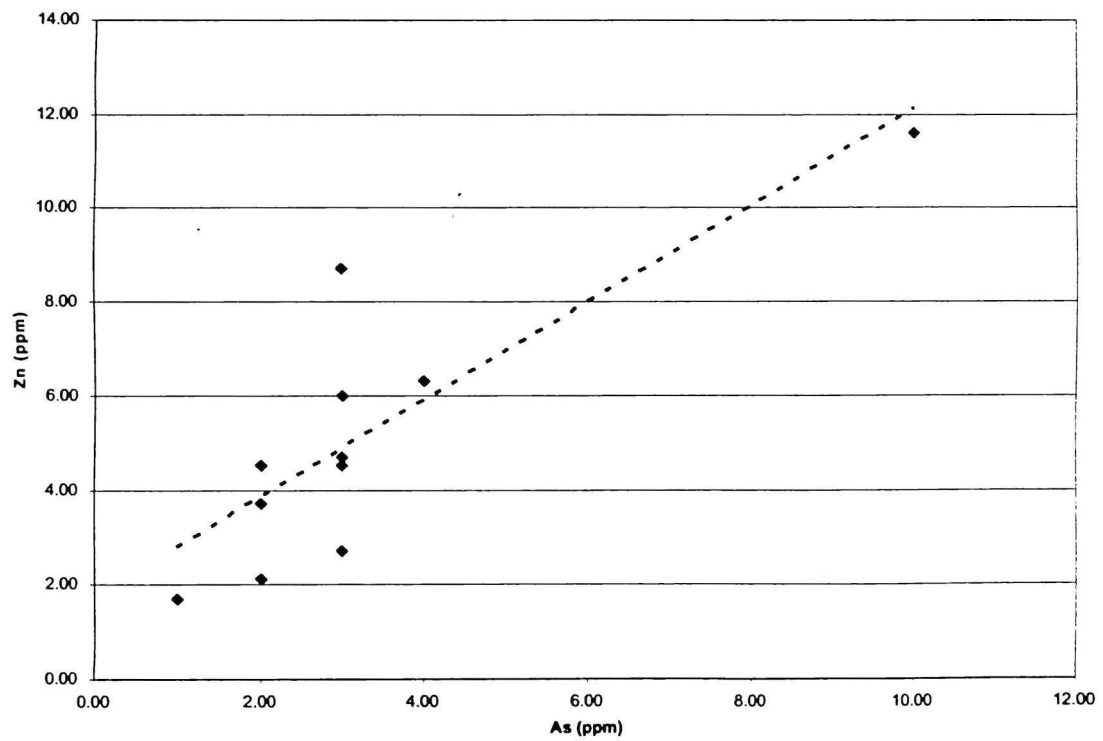


Figure 3. Zinc - As variation in Suwannee Limestone, Hillsborough County, Florida

The range of chemical compositions in these rocks provides some insight into the chemical heterogeneity in the aquifer system in this region (Tables 1, 2 and 3). Based on this variability, one may conclude that water-rock interaction modeling based on laboratory experiments may not completely represent the hydrogeochemical processes taking place over large areas during ASR activities. Such laboratory ground work, however, is important and geochemical analyses of core samples are required to provide control in these models and to help understand observed water quality trends during ASR.

Rare-earth elements

To allow comparison of REE distributions between samples, all REE data in this report have been normalized to the North American Shale Composite (Grommet and others, 1984). The REE patterns for samples from the three boreholes in this study (Figures 4, 5 and 6) all cluster around an NASC normalized value of 0.1, which is typical of carbonate compositions (Bellanca and others, 1997). Moreover, the nearly ubiquitous negative Ce anomaly is consistent with a marine depositional origin (Bellanca and others, 1997), and indicates that post-depositional chemical changes may not have greatly influenced the REE distributions. Variations in REE patterns do, however, exist relative to trace metal concentrations and depth. The somewhat fragmented REE pattern (i.e., elements not analyzed or detected) in Figure 4, when compared to the samples from other wells (Figures 5 and 6), is due to use of a different analytical package for these samples.

A comparison of all patterns indicates that the high-As sample, FGS-3, as well as samples FGS-5 and FGS-6 plot at the high end of the REE-normalized range. Upon analysis of all available data, these three samples share two common characteristics. First, the samples contain organic material. This characteristic, however, is not unique to these samples. Seven other samples also contain organics (possibly as grain coatings), thus the enrichment may not be related. The second characteristic is the Cr content of these samples, which is higher than any other sample in this data set. The relation between Cr and total REE is the subject of further study.

Slight differences in the slope of each REE pattern indicates enrichment or depletion in light or heavy REE's. Ratios of Sm to Yb and to Pr allow an alternative to comparing REE patterns for heavy (HREE) and light (LREE) pattern enrichment or depletion. This distribution of REE ratios (Figure 7), indicates that Suwannee Limestone samples exhibit a variety of enrichment from LREE to HREE. At present, no discernable relationships are observed between LREE and HREE and other chemical or physical characteristics of the rocks. None of

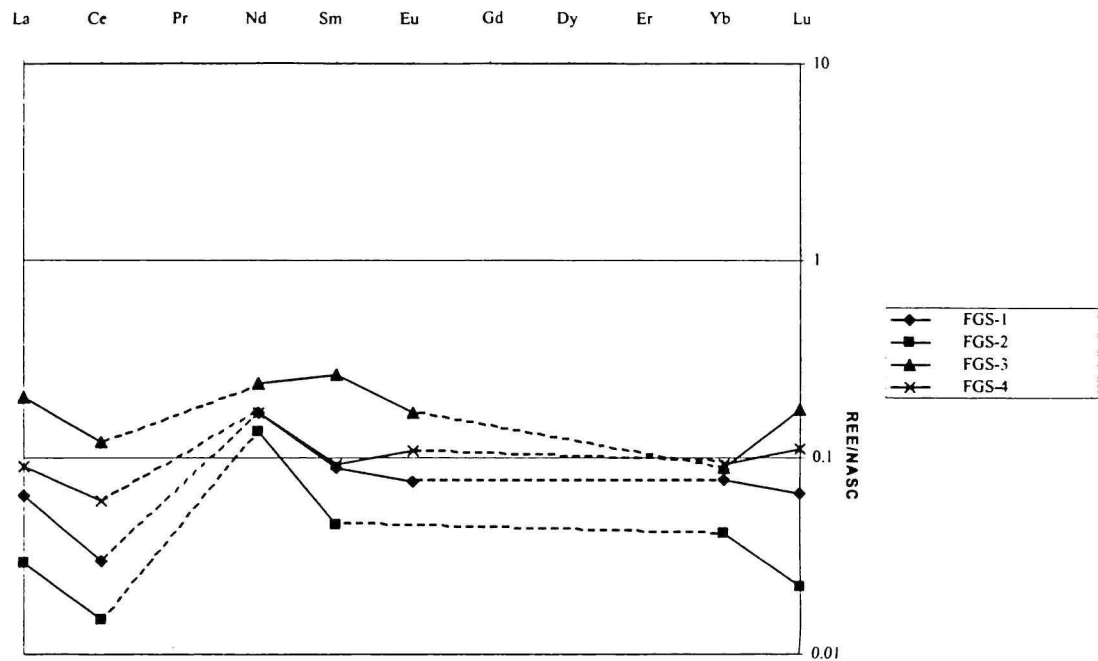


Figure 4. Normalized rare earth element distribution in Suwannee Limestone samples from W-16618, Hillsborough County, Florida.

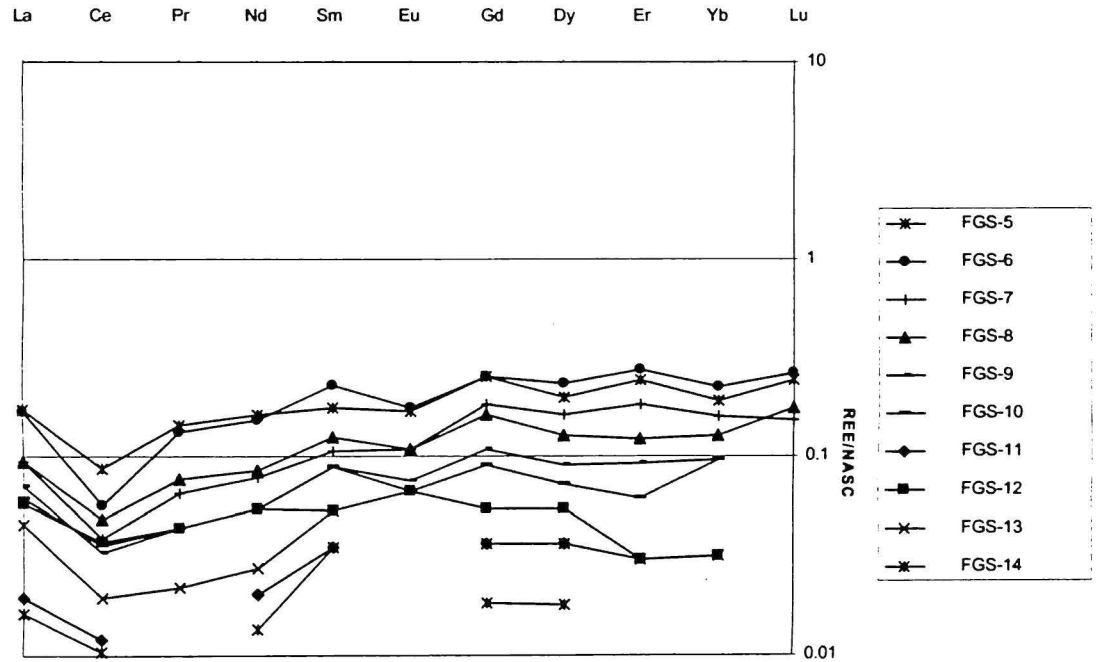


Figure 5. Normalized rare earth element distribution in Suwannee Limestone samples from W-17687, Hillsborough County, Florida.

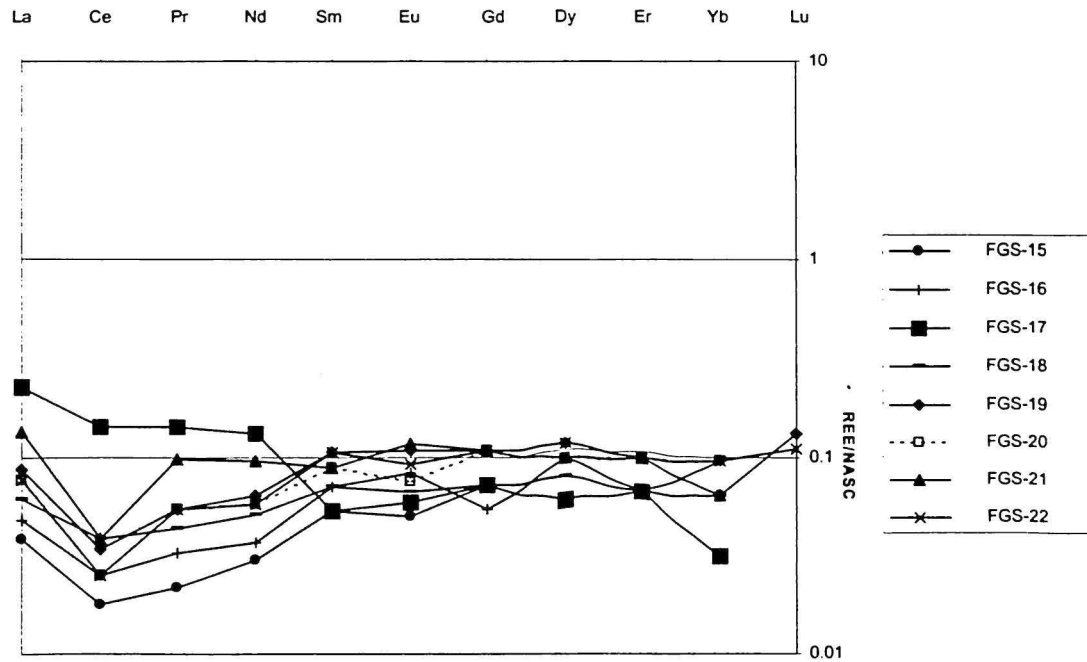


Figure 6. Normalized rare earth element distribution in Suwannee Limestone samples from W-16574, Hillsborough County, Florida.

