



Reclaimed Water Aquifer Storage and Recovery

Potential Changes in Water Quality



**WaterReuse
Foundation**

Reclaimed Water Aquifer Storage and Recovery

About the WateReuse Foundation

The mission of the WateReuse Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the U.S. Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations. The Foundation also conducts research in cooperation with the Global Water Research Coalition.

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Tracy Clinton
Carollo Engineers

Cosponsors

California State Water Resources Control Board
Southwest Florida Water Management District
United States Bureau of Reclamation



Published by the WaterReuse Foundation
Alexandria, VA

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For more information, contact:

WateReuse Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

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WateReuse Foundation Project Number: WRF-03-009
WateReuse Foundation Product Number: 03-009-01

ISBN: 978-1-934183-03-8
Library of Congress Control Number: 2007931232

Printed in the United States of America

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ABBREVIATIONS

ASR	aquifer storage recovery
BHT	butylated hydroxytoluene
DBP	disinfection byproduct
DHS	Department of Health Services (CA)
DO	dissolved oxygen
EC	electrical conductivity
EDC	endocrine-disrupting compound
EPA	U.S. Environmental Protection Agency
FDEP	Florida Department of Environmental Protection
gpd	gallons per day
HAAs	haloacetic acids
HPC	heterotrophic plate count
MAU	middle alluvial unit
MCL	maximum contaminant level
MDL	method detection limit
MG	million gallons
mgd	million gallons per day
ML	million liters
MW	molecular weight
NTU	nephelometric turbidity unit
ORP	oxidation–reduction potential
PBDEs	polybrominated diphenyl ethers
PPCPs	pharmaceutical and personal care products
RWQCB	Regional Water Quality Control Board (CA)
SNWA	Southern Nevada Water Authority
SWFWMD	Southwest Florida Water Management District
TCEP	tri(2-chloroethyl) phosphate
TDS	total dissolved solids
THMs	trihalomethanes
TOC	total organic carbon
TSV	target storage volume
TSS	total suspended solids
TTHMs	total THMs
UAU	upper alluvial unit
UIC	underground injection control
WRF	WateReuse Foundation

FOREWORD

The WateReuse Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics including the following:

- Defining and addressing emerging contaminants;
- Public perceptions of the benefits and risks of water reuse;
- Management practices related to indirect potable reuse;
- Groundwater recharge and aquifer storage and recovery;
- Evaluating methods for managing salinity and desalination; and
- Economics and marketing of water reuse.

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consists of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's funding partners are the U.S. Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, the California Department of Water Resources, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships. The Foundation is also a member of the Global Water Research Coalition.

This publication is the result of a study sponsored by the Foundation and is intended to communicate the results of this research project. The objectives of this report were to

- Describe the state of the practice of reclaimed water ASR;
- Identify wastewater constituents and water quality parameters of significance for designing, monitoring, and evaluating reclaimed water ASR;

- Measure concentrations of contaminants at various stages of recharge, storage, and recovery of reclaimed water; and
- Analyze observed data with respect to attenuation mechanisms and rates to characterize water quality changes through ASR.

Ronald E. Young
President
WateReuse Foundation

G. Wade Miller
Executive Director
WateReuse Foundation

ACKNOWLEDGMENTS

This project was funded by the WaterReuse Foundation in cooperation with the Southwest Florida Water Management District, the California State Water Resources Control Board, and the U.S. Bureau of Reclamation. The project team acknowledges and thanks the many individuals and organizations that contributed to this project. The project team members who contributed to the project are listed below.