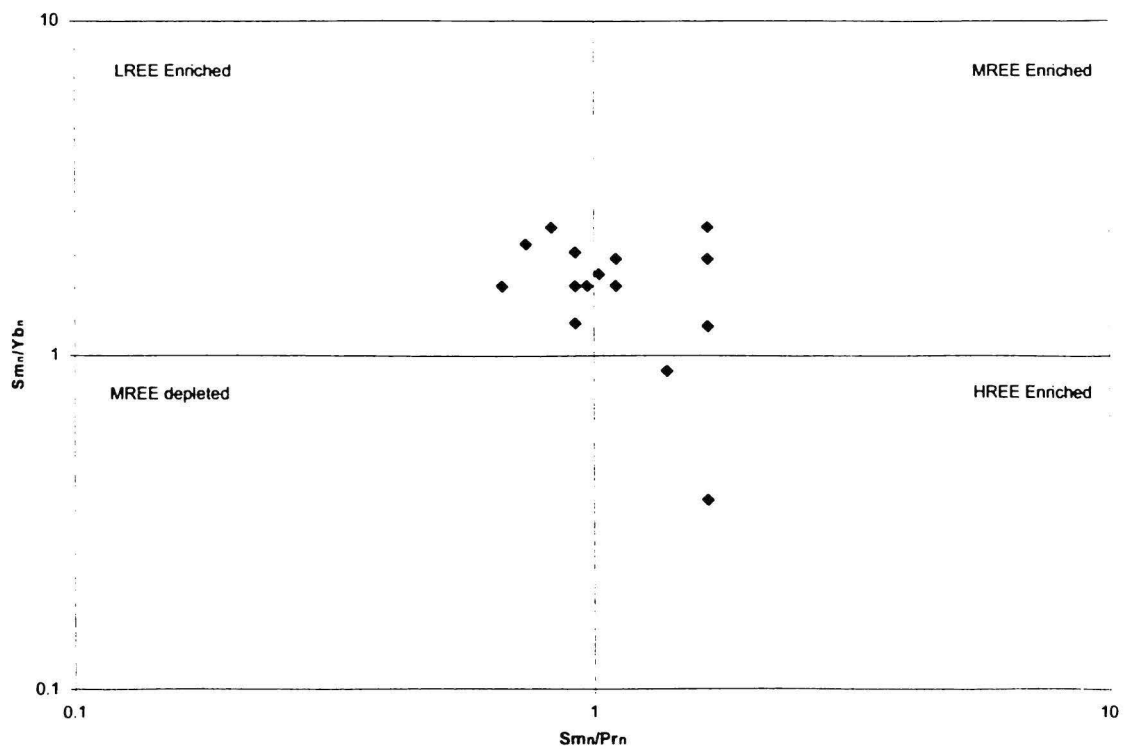


Figure 7. Normalized rare earth elements ratios showing Suwannee Limestone samples relative to fields of enrichment and depletion (LREE - light REE, MREE - middle REE, and HREE - heavy REE).

the samples in this study are depleted in middle REE's (MREE; Figure 7).

Total REE concentrations in the samples are estimated from the sum of all REE data plus the detection limits for those elements reported as "n.d." in Tables 1, 2 and 3. Any error or uncertainty associated with this estimation is minimal compared to observed trends. In fact, the same trends are observed when replacing "n.d." with null values.

Figure 8 is a plot of total estimated REE concentrations versus loss on ignition (LOI). LOI is a measure of the volatile content of a lithologic sample. Among other minor constituents, LOI includes structural water from phyllosilicates, adsorbed/absorbed water, CO₂ from carbonate material, and reflects weight changes due to oxidation of organics and metals (e.g., Fe). Most carbonates in this study have LOI values centered around 43 percent. Five samples, however, show a negative correlation with REE concentrations. This variation is the result of two overprinting lithologic characteristics: 1) the high LOI samples are the only two dolomitic samples in the data set, and 2) low LOI (<42%) samples increase in Si and Al with increasing REE content. The latter association is also observed in a plot of SiO₂ plus Al₂O₃ versus total REE (not shown).

Samples from W-17687 also indicate lithologic/depositional control of REE concentrations. With one exception, total REE content decreases with depth from 310 to 430 feet below land surface in that borehole (Table 3). Measured trace metals do not exhibit such variation with depth. Further sampling may or may not confirm this trend. Significance of the possible relation between high Cr, (and As in one sample) and total REE content may become more apparent during chemical investigation of mineral phases in the rocks during future FGS studies.

WATER CHEMISTRY

Uranium

In an aquifer system, the behavior and relationship between uranium concentration and uranium isotope ratios released by the action of aggressive waters is thought to be a function of the geochemical history of the rocks and the permeating waters. An idealized schematic model of the behavior of uranium under different conditions is presented along with a comparison between actual measurements and those predicted by the model.

In the following discussion, it will be assumed that recoil of the nucleus resulting from

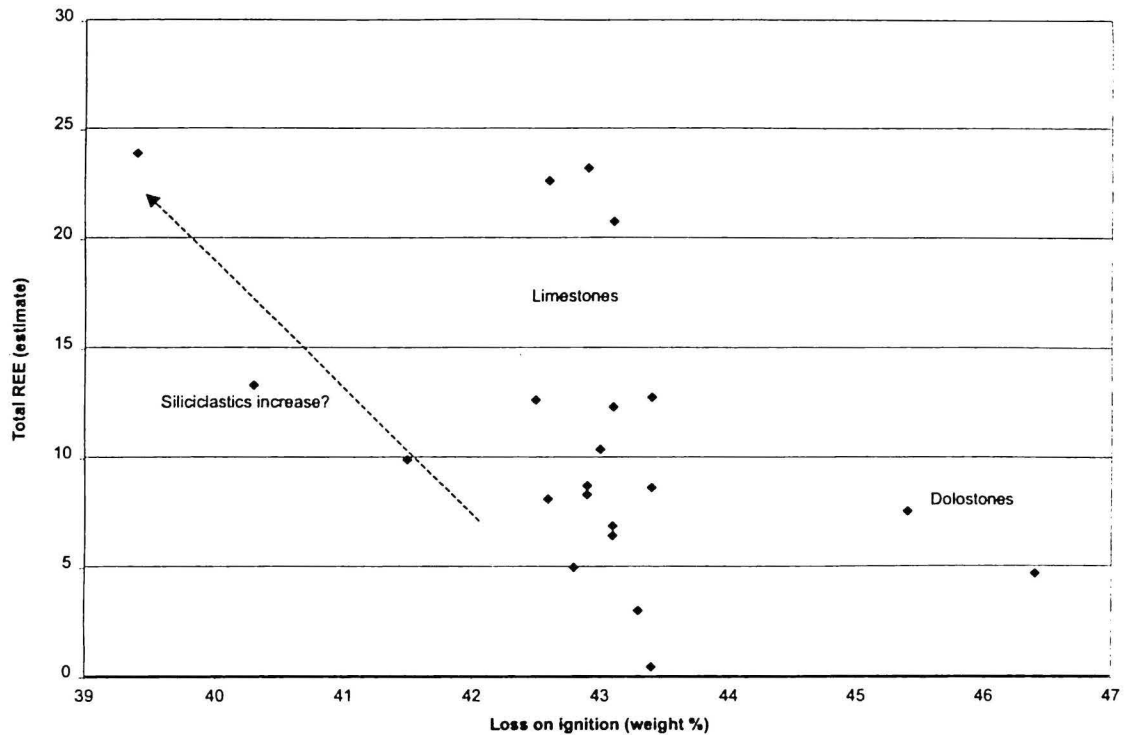


Figure 8. Total rare earth element (estimated, see text) distribution in Suwannee Limestone samples versus loss on ignition (LOI.)

the alpha particle decay of an atom is the most prominent mechanism affecting uranium isotope fractionation. Selective leaching of ^{234}U atoms can also play an important role in fractionating uranium isotopes in locations where oxic waters have continuously permeated a rock; however, in the present study area, it is probable that reducing waters have been in contact with the aquifer system matrix until the introduction of oxic waters by injection.

The redox environment is important because the oxidized uranium ion, U^{6+} , is highly mobile whereas the reduced uranium ion, U^{4+} , is quite immobile. In oxygenated water uranium is easily transported but if that water becomes reduced, the uranium contained in it will precipitate. This being the case, selective leaching of any isotope of uranium is suppressed. On the other hand, ejection of the nucleus resulting from the alpha decay of ^{238}U , which is in effect ^{234}U , is not inhibited because it is a physical mechanism, not a chemical one. If the ^{234}U is ejected from a rock into moving, albeit reduced water, the rock containing the uranium will become depleted in ^{234}U relative to ^{238}U because the ^{238}U can only become mobile through chemical means and some portion of the ^{234}U has been transported away. Therefore, if aggressive oxygenated waters invade a reduced aquifer, the initial uranium released from the rock will usually be deficient in ^{234}U .

With the above in mind, four scenarios are presented which provide insight into behavior of the uranium isotopes as shown by the measurements made of the waters recovered from several ASR sites (Table 4). In all the cases, the water in the aquifer is assumed to have been reducing before the injection of oxygen-rich surface waters. In two of the cases (1 and 2) the water bathing the rock is moving and in the other two cases (3 and 4) the water is assumed to have no significant motion (Figure 9). Each of the diagrams is meant to convey the uranium concentration and isotope ratio ($^{234}\text{U}/^{238}\text{U}$) for a **single grain** as oxic water mobilizes the uranium at deeper and deeper levels within that grain. In a manner of speaking, we are peeling off onion-like layers that contain the variously affected uranium. It should be noted that the concentration of uranium depends almost totally on the amount of ^{238}U present and is not measurably affected by the deficiency or excess of ^{234}U .

Case 1. A grain containing uranium homogeneously distributed within it (Figure 9). The nucleus recoiled from a ^{238}U atom originally sited at the grain-water boundary has a 50% chance of recoiling into the water. The nucleus recoiling from a ^{238}U atom located a small distance below the grain-water boundary would have a smaller probability of being ejected into the water and so on down to a distance equal to the recoil distance at which point no recoiling nucleus would be able to be ejected. In this case 0.50 would be the lowest uranium isotope ratio and it would be seen first (as the uranium in the outermost layer of the grain is mobilized), followed by ratios tending towards 1.00, the ratio of the interior of the grain.

Case 2. A grain having a very thin coating or layer of relatively high concentration uranium resting on top of a grain having uranium homogeneously distributed within it (Figure 9). The coating might consist of organic material or might result from precipitation of uranium due to changing redox character of the aquifer in the past - a mechanism responsible for the formation of many sedimentary uranium ore bodies. It is assumed that the layer is significantly thinner than the recoil distance of recoiling uranium nuclei. In this case the lowest $^{234}\text{U}/^{238}\text{U}$ ratio can be less than 0.50 because both above and below the coating the uranium concentration is less than that of the coating. Those nuclei recoiling into the water will be carried off as in Case 1. Those recoiling downward into the grain engender a zone in which the ^{234}U is in excess relative to ^{238}U and below the recoil distance the $^{234}\text{U}/^{238}\text{U}$ ratio is 1.00. Invading oxic waters first mobilize the coating so that the concentration rises rapidly but then decreases as the coating is dissipated. The concentration is then dictated by mobilization of uranium from the underlying unenriched rock material. The zone directly beneath the high

Table 4. Uranium analyses for Cycle Test samples from Punta Gorda ASR. Uranium detection limit is 0.01 ug/l

Sample No. (FLW)	Date	U (ug/l)	Activity Ratio 234U/238U
NATIVE			
5173	6/28/99 6:00 PM	2.99	0.85
INJECTION			
5174	7/1/99 12:00 PM	0.03	1.21
5176	7/19/99 10:00 AM	0.025	2.4
5195	8/17/99 2:30 PM	0.064	1.37
5196	8/18/99 11:00 AM	0.056	1.02
5197	8/19/99 12:00 AM	0.708	0.93
5198	8/30/99 1:00 PM	0.038	2.4
RECOVERY			
5177	7/22/99 9:15 AM	0.027	1.08
5178	7/22/99 10:00 PM	2.03	0.74
5179	7/23/99 10:00 AM	3.79	0.76
5180	7/23/99 10:00 PM	4.75	0.81
5181	7/24/99 10:00 AM	5.79	0.81
5182	7/24/99 10:00 PM	5.88	0.84
5183	7/25/99 10:00 AM	7.93	0.83
5184	7/25/99 10:00 PM	7.92	0.83
5185	7/26/99 10:00 AM	7.23	0.86
5186	7/26/99 10:00 PM	7.08	0.87
5187	7/27/99 10:00 AM	7.85	0.85
5188	7/27/99 10:00 PM	7.42	0.84
5189	7/28/99 10:00 AM	7.2	0.84
5190	7/28/99 10:00 PM	7.37	0.84
5191	8/5/99 12:00 AM	3.6	0.82
5193	8/5/99 12:00 AM	4.08	0.85
5192	8/6/99 12:00 AM	6.23	0.87
5194	8/6/99 12:00 AM	7.1	0.85
5200	9/1/99 2:30 PM	1.56	0.85
5201	9/1/99 10:00 PM	2.07	0.86
5202	9/2/99 2:00 PM	3.76	0.87
5203	9/2/99 10:00 PM	3.98	0.91
5204	9/3/99 10:00 AM	4.58	0.9
5205	9/4/99 10:00 AM	3.9	0.88
5206	9/5/99 10:00 AM	2.92	0.9
5207	9/6/99 10:00 AM	2.36	0.88
5208	9/8/99 9:30 AM	2.14	0.96

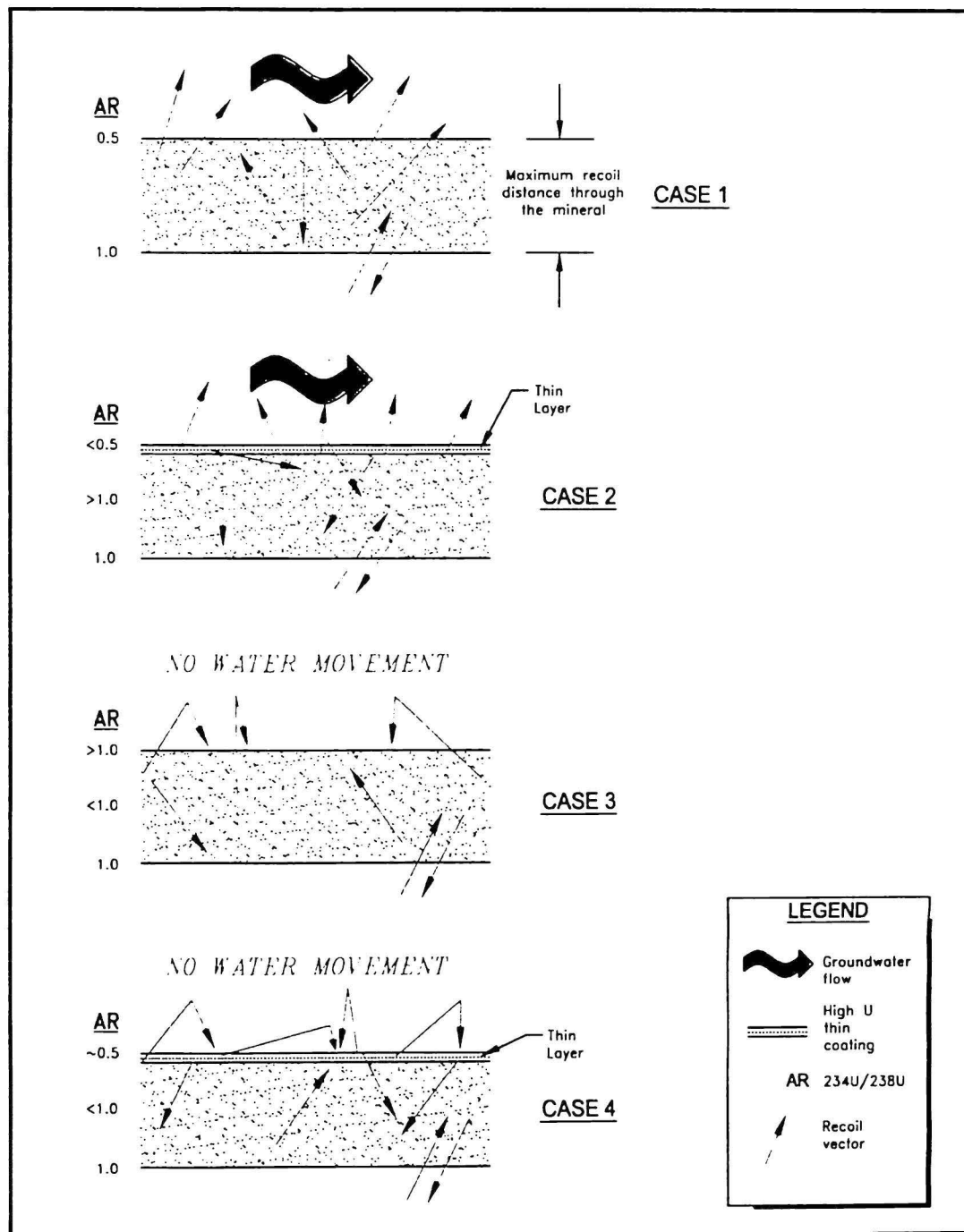


Figure 9. Uranium mobilization models for single carbonate grains (coated and uncoated) exposed to flowing and non-flowing groundwater. Cases 1-4 reflect conditions that may occur during ASR.

concentration layer has a $^{234}\text{U}/^{238}\text{U}$ ratio greater than 1.0 because the number of nuclei that recoiled down into this zone far exceed those moving upward.

Case 3. In this case and in Case 4, the water surrounding the grain is both reducing and essentially “stagnant” (Figure 9). In Case 3, as in Case 1, the rock material is homogeneous with regard to uranium distribution. However, in this situation, for those recoiling nuclei that reach the water there is no transport away from the grain but rather an eventual precipitation of the ^{234}U on the surface of the grain. The effect is that all the nuclei that reach the water end up on the grain boundary so that invading oxic water will first mobilize uranium which is enriched in ^{234}U so that the $^{234}\text{U}/^{238}\text{U}$ ratio will be greater than 1.00. After this ^{234}U -enriched zone has been mobilized, the uranium will have a ratio of less than 1.00, even approaching 0.5. Finally the ratio will approach 1.00 as the limit of recoil within the rock material is reached. Because ^{234}U does not contribute significantly to total uranium concentration, the initial concentration will be high.

Case 4. In this case, as in Case 2, an initial coating with a relatively high concentration of uranium is hypothesized (Figure 9). In such a situation, those nuclei recoiled into the water will eventually be precipitated onto the grain boundary and those recoiled downward will generate a zone enriched in ^{234}U . Invading oxic water mobilizes the high uranium concentration coating first so that the $^{234}\text{U}/^{238}\text{U}$ ratio will initially be less than 1.00 (although probably not approaching 0.5) followed by the mobilization of the zone just below the high uranium concentration coating, which has a ratio greater than 1.00. Finally the ratio will approach 1.00. Because there is a coating, the initial concentration will tend to be relatively high, followed by a lower concentration, reflecting the difference in uranium concentration between the coating and the underlying grain.

The scenarios described above are based on a single grain being acted upon by waters that promote the mobilization of the uranium present. In an actual aquifer the mobilizing water affects many grains, not all of which are identical. Further, the injected water can mix with native waters or with waters that affected the same grains, but at a different time. Nevertheless, the wide range of isotopic values and changing uranium concentrations appear to reflect the behavior suggested by some of these scenarios.

Rome Avenue

The Rome Avenue, Tampa (Hillsborough County) ASR Test Production Well (TPW-1)

provided samples that appear similar to those of Case 2. No samples were taken during the first cycle of testing. The initial isotope ratios measured during Cycle 2 were somewhat below 0.5 and as more of the injected water was recovered the ratio increased such that the final three samples had ratios of about 0.85 (Figure 10). The uranium concentration increased in the first few samples taken, peaked, and then decreased (Figure 11). It is likely that the samples collected during Cycle 2 were somewhat modified by the previous exposure of the aquifer rocks to injected oxic waters.

Cycle 3 consisted of a long period of injection followed by storage. The only discharge samples that were available from TPW-1 were taken during a short period of recovery. Each of the five samples taken during this time had a uranium concentration of about 1.0 ug/l (Figure 11) and an isotope ratio which was very low (approximately 0.38; Figure 10). These values are very similar to the initial samples taken during Cycle 2 recovery. The interpretation of these low-isotope ratio samples is that they are found in injected oxic waters that have had time to penetrate into the micropores found in all aquifer rocks and have mobilized the uranium located there. With increased flow back to the well (as in Cycle 2) the isotope ratio increases and the concentration increases as the uranium is mobilized from the previously somewhat leached grains along the major conduits or flow passages.

Punta Gorda

Two injection zones were tested at the Punta Gorda (Charlotte County) ASR facility. Appendix 2 summarizes relevant drilling, cycle testing and chemical modeling activities at this site. The upper zone tested at Punta Gorda (Cycle 1) seems to fit Case 3 in which the recovered waters first have an isotope ratio greater than 1.00 (Figure 12). Relatively small amounts of water were input during Cycle 1 injection, thus only the first part of Case 3 was observed, suggesting that native water in that zone migrated little, if at all. This is consistent with the assumptions of Case 3.

The lower injection zone at Punta Gorda (Cycles 1A and 2A) is more difficult to assign to a particular scenario. The initial isotope ratios are less than 1.00 but not in the vicinity of 0.5 and, in fact, they remain more-or-less constant through time (Figure 13). A possibility is that some water movement has occurred in this zone (which has a greater acceptance of injected water than does the upper zone) so that some portion of the recoiled ^{234}U was transported away in the past. This would result in an initial mobilization ratio between 0.5 and 1.0. A combination of environments combining Cases 1 and 4 approximate this suite of measurements.

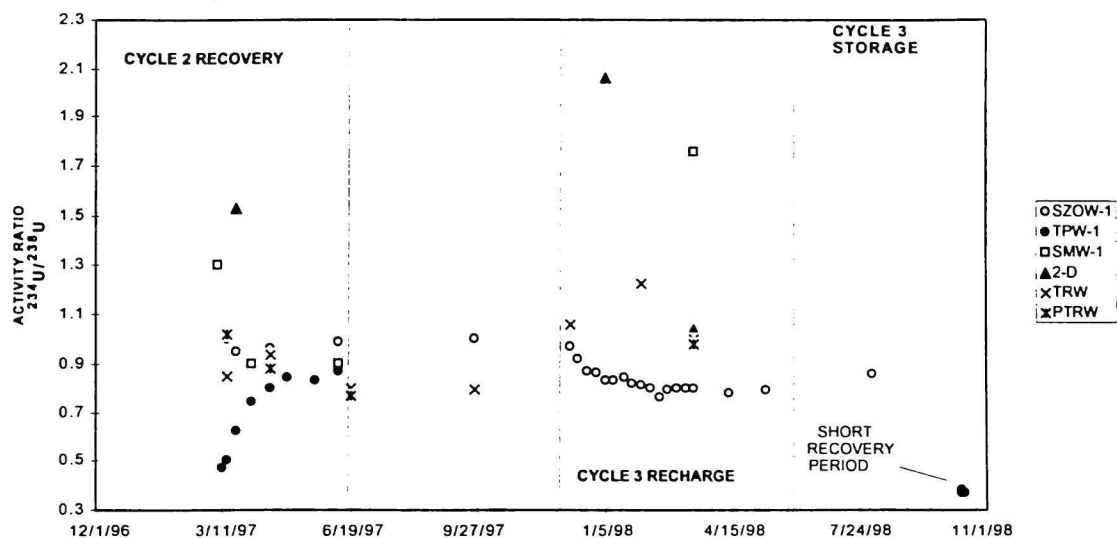


Figure 10. Uranium activity ratios through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida.

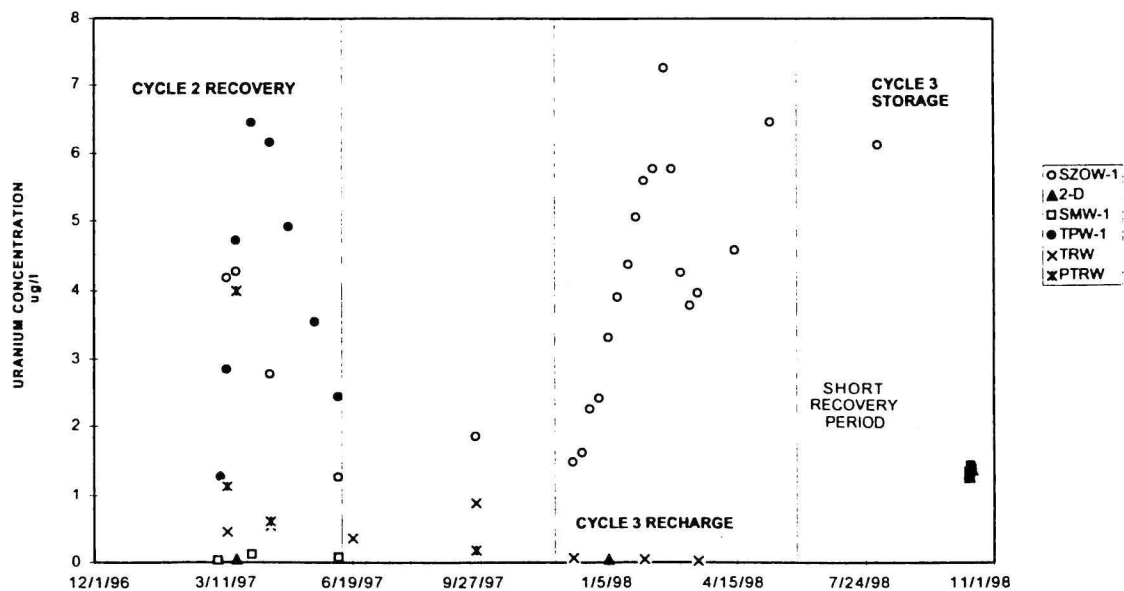


Figure 11. Uranium concentration through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida (data source: Williams and others, in review). All concentrations are below the proposed 20 ug/l MCL for U.

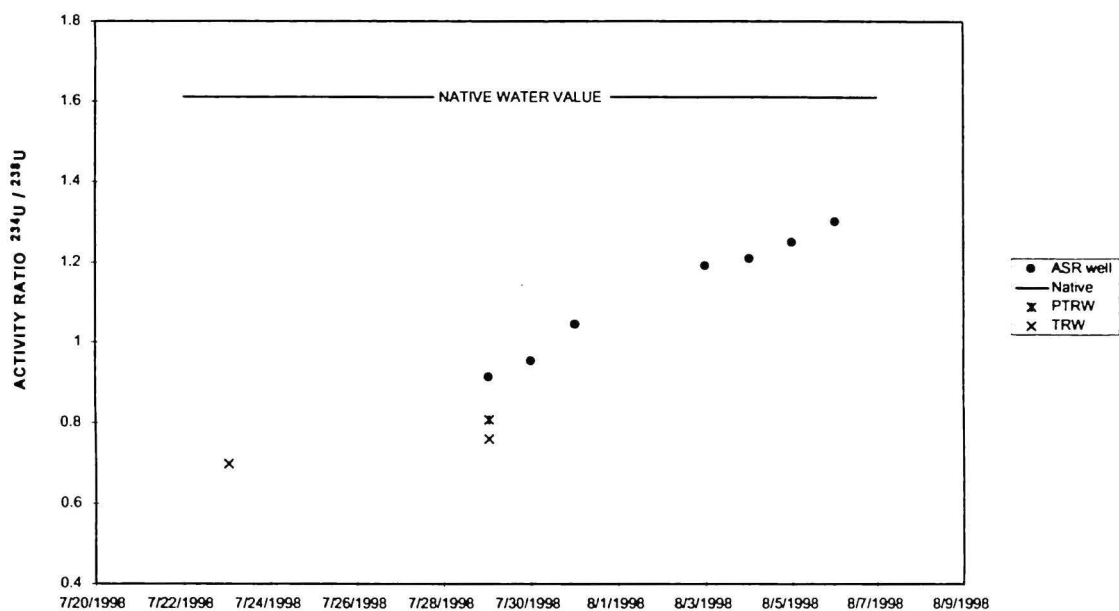


Figure 12. Uranium activity ratio through time for Cycle 1 (Upper Zone), Punta Gorda ASR, Charlotte County, Florida.