Principal Investigator

Tracy Clinton, Carollo Engineers

Project Team

Karen Barry, CSIRO Land and Water
Jess Brown, Carollo Engineers
Jim Crook, Water Reuse Consultant
Peter Dillon, CSIRO Land and Water
Don Ellison, Southwest Florida Water Management District
Janie Holady, Southern Nevada Water Authority
Debra Huffman, University of South Florida
Rai Kookana, CSIRO Land and Water
Steve McDonald, Carollo Engineers
Michael Micheau, PBS&J
Rebecca Overacre, Carollo Engineers
Declan Page, CSIRO Land and Water
Paul Pavelic, CSIRO Land and Water
David Pyne, ASR Systems, Incorporated
Shane Snyder, Southern Nevada Water Authority
Rebecca Trenholm, Southern Nevada Water Authority
Brett Vanderford, Southern Nevada Water Authority
Joanne Vanderzalm, CSIRO Land and Water
G. G. Ying, CSIRO Land and Water

Technical Advisors

Charles Haas, Drexel University
Joan Rose, Michigan State University
David York, Florida Department of Environmental Protection

Participating Agencies

Bolivar, SA, Australia, Bolivar Water Reclamation Plant
Chandler, AZ, Tumbleweed Recharge Facility
Englewood, FL, South Regional Wastewater Treatment Plant
Manatee County, FL, Southwest Water Reclamation Facility

Project Advisory Committee

Anthony Andrade, Southwest Florida Water Management District

Joe Cotruvo, Joseph Cotruvo & Associates

Audrey Levine, University of South Florida

Rich Mills, California State Water Resources Control Board

Judy Richtar, Florida Department of Environmental Protection

Eric Stiles, U.S. Bureau of Reclamation

Mike Wehner, Orange County (CA) Water District

EXECUTIVE SUMMARY

Aquifer storage recovery (ASR) is defined as the storage of water in a suitable aquifer through a well during times when water is available and recovery of the water from the same well during times when it is needed. The water sources used for ASR include potable water, reclaimed water, and stormwater.

To date, significant experience has been gained in the practice of reclaimed water ASR through several testing programs and operational facilities. Collectively, the data from these programs can be used to help identify water quality issues associated with reclaimed water ASR and to better understand fate and transport properties of residual contaminants in reclaimed water. The major objectives of this report are to:

- Describe the state of the practice of reclaimed water ASR
- Identify wastewater constituents and water quality parameters of significance for designing, monitoring, and evaluating reclaimed water ASR
- Measure concentrations of contaminants at various stages of recharge, storage, and recovery of reclaimed water and analyze observed data with respect to attenuation mechanisms and rates to characterize water quality changes through ASR

Reclaimed water ASR projects located in Florida, Arizona, California, Texas, Hawaii, Australia, and Kuwait were surveyed to determine the state of the practice and screen for potential study sites. Four operating reclaimed water ASR sites were selected for participation in the water quality monitoring study. These were the Englewood Water District in Englewood, FL, Manatee County Utilities in Manatee County, FL, the Tumbleweed Recharge Facility in Chandler, AZ, and the recharge facility in Bolivar, SA, Australia. Conditions at each site covered a broad range of lithologies, salinities, redox states, temperatures, operational histories, and reclaimed water quality. They also allowed for monitoring over different storage periods, which ranged from 1 week to 11 months.

A sampling plan was developed for each of the four testing sites to capture unique environmental and operational conditions. Sampling events were integrated with planned operating and monitoring activities where possible. The target parameters were chosen based on several criteria, including applicability to water quality regulations, usefulness in aquifer characterization, degree of public concern, and importance to irrigation water quality. Compounds satisfying these criteria were narrowed to those that were capable of being analyzed precisely and within budget. Water quality samples were analyzed at local laboratories for most constituents and at the Southern Nevada Water Authority for trace organics, which were largely comprised of pharmaceuticals and personal care products.

The study found that the accuracy of field measurements of dissolved oxygen and oxidation–reduction potential were generally poor; this is especially important given that these conditions have been found to have an important influence on degradation of some organics in aquifers for several endocrine-disrupting compounds and for trihalomethanes. While anoxic and low-redox conditions are reasonably expected to occur in the storage zone at all four reclaimed ASR sites, the field data fail to show this. This finding is particularly important given the abundance of carbon and nutrients and the aquifer confinement. This is

probably due to the sampling methods that were utilized at some sites for these two field measurements.

Total organic carbon, pH, and nutrient reductions observed in this study generally supported the theory that notable microbial and chemical activities occur in the zone closest to the wellhead, where the influx of dissolved oxygen enhances many processes. Pathogens and indicator organisms were rarely detected in monitor programs at ASR sites.