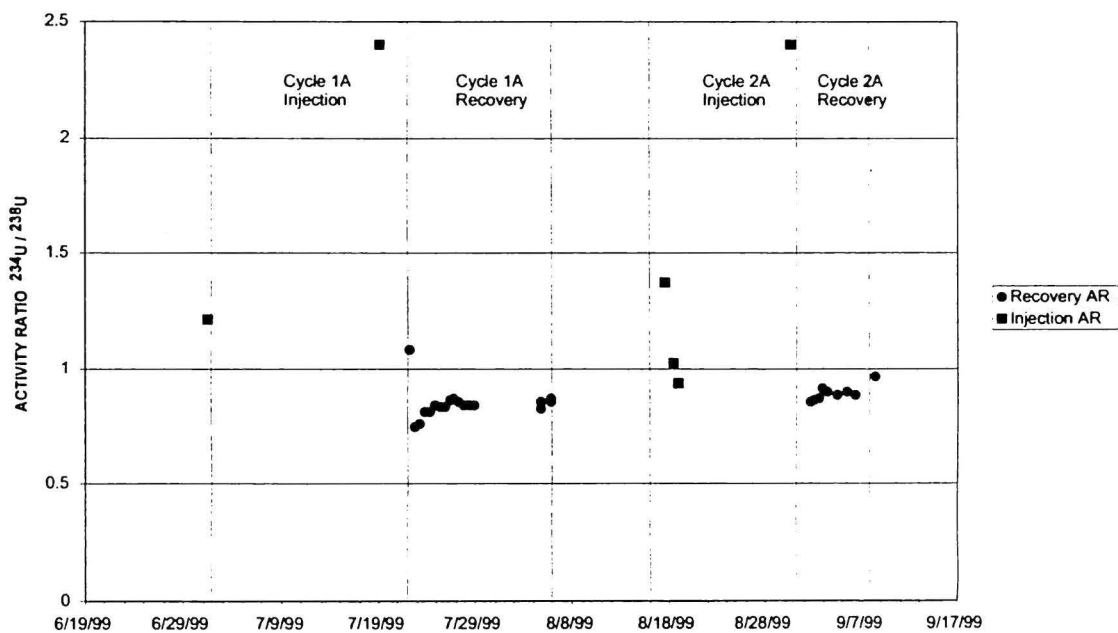


Figure 13. Uranium activity ratio through time for Cycles 1A and 2A, Punta Gorda ASR, Charlotte County, Florida.

Thus far in this multi-year investigation, cycle testing at Punta Gorda (Lower Zone) provides the only opportunity to compare chemical trends in two successive cycles. In Cycle 1A, U concentrations approach 8 ug/l, whereas in 2A, the maximum U concentration observed is 4.6 ug/l (Figure 14). The observed trends indicate leaching of total U from the aquifer system matrix. Significance of the observed decrease in maximum U values between Cycles 1A and 2A is difficult to ascertain. Had cycle testing conditions been consistent (and the results directly comparable), the data would suggest that with continued cycling U is being successively depleted from the source and may ultimately decline to native groundwater values. Conditions, however, were not consistent; differences exist in injection duration, injection and recovery rates, and probable FeOH precipitation in the borehole (see Appendix 2). Further study under more controlled conditions is required to determine if U concentrations (and other metals) in recovered waters decrease with increasing ASR cycling.

Other trace metals

Rome Avenue

Williams and others (in review) report As values up to 36 ug/l during the Cycle 2 recovery phase for TPW-1. Although the observed values for that cycle were below the current As MCL of 50 ug/l, the increase in As warranted further study at this site. Subsequent to the first progress report (Williams and others, in review), additional Cycle 2 samples were analyzed. These additional Cycle 2 samples were initially collected as 5 gallons samples for U analysis. These splits did not meet FDEP sample preservation protocol; however, they were the only samples available to improve resolution of the observed Cycle 2 trend. It was hoped that analysis of these additional samples would better delineate the behavior of As, at least to the degree that changes in water quality monitoring could be suggested, if necessary. Given that the Cycle 2 samples did not meet FDEP protocol, the results are only considered an indication of the geochemical processes that occur during this ASR cycle.

The As distribution through time for Cycle 2 recovery and all of Cycle 3 is shown in Figure 15. This data set includes 24 new analyses (Table 5). Because Cycle 3 took place over a period of only three days and likely represents only a partial recovery trend, a quantitative comparison of results from the two cycles is not possible. The pre-treated river water sample (PTRW) represents an As concentration for injected water (< 1 ug/l As). During the recovery period for both cycles, a distinctive increase in As is observed, with one sample exceeding the

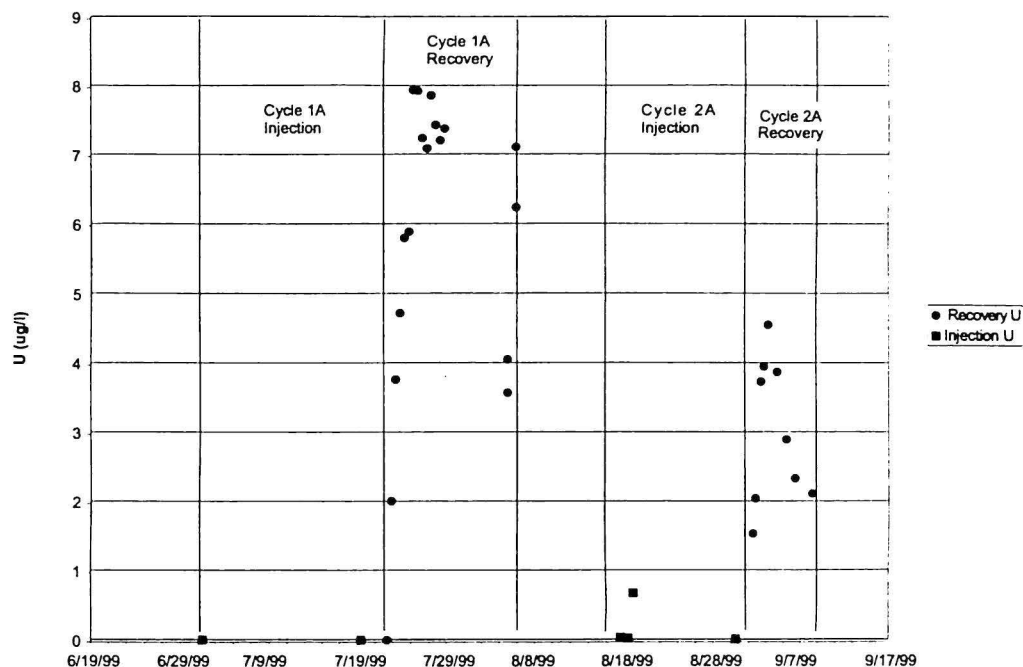


Figure 14. Uranium concentration through time for Cycles 1A and 2A, Punta Gorda ASR, Charlotte County, Florida

As MCL. (This sample, although significant, did not meet all FDEP sampling protocols.) Although the cycles did not continue to the extent that native groundwater As levels (< 2 ug/l; Maddox and others, 1992) were reached, both trends show a peak in As, followed by a decline. The decline represents mixing of the injected waters with low-As native groundwater.

Collection of samples from SZOW-1, the storage zone monitor well, began in March, 1997 at values likely representing the outer edge of the injection bubble (Figure 15). During Cycle 2 recovery, the injected “bubble” is withdrawn from the SZOW-1 well and the concentration decreases toward background groundwater levels for As. An increase is again observed in SZOW-1 as Cycle 3 recharge begins, reflecting migration of reactive injected waters across the location of that well, which is 192.5 feet south of TPW-1.

To address the issue of mobilized metals in recovered waters at Rome Avenue, the project consultants, CH2M Hill, conducted a cycle test during May and June, 1999. Abatement of As mobility was evaluated through a pH-adjusted cycle test. The pH of injected waters was elevated in an attempt to reduce As concentrations in recovered waters. Changes in As concentration during the test are shown in Figure 16. During the initial pump-out (May 10, 1999 to May 24, 1999) for this cycle, As concentrations vary similarly to those found during

Table 5. Trace metal analyses for Rome Ave. ASR samples. Shaded data are from Williams and others (1999). Non-shaded data do not fully meet FDEP sampling protocols. See text for further explanation. "BD"- Below detection.

	As ug/l	Ba ug/l	Cd ug/l	Ca mg/l	Mn ug/l	K mg/l	Na mg/l	Sr ug/l	Zn ug/l
DETECTION LIMIT	4.0	0.7	0.4	0.1	0.25	0.01	0.1	0.4	1.5
SMW-1									
3/7/97	BD	14.6	BD	62.8	6.20	0.733	7.9	137	BD
3/14/97	BD	15.9	BD	62.7	6.82	0.743	8.4	137	BD
6/9/97	BD	14.3	BD	64.0	5.44	0.778	9.4	139	BD
1/5/98	BD								
3/16/98	BD								
SZOW-1									
3/7/97	35	14.2	BD	77.6	7.29	2.45	26.7	197	18
3/14/97	24	14.1	BD	70.7	13.8	2.29	21.2	178	23
4/1/97	7							146	
6/9/97	4							145	
9/24/97	5								
12/8/97	4								
12/15/97	8								
12/22/97	4								
12/29/97	BD								
1/12/98	5								
1/26/98	6								
2/9/98	8								
2/23/98	9								
3/9/98	8								
3/21/98	16							169	
5/11/98	13								
8/3/98	17	11.9		72.1	5.54		31.8	185	
TPW-1									
3/10/97	BD	16.0	BD	117	335	2.50	34.5	496	58
3/11/97	9	12.5	BD	91.9	59.2	1.97	24.2	470	167
3/14/97	11	11.3	BD	84.9	9.40	2.08	25.6	413	73
3/20/97	22	11.4	BD	80.4	12.0	2.15	26.4	330	42
3/21/97								320	
4/3/97								236	
4/17/97	53							207	
5/1/97	45							201	
5/22/97	29							199	
6/9/97	36	11.9	BD	70.5	6.04	1.64	23.9	216	BD
2-D									
3/7/97	BD	31.4	BD	134	13.2	6.88	219	2400	13
3/14/97	BD	30.1	BD	133	10.8	7.00	218	2350	13
1/5/98	BD								
3/16/98	BD								
PTRW									
3/20/97	BD	12.5	BD	65.9	9.25	1.64	10.7	553	29
TRW									
3/14/97								552	

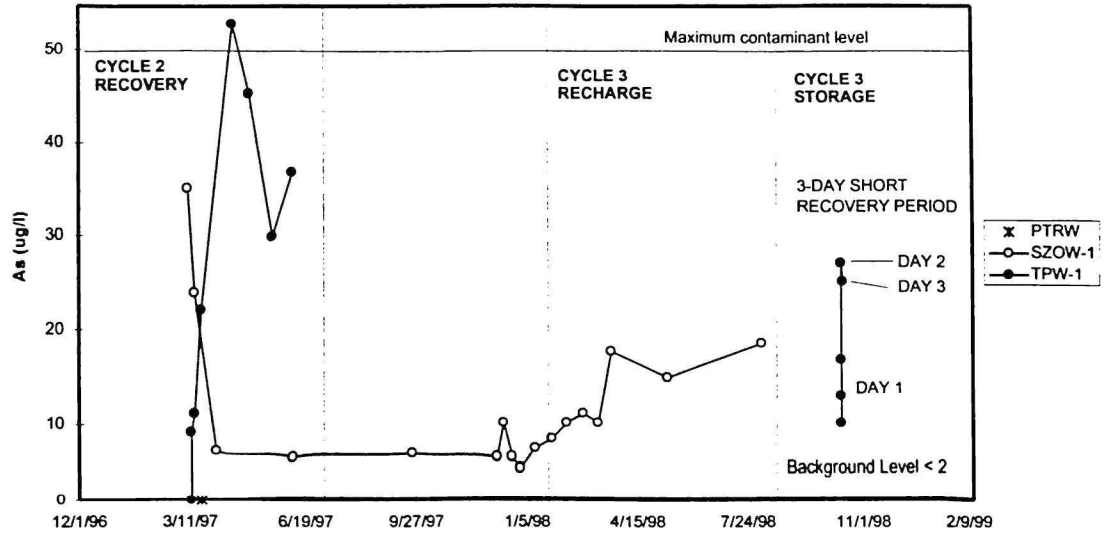


Figure 15. Arsenic concentration through time for Cycles 2 and 3, Rome Avenue ASR, Hillsborough County, Florida. (Note: some high-As samples do not meet FDEP protocol for regulatory purposes.)