Concentrations of regulated disinfection byproducts, including total trihalomethanes and haloacetic acids, decreased between recharge and recovery at three of four sites. It is likely that microbial degradation occurred and that much of this degradation occurred close to the well.

A large emphasis was placed on the microcontaminant portion of this study, which attempted to use the physical characteristics of a strategically selected group of contaminants to indicate removal mechanisms in the aquifer. Several microcontaminants appeared in significantly higher concentrations in the recovered water than recharge water. These included carbamazepine, gemfibrozil, ibuprofen, iopromide, *N*-nitrosodimethylamine, and sulfamethoxazole. It is unlikely that these specific analytes are degradation byproducts of each other or of other effluent-derived organic matter. Several possible causes for the increased concentrations were considered, but the findings most likely indicated highly variable concentrations of endocrine-disrupting compounds, pharmaceuticals, and personal care products in reclaimed water. The concentrations measured in the recharge water were considered low and possibly not representative of typical conditions. Monitoring well data at sites where these were sampled were also inconsistent with source water and recovered water concentrations, a further indication of variability of input concentrations as the largest factor affecting measured concentrations in monitoring wells and in recovered water.

In order to account for possible recharge water variability, the microcontaminant data were analyzed via two approaches. The first utilized the recharge water concentration as a viable benchmark, and the second dismissed the recharge water concentrations and compared only recovered water concentrations. Few trends were seen with either approach, and few correlations were observed with expected degradation rates.

The most notable microcontaminant trend was with atrazine, which decreased at the three sites where it was detected. Chlorate was reduced at three sites compared to recharge concentrations but exhibited ambiguous results at the Bolivar site, over the longest storage period. Discounting recharge concentrations and comparing recovered water samples only, tri(2-chloroethyl) phosphate decreased at the three sites where it was detected. In general, the data compilation showed that residence times and degradation rates in the aquifers were insufficient to claim biodegradation of trace organics to a degree that eclipses source concentration variability at the four sites.

By observing changes in concentrations of over 90 compounds at four ASR sites with many variables, this study intentionally took a broad assessment of water quality changes in reclaimed water ASR storage. The study was designed to investigate the variables of aquifer characteristics, storage time, travel distance, recharge water quality, and operational history. The data support many aquifer process assumptions, such as enhanced activity near the well, but do not statistically support conclusions regarding specific degradation rates for most of the parameters observed. With further research, however, it will be possible to better define the subsurface processes and associated treatment effectiveness.

CHAPTER 1

INTRODUCTION

Aquifer storage recovery (ASR) is defined as the storage of water in a suitable aquifer through a well during times when water is available and recovery of the water from the same well during times when it is needed. The water sources used for ASR include potable water, reclaimed water, and stormwater.

Storage of reclaimed water through ASR represents a powerful tool for effectively using a valuable water resource. However, many technical, regulatory, public health, and public perception constraints limit current applications. A significant problem challenging more widespread application of reclaimed water ASR is the uncertainty regarding the impact of recharged water on native groundwater resources. This concern, and the concern for the quality of the reclaimed water after it is stored, drive the need for an understanding of the fate of contaminants present in the recharge water, from common wastewater compounds to trace organics not addressed by primary or secondary drinking water standards.

In regulated reclaimed water applications, public health is protected by a series of barriers, such as source water control, advanced wastewater treatment processes, and cross-connection control. By adding time and travel through the subsurface, ASR potentially offers another in the series of barriers that protect public health in the use of reclaimed water. The effectiveness of ASR to provide not only safe seasonal and long-term storage but also potential additional subsurface natural treatment of reclaimed water is the subject of this research.