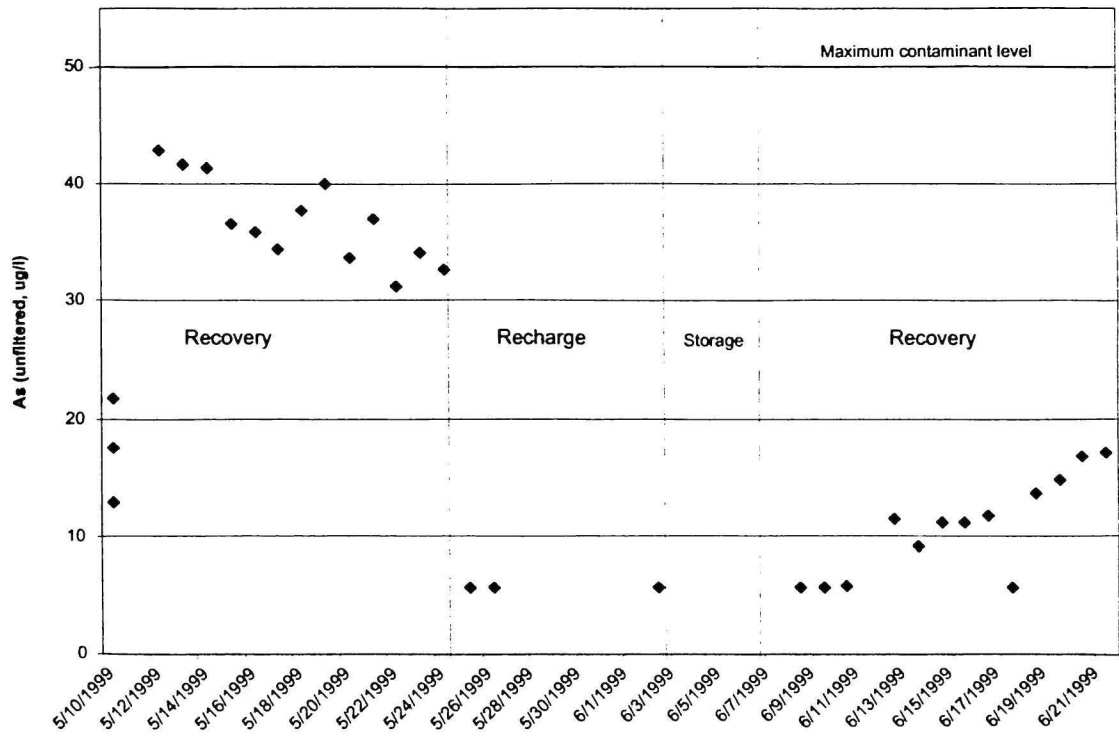


Figure 16. Arsenic concentrations through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999 (data source: CH2M Hill, December, 1999).

Cycles 1 and 2. These recovered waters represent the unrecovered injected waters from Cycle 3 recharge during Spring/Summer, 1998.

Cycle 3 storage began in August 1998 and aside from a brief (3 day) recovery in October (Figure 14), the injected waters were not withdrawn until mid-May, 1999 – approximately a 10-month storage period. Initial pump-out waters collected before the pH-adjusted cycle test did not reach the As MCL (i.e., <50 ug/l; Figure 16). This suggests that with increasing storage time, As did not continue to leach from the aquifer system carbonates to yield higher concentrations. Although As did not reach levels observed during earlier cycles, it is likely that the As “front” increases in size because of the increase in storage time and thus has more of an opportunity for leaching to reach its full extent within the injected “bubble.” It is also possible that As reached higher levels, but injected waters equilibrated and metals had time to precipitate or resorb in the aquifer-system matrix. For reference, Stuyfzand (1998) reports that 10-100 days were required in Netherlands ASR sites for pyrite oxidation to consume O_2 and NO_3^- in the injected waters.

For the pH-adjusted cycle test, surface waters with an adjusted pH of approximately 7.8 were injected from May 25, 1999 to June 3, 1999. Reported pH of previously injected waters (PTRW) is less than 7.2 (CH2M Hill, 1999). Native ground-water pH, based on an earlier aquifer performance test (February, 1996) is approximately 7.5. Input waters were stored in the aquifer from May 10, 1999 to May 24, 1999. Recovery extended from June 7, 1999 to June 22, 1999. Although the pH-adjusted cycle test was successful in that the maximum observed As concentrations were significantly reduced (Figure 16), As concentrations still increase with time during recovery.

Despite the positive results of the pH-adjusted cycle test in reducing observed As, mechanical complications occurred. Upon raising the pH to a more basic level, excessive scaling occurred in the physical plant (pumps, valves, etc.). Moreover, Fe and Mn in some samples (CH2M Hill, 1999) exceeded secondary drinking water standards. The pH-adjusted solution was not cost-effective.

The Rome Avenue facility currently has seven additional ASR wells being drilled as part of a major expansion project. Once online, these wells will be connected with TPW-1 via a pipeline that will allow blending of the recovered water. Carefully monitored, it is expected that the blended water will result in reduction of dissolved metals concentrations.

Punta Gorda

Relevant drilling, chemical modeling and cycle-testing activities at the Punta Gorda ASR facility are summarized in Appendix 2. The distributions of As concentrations during Cycle tests 1 and 2, and 1A and 2A, are shown in Figures 17 and 18, respectively. Although no samples exceed the current MCL for As, the trend observed in Cycle 1 (Williams and others, in review) is clearly repeated in Cycles 2 (Upper Zone) and 1A and 2A (Lower Zone) indicating that a similar geochemical process occurs in both zones during ASR cycle testing. Similar to the U concentrations for these cycles (Figure 14), As maximum concentrations decrease from Cycle 1A to Cycle 2A (Figure 18). Iron exhibits a similar pattern (Figure 19) and some samples exceed the MCL for Fe. The same observations presented above (e.g., the need for improved experimentation control) apply here for As, and to a lesser extent, Fe. Although depletion (i.e., leaching) of the As (and perhaps Fe) source in the aquifer system may be taking place during successive cycle tests, other chemical processes may be involved. We are fortunate that native concentrations and injection concentrations for Fe and As are low, thus enabling the patterns to be observed in time-transgressive plots without being masked or overprinted by trends representing mixing of the two waters.

Other metals analyzed in Punta Gorda samples are listed in Table 6. Distribution of these metals (e.g., Ca, Mn, Na and Sr; Figures 20-23) reveals mixing of injected and native waters. For these parameters, the mixing curves mask any geochemical effects due to water-rock interaction.

Origin of the mobilized metals

The association of As and Fe in recovered waters from the Rome Avenue and Punta Gorda wells suggests that oxidation of an As and Fe-bearing phase (or organic material) is taking place during the cycle tests. With the available data, it is not possible to determine if the source is pyrite, Fe-hydroxide grain coatings or organics. If oxidation of pyrite is occurring, a release of SO_4^{2-} , and perhaps Co, Ni and Zn would be observed. Pyrite has been observed (FGS lithologic data) in carbonates of the Floridan aquifer system in southwest Florida. Input waters at Rome Avenue and native groundwater at Punta Gorda have SO_4^{2-} concentrations that, due to mixing, mask any trends that could otherwise be attributed to pyrite oxidation (Figure 24). The metals Co, Ni and Zn have not been analyzed in the recovered water, however, these metals will be investigated in the Year 2000 study.

The relation between Fe and Mn during the Rome Avenue pH-adjusted cycle test (Figure 25)

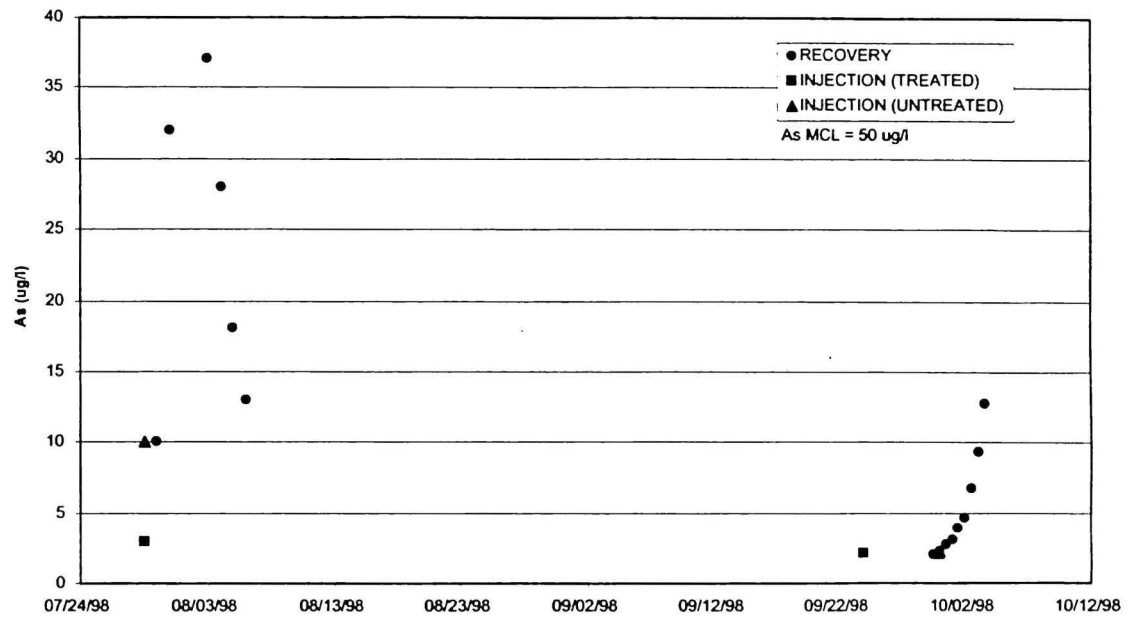


Figure 17. Arsenic concentration through time for Cycles 1 and 2 (Upper Zone), Punta Gorda ASR, Charlotte County, Florida

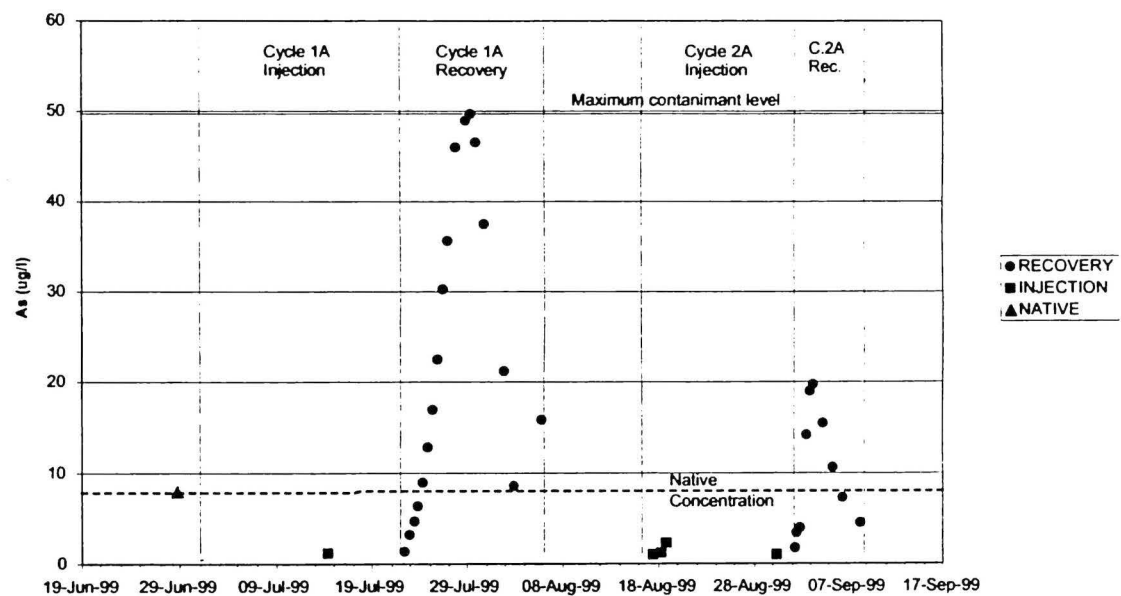


Figure 18. Arsenic concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida

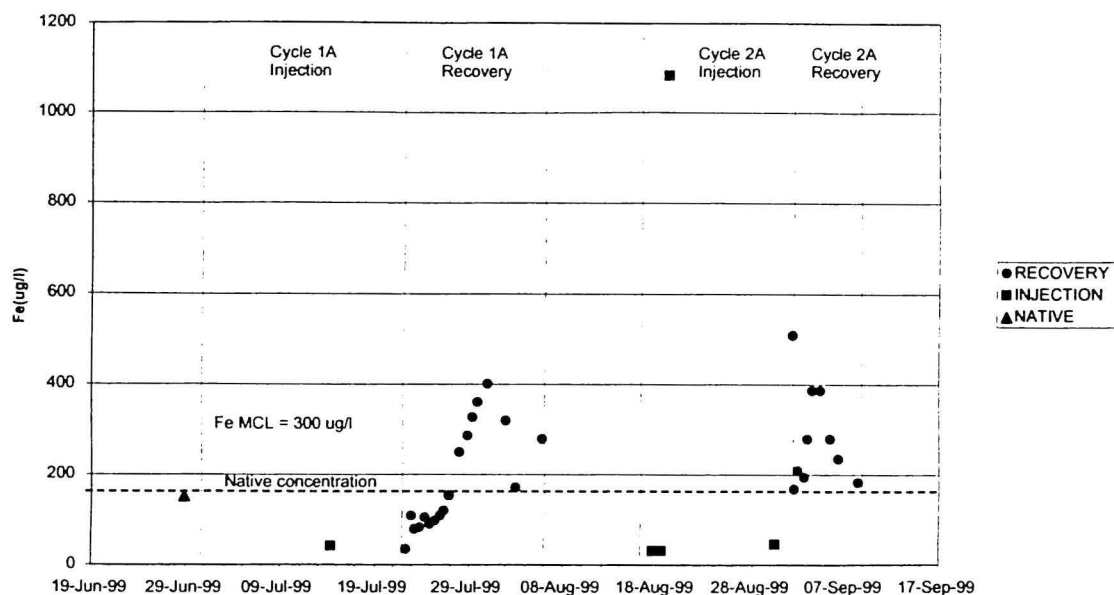


Figure 19. Iron concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida

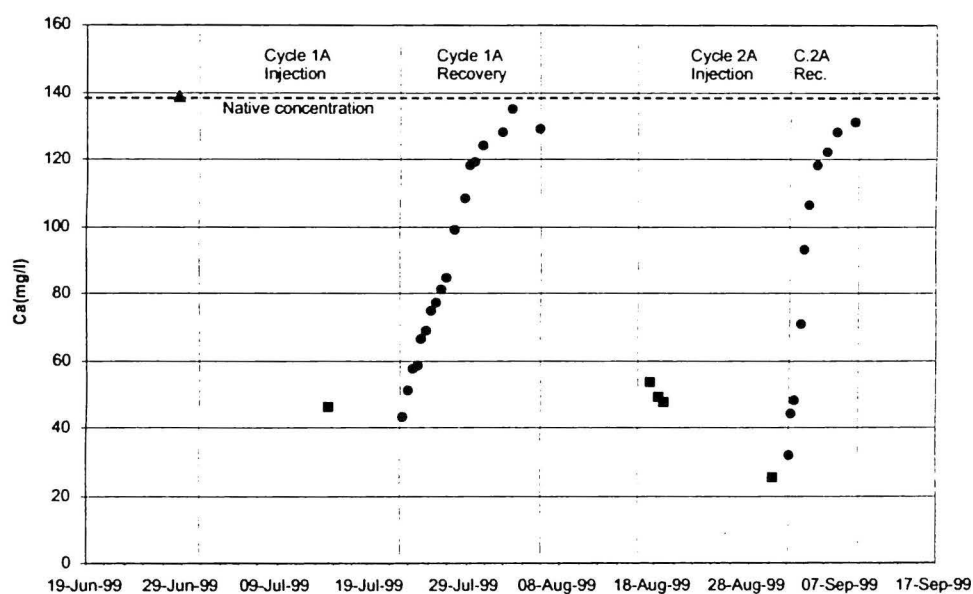


Figure 20. Calcium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida

Table 6. Trace metal analyses of water samples from Cycles 1 and 2 (Upper Zone) and Cycles 1A and 2A (Lower Zone), Punta Gorda ASR. Shaded data are from Williams and others (in review).

	As ug/l	Ba ug/l	Ca mg/l	Mn ug/l	Na mg/l	Sr ug/l	Fe ug/l	Pb ug/l	Cd ug/l
DETECTION LIMIT	4.0	0.7	0.1	0.25	0.1	0.4	10	10	0.4
NATIVE									
6/28/99 6:00 PM	7.96	45	139	5.9	403	34500	153		
INJECTION									
7/14/99 10:00 AM	BD	26	45.7	41.9	57	2540	41		
8/17/99 2:30 PM	BD	33.7	53.5	22.1	64.5	3140	29		
8/18/99 11:00 AM	BD	29.9	49.1	12.6	60.9	2980	28		
8/19/99 12:00 AM	BD	801	47.2	49.4	58.9	2900	1080		
8/30/99 1:00 PM	BD	15.5	25.3	7	38.5	1250	43		
RECOVERY									
7/22/99 9:15 AM	BD	23	43.1	20.7	54.2	2100	35		
7/22/99 10:00 PM	BD	112	50.7	22.8	60	3190	107		
7/23/99 10:00 AM	4.69	42	57.2	23.9	74.3	4390	78		
7/23/99 10:00 PM	6.33	66	58.4	18.9	87.6	5350	80		
7/24/99 10:00 AM	8.87	41	66.1	17.9	111	7000	102		
7/24/99 10:00 PM	12.7	36	68.7	16.4	128	8540	89		
7/25/99 10:00 AM	16.8	42	74.5	16.3	154	10900	98		
7/25/99 10:00 PM	22.4	35	76.8	15.5	164	12800	106		
7/26/99 10:00 AM	30.1	34.7	80.9	15	186	15100	118		
7/26/99 10:00 PM	35.6	39.4	84.2	14.3	204	17000	152		
7/27/99 10:00 PM	45.9	48.8	98.6	15.2	256	21900	250		
7/28/99 10:00 PM	48.9	68.4	108	11.3	303	25700	285		
7/29/99 10:00 AM	49.7	63	118	10.9	327	28000	326		
7/29/99 10:00 PM	46.5	99.6	119	10.5	339	28900	361		
7/30/99 10:00 PM	37.5	49.6	124	9.3	362	30900	400		
8/1/99 10:00 PM	21.2	52.5	128	7.6	373	31800	317		
8/2/99 10:00 PM	8.57	44.9	135	4.5	388	32900	169		
8/5/99 10:00 PM	15.8	44.3	129	6.3	381	32400	276		
9/1/99 9:00 AM	BD	151	31.7	27.3	37.1	1500	508		
9/1/99 2:30 PM	BD	50	43.8	21.8	53.5	3200	166		
9/1/99 10:00 P	BD	256	48	21.2	67.2	4380	206		
9/2/99 2:00 PM	14.1	39.4	70.4	20	139	11500	194		
9/2/99 10:00 PM	18.9	42.7	93	18	227	19200	276		
9/3/99 10:00 AM	19.7	50.9	106	14.9	289	23900	384		
9/4/99 10:00 AM	15.4	49.9	118	11.4	339	28400	384		
9/5/99 10:00 AM	10.5	43.5	122	8.8	351	29500	278		
9/6/99 10:00 AM	7.15	46.4	128	7.7	372	31600	234		
9/8/99 9:30 AM	4.38	44	131	5.2	379	32300	182		
INJECTION (UNTREATED)									
7/29/98 12:00 AM	10	41.5	65.8	48.6	55.5	4590		BD	
9/30/98 12:00 AM	BD	18.2	31.7	11.9	22.2	1470		BD	BD
INJECTION (TREATED)									
7/29/98 12:00 AM	BD	40.7	63.1	22.8	80.5	4460		BD	
9/24/98 12:00 AM	BD	26.6	35.9	10.2	56.3	1860		BD	BD
9/30/98 12:00 AM	BD	16.3	32.7	6	41.4	1460		BD	BD
RECOVERY									
7/29/98 12:00 AM	BD		65	29.9	82.8	4570		BD	
7/30/98 12:00 AM	10	53.7	84.6	14.3	123	10200		BD	
7/31/98 12:00 AM	32	52.2	104	9.52	206	19100		BD	
8/3/98 12:00 AM	37	57	133	3.73	319	30900		BD	
8/4/98 12:00 AM	28	56.8	135	3.93	327	33000		BD	
8/5/98 12:00 AM	18		141	3.85	354	32700		BD	
8/6/98 12:00 AM	13	79.2	140	2.87	341	32700		BD	
9/29/98 2:00 PM	BD	45.4	43.3	18.7	47.3	2100		BD	BD
9/30/98 2:00 AM	BD	39.2	57.9	20.4	65.2	3500		BD	BD
9/30/98 2:00 PM	BD	39.5	66.5	19.7	81.9	4820		BD	BD
10/1/98 2:00 AM	BD	38.9	71.7	18.1	94.5	5990		BD	BD
10/1/98 2:00 PM	BD	40.3	75.5	16.7	112	7440		BD	BD
10/2/98 2:00 AM	4.6	41.2	79.5	14.3	127	8970		BD	BD
10/2/98 2:00 PM	6.7	40.7	83.8	13.7	144	10900		BD	BD
10/3/98 2:00 AM	9.3	40.8	86.6	12.6	157	12400		BD	BD
10/3/98 2:00 PM	12.8	42.5	84.9	11.7	172	13900		BD	BD

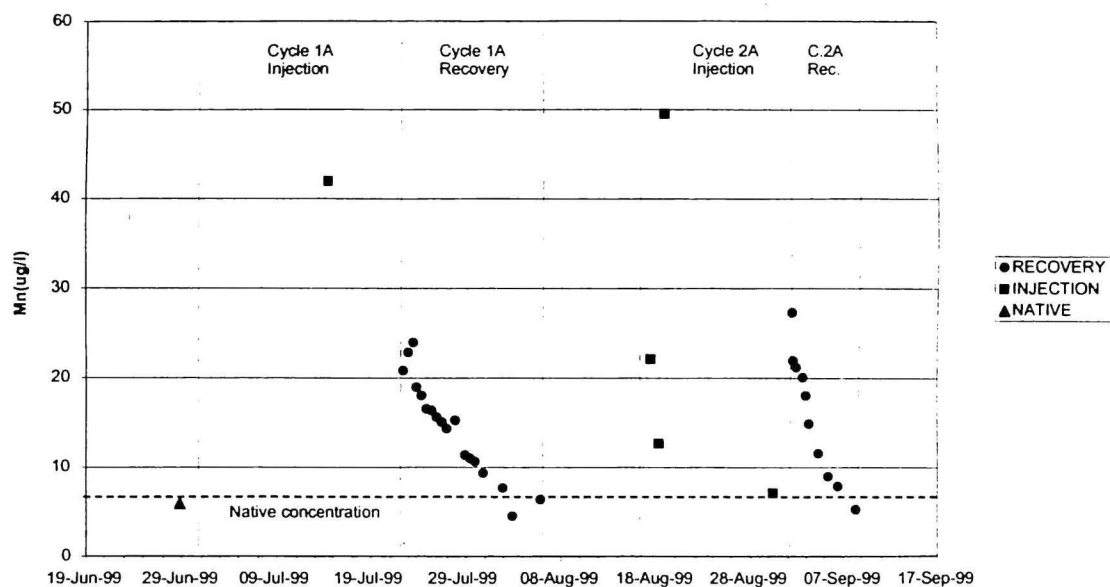


Figure 21. Manganese concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida.

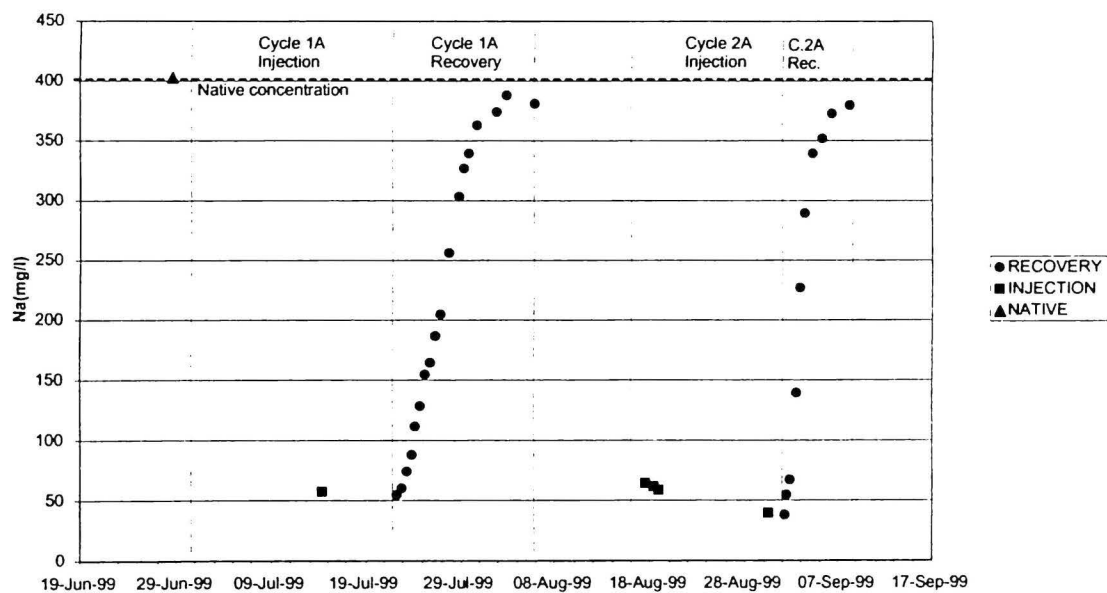


Figure 22. Sodium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida

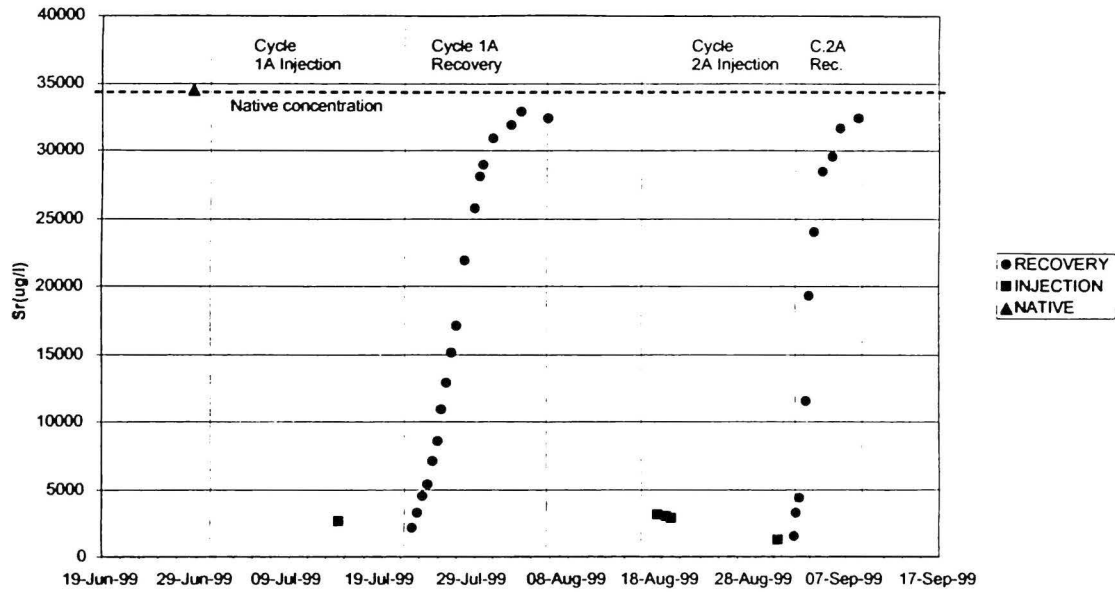


Figure 23. Strontium concentration through time for Cycles 1A and 2A (Lower Zone), Punta Gorda ASR, Charlotte County, Florida.

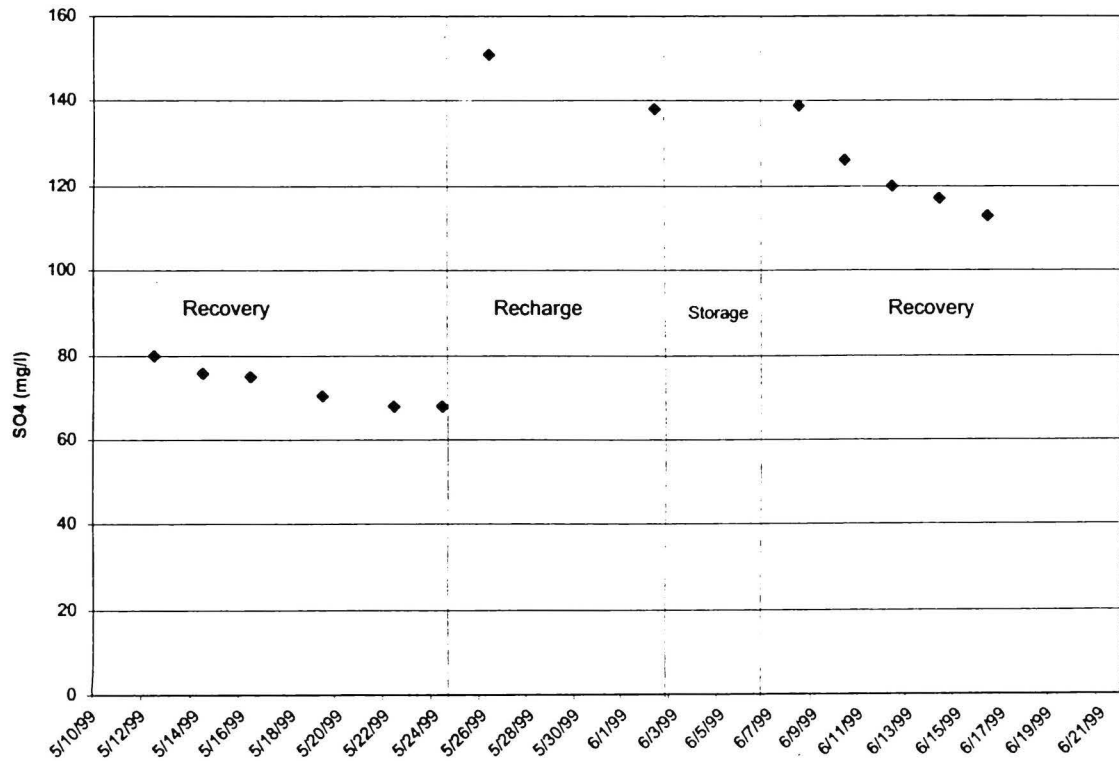


Figure 24. Sulfate concentration through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999 (data source: CH2M Hill, December, 1999).

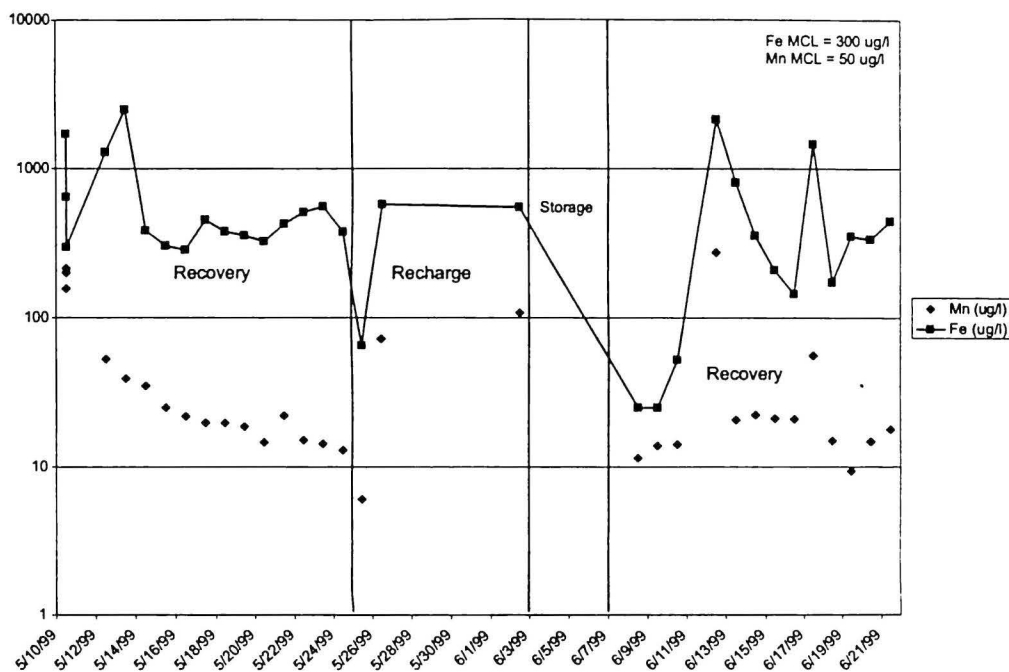


Figure 25. Iron and Manganese concentrations through time for Rome Avenue ASR pH-adjusted cycle test, May-June, 1999 (source: CH2M Hill, December, 1999) .

is similar to As in that the metals show an increase with time during recovery. Association of As-Fe-Zn (and Mn) in rocks (Figures 2 and 3) suggests pyrite involvement, however, the trends are not well developed and require additional data.

PLANNED RESEARCH

Sampling of waters from ASR cycle tests at Rome Avenue and Punta Gorda are continuing. Given the association of Co, Ni and Zn to pyrite and the possible oxidation of pyrite in the aquifer system during cycle testing, these metals will be added to those being monitored.

Cores from the Rome Avenue expansion have already been received and are being described by Florida Geological Survey (FGS) staff. Moreover, the FGS is performing hydraulic conductivity analyses on the core samples. In cooperation with the FGS, CH2M Hill consultants have agreed to core targeted intervals in the expansion wells. This core and the accompanying gamma-ray log for the well will allow comparison of whole rock chemistry, organic content and gamma-ray activity in a given borehole. If time and funds permit, chemistry of phases within the rock samples (e.g., grain coatings, interstitial minerals) will be

determined from microprobe analysis. Moreover, total organic carbon will be measured in selected samples.

As other ASR facilities come online and begin cycle testing, suites of samples from those sites will likely be included in the ongoing study. These sites include the NW Hillsborough County Reclaimed Water ASR, Englewood Reclaimed Water ASR and Bonita Springs ASR.

The results of this continuing investigation are extremely relevant to the ASR pilot studies proposed under the Comprehensive Everglades Restoration Plan. The site-specific nature of geochemical processes during ASR cycles warrants appropriate sampling of core material from the aquifer system as well as appropriate water sampling schedules during ASR cycle testing. During the Restudy pilot ASR programs, we hope that cycle tests can be designed to accommodate the need for evaluating water-rock geochemical interactions taking place in the Floridan aquifer system and their affect on recovered water quality through time. This would include coring of selected injection-zone horizons, native ground-water sampling, collection of a comprehensive suite of geophysical logs, and trace metal analyses of test cycle waters. As demonstrated herein and in our Year One - Year Two study (Williams and others, in review), chemical variability exists within Floridan aquifer system carbonates. As such, geochemical processes taking place during ASR operation can be site specific.

REFERENCES

- Ahmann, D., 1999, Microbial arsenic reduction: A new, ubiquitous, yet still mysterious factor in aquatic arsenic mobility: *Eos* v. 80, no. 17 Supplement, p. S148.
- Ahmed, K.M., Imam, M.B., Akhter, S.H., Hasan, M.A., and Khan, A.A., 1999, Sedimentology and mineralogy of the arsenic contaminated aquifers in the Bengal Delta of Bangladesh, Kth-Dhaka University Seminar on ground-water arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Bellanca, A., Masetti, D., and Neri, R., 1997, Rare earth elements in limestone/marlstone couplets from the Albanian-Cenomanian Cismon section (Venetian region, northern Italy): Assessing REE sensitivity to environmental changes: *Chemical Geology*, v. 141, p. 141-152.
- Bhattacharya, P., Jacks, G., Gustafsson, J.P., Sracek, A., Olofsson, B., Aaltonen, J., Khan, A.A., Akhter, S.H., and Ahmed, K.M., 1999a, High arsenic in the alluvial aquifers of Bengal Delta Plains in Bangladesh: Genesis and low-cost remediation, 1999 [abstracts] Kth-Dhaka University Seminar on groundwater arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Bhattachaya, P., Jacks, J., Sracek, A., Gustafsson, J.P., and Chatterjee, D., 1999b, Geochemistry of the Holocene alluvial sediments in the Bengal Delta Plains and their implications in ground-water arsenic contamination [abstracts] Kth-Dhaka University Seminar on ground-water arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Brandon, W., Byrne, J., McTigue, D., and Stein, C., 1999, Arsenic contaminated sediment and groundwater: A case study in central Massachusetts: *Eos* v. 80, no. 17 Supplement, p. S146.
- Brun, A., Christensen, F.D., Christiansen, J.S., Stuyfzand, P.J., and Timmer, H., 1998, Water quality modeling at the Langerak deep-well recharge site: *in* Peters, J.H., et al., eds., *Artificial Recharge of Groundwater*: Rotterdam, Netherlands, A.A. Balkema, 474 p.
- Campbell, K.M., and Arthur, J.D., 1993, Geologic map of Hillsborough County: Florida Geological Survey Open File Map Series No. 45.
- CH2M Hill, 1999, Rome Avenue Park cycle test unpublished analytical data, May/June, 1999 (provided by M.Clasen, CH2M Hill, December, 1999).
- Colman, J.A. and Lyford, F.P., 1999, Sources and geochemical associations of arsenic in leachate plumes from a landfill in Saco, Maine: *Eos* v. 80, no. 17 Supplement, p. S148.
- Cowart, J.B., Williams, H.K., and Arthur, J.D., 1998, Mobilization of U isotopes by the introduction of surface waters into a carbonate aquifer: *Geological Society of America Abstracts with Programs*, v. 30, no. 7, p. A-86.

REFERENCES (continued)

- Das, D., Samanta, G., Mandal, B.K., Chowdhury, T.R., Chanda, C.R., Chowdhury, P.P., Basu, G.K., and Chakraborti, D., 1996, Arsenic in groundwater in six districts of West Bengal, India: Environmental Geochemistry and Health, v. 18, p. 5-15.
- Deer, W.A., Howie, R.A., and Zussman, J., 1992, An introduction to rock forming minerals – Second edition, Longman Scientific and Technical, Hong Kong, 696 p.
- Federal Register, 2000, 40 CFR Parts 141 and 142, National Primary Drinking Water Regulations; Arsenic and clarifications to compliance and new source contaminants monitoring; Proposed rule: v. 65, no. 121, p. 38888-38893.
- Federal Register, 2001, 40 CFR Parts 9, 141 and 142, National Primary Drinking Water Regulations; Arsenic and clarifications to compliance and new source contaminants monitoring; Final rule: v. 66, no. 14, p. 6975-7066.
- Green, R., Arthur, J.D., and DeWitt, D., 1995, Lithostratigraphic and hydrostratigraphic cross sections through Pinellas and Hillsborough Counties, Southwest Florida: Florida Geological Survey Open File Report 61, 26 p.
- Grommet, L.P., Dymek, R.F., Haskin, L.A., and Korteve, R.L., 1984, The “North American shale composite”: Its compilation, major and trace element characteristics: *Geochimica et Cosmochimica Acta*, v. 48, p. 2469-2482.
- Hemm, J.D., 1985, Study and interpretation of chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- Jacks, G., Bhattacharya, P., and Chatterjee, D., 1999, Artificial recharge as a remedial measure, [abstracts] Kth-Dhaka University Seminar on groundwater arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Kolker, A., Cannon, W.F., Woodruff, L.G., Westjohn, D.B., Haack, S.K. and Kim, M., 1999, Arsenic in southeastern Michigan groundwater: Results of USGS test drilling: *Eos* v. 80, no. 17 Supplement, p. S146.
- Maddox, G.L., Lloyd, J.M., Scott, T.M., Upchurch, S.B., and Copeland, R., 1992, Florida's groundwater quality monitoring program: Background hydrogeochemistry: Florida Geological Survey Special Publication 34, 364 p.
- Montgomery-Watson, 1999, Punta Gorda ASR Exploratory Well, Cycle Test 1a and 2a Results, Memorandum dated November 15, 1999, 32 p.
- National Research Council, 1999, Arsenic in Drinking Water: Washington D.C., National Academy Press, 310 p.
- Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., and Ahmed, K.M., 2000, Mechanism of arsenic release to groundwater, Bangladesh and West Bengal: *Applied Geochemistry*, v. 15, p. 403-413.
- Ruiter, H. and Stuyfzand, P.J., 1998, An experiment on well recharge of oxic water into an anoxic aquifer: in Peters, J.H., et al., eds., *Artificial Recharge of Groundwater*: Rotterdam, Netherlands, A.A. Balkema, 474 p.

REFERENCES (continued)

- Schlottmann, J.L., and Briet, G.N., 1992, Mobilization of As and U in the central Oklahoma aquifer, USA: *in* Kharaka, Y.K. and Maest, A.S., eds., *Water-Rock Interaction: Rotterdam, Netherlands, A.A. Balkema*, p. 835-838.
- Sracek, A., Bhattacharya, P., and Jacks, G., 1999, Basic principles of groundwater flow and considerations for sampling of arsenic, [abstracts] Kth-Dhaka University Seminar on groundwater arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Sracek, A., Bhattacharya, P., Jacks, G., and Gustafsson, J.P., 1999, Mobility of arsenic and geochemical modeling applications [abstracts] Kth-Dhaka University Seminar on groundwater arsenic contamination in the Bengal Delta Plains of Bangladesh, Feb. 7-8, 1999 (see http://phys4.harvard.edu/~wilson/arsenic_project_Dhaka_conference_abstracts.html).
- Stollenwerk, K.G. and Colman, J.A., 1999, Natural remediation of arsenic contaminated groundwater: Solute-transport model predictions: *Eos* v. 80, no. 17 Supplement, p. S148.
- Stuyfzand, P.J., 1998, Quality changes upon injection into anoxic aquifers in the Netherlands: Evaluation of 11 experiments, *in* Peters, J.H., et al., eds., *Artificial Recharge of Groundwater: Rotterdam, Netherlands, A.A. Balkema*, 474 p.
- Thomas, R.C. and Saunders, J.A., 1998, Arsenic co-precipitation in low-temperature pyrites: implications for bioremediation via sulfate reducing bacteria: *Geological Society of America Abstracts with Program*, v. 30, no. 7, p. A-58.
- Welch, A.H. and Lico, M.S., 1998, Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada: *Applied Geochemistry*, v. 13, no. 4, p. 521-539.
- Welch, A.H., 1999, Arsenic in groundwater of the United States: Processes leading to widespread high concentrations: *Eos* v. 80, no. 17 Supplement, p. S147.
- Wendell, D. and Glanzman, D., 1998, Well recharge in California: Water quantity and quality considerations: *in* Peters, J.H., et al., eds., *Artificial Recharge of Groundwater: Rotterdam, Netherlands, A.A. Balkema*, 474 p.
- White, C.A. and Scully, M.V., 1999, An evaluation of potential arsenic sources to the groundwater at a landfill site in eastern Maine: *Eos* v. 80, no. 17 Supplement, p. S148.
- Williams, H., Cowart, J.B. and Arthur, J.D., in review, Florida aquifer storage and recovery (ASR) geochemical project: Year One and Year Two Progress Report Submitted to Bureau of Water Facilities Regulation, Florida Department of Environmental Protection, January, 1999, Florida Geological Survey Open File Report 82, 132 p.

Appendix 1. Lithologic descriptions of samples analyzed for whole rock chemistry. Wells include SWFWMD ROMP TR9-2 (W-16618), NW Hillsborough Recalimed ASR TPW-1 (W-17687) and SWFWMD WRAP 2D (W16574).

<u>Well Number</u>	<u>Depth (ft. below land surface)</u>	
16618	368	FGS-1 PACKSTONE; YELLOWISH GRAY POROSITY: INTERGRANULAR, LOW PERMEABILITY GRAIN TYPE: BIOGENIC, SKELETAL, CALCILUTITE GRAIN SIZE: MEDIUM; WELL-SORTED MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX SEDIMENTARY STRUCTURES: INTERBEDDED, MASSIVE OTHER FEATURES: WEATHERED, CHALKY, GRANULAR FOSSILS: FOSSIL FRAGMENTS
16618	382.5	FGS-2 MUDSTONE-WACKESTONE; YELLOWISH GRAY POROSITY: INTERGRANULAR, LOW PERMEABILITY GRAIN TYPE: BIOGENIC, SKELETAL, CALCILUTITE GRAIN SIZE: MEDIUM; WELL-SORTED MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX SEDIMENTARY STRUCTURES: INTERBEDDED, MASSIVE OTHER FEATURES: WEATHERED, CHALKY FOSSILS: FOSSIL FRAGMENTS
16618	392	FGS-3 MUDSTONE; LIGHT OLIVE POROSITY: INTERGRANULAR, LOW PERMEABILITY GRAIN TYPE: BIOGENIC, SKELETAL, CALCILUTITE GRAIN SIZE: MEDIUM; WELL-SORTED MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX SEDIMENTARY STRUCTURES: INTERBEDDED, MASSIVE OTHER FEATURES: WEATHERED, CHALKY FOSSILS: ORGANICS? (BLACK LAMINATIONS – COMPOSITION UNKNOWN)
16618	425	FGS-4 WACKESTONE; YELLOWISH GRAY POROSITY: INTERGRANULAR, LOW PERMEABILITY GRAIN TYPE: BIOGENIC, SKELETAL, CALCILUTITE GRAIN SIZE: MEDIUM; WELL-SORTED MODERATE TO GOOD INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX SEDIMENTARY STRUCTURES: INTERBEDDED, MASSIVE OTHER FEATURES: WEATHERED, CHALKY FOSSILS: FOSSIL MOLDS
17687	310-315	FGS-5 PACKSTONE-GRAINSTONE; YELLOWISH GRAY 20% POROSITY: INTERGRANULAR GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL GRAIN SIZE: MEDIUM; RANGE: CRYPTOCRYSTALLINE TO MEDIUM MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX OTHER FEATURES: LOW RECRYSTALLIZATION FOSSILS: MOLLUSKS TRACE ORGANICS PRESENT.

Appendix 1. (continued)

<u>Well</u> <u>Number</u>	<u>Depth</u> <u>(ft. below land surface)</u>	
17687	320-325	FGS-6 WACKESTONE; PALE YELLOWISH BROWN TO YELLOWISH GRAY 20% POROSITY: INTERGRANULAR GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL 45% ALLOCHEMICAL CONSTITUENTS GRAIN SIZE: MEDIUM; RANGE: CRYPTOCRYSTALLINE TO MEDIUM MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX OTHER FEATURES: LOW RECRYSTALLIZATION, DOLOMITIC? FOSSILS: MOLLUSKS SOME ORGANICS (OR GRAIN COATINGS; DARK BLEBS) PRESENT.
17687	325-330	FGS-7 AS ABOVE
17687	330-335	FGS-8 AS ABOVE; TWO LITHOLOGIES: MUDSTONE AND WACKESTONE, TRACE SILT? AND ORGANICS
17687	340-345	FGS-9 GRAINSTONE; YELLOWISH GRAY GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL GRAIN SIZE: MEDIUM; RANGE: MEDIUM - COARSE MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX OTHER FEATURES: LOW RECRYSTALLIZATION FOSSILS: MOLLUSKS
17687	360-365	FGS-10 PACKSTONE; YELLOWISH GRAY 25% POROSITY: INTERGRANULAR, MOLDIC GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL 55% ALLOCHEMICAL CONSTITUENTS GRAIN SIZE: MEDIUM; RANGE: CRYPTOCRYSTALLINE TO COARSE MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX OTHER FEATURES: LOW RECRYSTALLIZATION FOSSILS: MOLLUSKS, FOSSIL MOLDS SOME ORGANICS PRESENT AS FINELY INTERSPERSED SPECS.
17687	420-421	FGS-11 WACKESTONE; YELLOWISH GRAY 20% POROSITY: INTERGRANULAR GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL 40% ALLOCHEMICAL CONSTITUENTS GRAIN SIZE: FINE; RANGE: CRYPTOCRYSTALLINE TO MEDIUM MODERATE INDURATION CEMENT TYPE(S): CALCILUTITE MATRIX CORED INTERVAL 420'-421' IS A WACKESTONE WITH MEDIUM INDURATION AND MICRITE CEMENT. MOLLUSK MOLDS AND SOME ORGANICS ARE PRESENT AS TRACE FINELY DISPERSED SPECS.

Appendix 1. (continued)

<u>Well Number</u>	<u>Depth (ft. below land surface)</u>		
17687	429	FGS-12	WACKESTONE; GRAYISH BROWN 20% POROSITY; INTERGRANULAR GRAIN TYPE: BIOGENIC, CALCILUTITE, SKELETAL 15% ALLOCHEMICAL CONSTITUENTS GRAIN SIZE: VERY FINE; RANGE: CRYPTOCRYSTALLINE TO FINE MODERATE INDURATION CEMENT TYPE(S): DOLOMITE AND CALCILUTITE MATRIX OTHER FEATURES: MEDIUM RECRYSTALLIZATION FOSSILS: MOLLUSKS, FOSSIL MOLDS FINE GRAINED DOLOMITE MAKES UP ABOUT 50% OF THIS SAMPLE. SOME ORGANICS PRESENT. CORED INTERVAL 429'-430' IS A WACKESTONE WITH 15% POROSITY AND GOOD INDURATION WITH MICRITE CEMENT. FINE BLACK LAMINATIONS (PROBABLY ORGANIC LAYERS) WITHIN THE LIMESTONE ARE PRESENT. LAMINATIONS ARE UP TO 1/4 INCH THICK, WITH VARYING DISTANCES BETWEEN LAMINATIONS. POSSIBLE BURROW PERPENDICULAR TO CORE, FILLED WITH CALCILUTITE, ORGANIC MATERIAL AND FORAMINIFERA. FRACTURE OBSERVED IN THIS INTERVAL LIKELY FORMED DURING OR AFTER DRILLING. THIS OBSERVATION IS MADE DUE TO THE LACK OF SLICKENSIDES, MINERALIZATION, OR DISSOLUTION ON THE FRACTURE SURFACE.
17687	431	FGS-13	DOLOSTONE, YELLOWISH GRAY TO GRAYISH BROWN MOLDIC, GRANULAR, RECRYSTALLIZED, ORGANIC COATINGS?
17687	432	FGS-14	PACKSTONE, YELLOWISH GRAY, CHALKY, "OCALA" SPARRY ALLOCHEMS, TRACE BLACK SPECS (ORGANICS?)
16574	295-300	FGS-15	GRAINSTONE; YELLOWISH GRAY TO TAN POOR INDURATION ACCESSORY MINERALS: TRACE SPAR FOSSILS: BENTHIC FORAMINIFERA, ECHINOID POROUS.
16574	325-330	FGS-16	GRAINSTONE; YELLOWISH GRAY TO TAN POOR INDURATION; WELL SORTED ACCESSORY MINERALS: TRACE SPAR OTHER FEATURES: FOSSILIFEROUS
16574	330-335	FGS-17	AS ABOVE; VARIABLY RECRYSTALLIZED PACKSTONE TO GRAINSTONE; TRACE ORGANICS(?) INTERSPERSED
16574	335-340	FGS-18	AS ABOVE
16574	370-375	FGS-19	PACKSTONE-GRAINSTONE; LIGHT YELLOWISH GRAY POOR INDURATION ACCESSORY MINERALS: TRACE QUARTZ SAND/SILT OTHER FEATURES: FOSSILIFEROUS, CHALKY
16574	459	FGS-20	VERY FINE-GRAINED PACKSTONE (OR MUDSTONE); VERY PALE ORANGE TO YELLOWISH GRAY; GRAIN SIZE: FINE; RANGE: VERY FINE TO FINE CHALKY, FOSSILS: BENTHIC FORAMS
16574	459.5	FGS-21	AS ABOVE
16574	459	FGS-22	SPLIT SAMPLE OF FGS-20

Appendix 2. Cycle test and drilling activities at the Punta Gorda ASR (modified from Montgomery-Watson (1999)).

The Punta Gorda ASR well has undergone cycle testing in two permeable storage zones within the Suwannee Limestone, which comprises the upper part of the Floridan aquifer system. Cycle tests 1 and 2 utilize the Upper Zone, which includes an open borehole interval from 700' to 764' below land surface (bls). Cycle tests 1A and 2A utilize a Lower Zone, which extends from 764' to 933' bls.

Injection flow rates during cycle tests in the Upper Zone revealed significant decreases in average flow. During the injection period for cycle 2 (8/24/98 to 9/29/98), for example, daily average flows decreased from 200 gallons per minute (gpm) to 10 gpm. The decrease in injection flow rates for cycle tests 1 and 2 were attributed to formation plugging (Montgomery-Watson, 1999). Consultants attributed the plugging of pore space in the aquifer system matrix (or along borehole walls) to either particle rearrangement or precipitation of solids. Rather than acidizing the Upper Zone or making chemical adjustments to the recharge water, consultants opted to utilize a lower flow zone in the well for further cycle tests and possibly full ASR implementation. Similar injection-rate declines were observed in the Lower Zone during cycle tests 1A and 2A.

During Cycle 1A, several water quality parameters were monitored and later used to compare to geochemical model results from PHREEQC (Parkhurst, 1995). As demonstrated in the MW (1999) report, it is clear that the PHREEQC model is a very useful predictive tool concerning the movement of cations and anions from the aquifer system matrix to the injected "bubble" during an ASR cycle test. The model also predicts that Fe-hydroxide precipitation may be occurring in the aquifer. Moreover, the model was used to predict the ability to reduce the observed pore plugging by the acid addition during injection.

3938000015011V



FLORIDA GEOLOGICAL SURVEY