The goal of this project was to combine a fundamental understanding, practical experience, and physical research to promote progress in the proper practice of reclaimed water ASR. To date, significant experience has been gained in the practice of reclaimed water ASR through several testing programs and operational facilities. Collectively, the data from these programs can be used to help identify water quality issues associated with reclaimed water ASR and to better understand fate and transport properties of residual contaminants in reclaimed water. The major objectives of this report are to:

- Describe the state of the practice of reclaimed water ASR
- Identify wastewater constituents and water quality parameters of significance for designing, monitoring, and evaluating reclaimed water ASR
- Measure concentrations of contaminants at various stages of recharge, storage, and recovery of reclaimed water and analyze observed data with respect to attenuation mechanisms and rates to characterize water quality changes through ASR

The project tasks to achieve these objectives were to (1) conduct a technical workshop, (2) conduct a literature survey, (3) develop a list of constituents to be tested and their basis, (4) develop sampling plans and conduct the necessary sampling, and (5) compare the data and draw conclusions if possible.

CHAPTER 2

STATE OF THE PRACTICE OF RECLAIMED WATER ASR

2.1 CURRENT RECLAIMED WATER ASR OPERATIONS

Storage of reclaimed water through ASR is much less common than groundwater recharge with reclaimed water or ASR with potable or surface water (Pyne, 2005). The state of the practice lags not only due to the uncertainty of the impact of recharged water on native groundwater resources, but also due to the unique regulatory challenges presented by this combination of emerging practices. The regulatory framework, largely undeveloped worldwide, must address reclaimed water regulations, groundwater regulations specific to ASR, and water rights issues. Several regions are pioneering this practice, however, using combined permits, monitoring programs, and protective barriers to implement successful reclaimed water ASR operations.

In order to screen for potential study sites and to gain an understanding for the current state of the practice, a survey was conducted of all known reclaimed water ASR projects. Administrators of reclaimed water ASR sites in Florida, Arizona, California, Texas, Hawaii, Australia, and Kuwait were interviewed for information on the institutional issues surrounding their projects. Table 2.1 provides a summary of the sites and their operational status. Further information on each facility's project background, purpose, and operations can be found in Appendix A. Extensive descriptions of research conducted at the Bolivar and Willunga, Australia, sites are also available in Appendix A. It is important to note that many of the sites surveyed are dynamic, and the information gathered may have changed by the time of publication of this report.

2.2 GENERIC ASR WATER QUALITY CONCEPTUAL MODEL

Based upon operational and testing data from ASR wells in brackish limestone artesian aquifers in both Florida and Australia, a generic conceptual water quality model has been proposed to describe a single ASR well and monitor well system (Pyne, 2005). Supplemental investigations have been completed that have refined this conceptual model by utilizing operational data from 52 ASR wells and 41 storage zone monitor wells at 12 ASR wellfields in southwest Florida. The data from Australia include monitor wells located 12 ft from the ASR well and also at greater distances exceeding 150 ft. The Florida data do not include monitor wells closer than 90 ft from an ASR well.

A typical ASR operating cycle includes recharge of water into one or more ASR wells for several weeks to months during the year, particularly during wet months and wet years. The stored water remains in storage typically for a few weeks to months and is then recovered during dry months, extended drought periods, and emergencies, with the water recovered from the same wells. At a few ASR wellfields storage occurs for shorter periods, such as storage during nights and weekends for recovery during the day to meet peak diurnal demands. At other ASR wellfields, particularly in southwestern states, storage is primarily for water banking purposes, storing water during wet years for recovery during droughts. In these areas, seasonal storage is an important, secondary consideration.

Usually, the same volume that is stored is recovered. However, for some ASR wellfield locations, particularly those in brackish aquifers exceeding about 5000 mg of total dissolved solids (TDS)/L, ultimate recovery efficiency may be less than 100%. Formation of a buffer zone is required in order to achieve full recovery efficiency in brackish aquifers. The buffer zone is best formed in one step, prior to the beginning of operational cycles; however, it may also be formed incrementally over several initial cycles during each of which a portion of the stored water remains underground. The same end point is ultimately achieved; however, the second approach typically requires several years, whereas the first typically requires a few weeks or months.

Table 2.1. Operational Status of Surveyed Reclaimed Water ASR Projects

State or Country	City or County	Operational Status
Arizona	Chandler	Full operation (two sites)
Arizona	Fountain Hills	Full operation
Arizona	Scottsdale	Full operation
Texas	El Paso	Aquifer recharge mode
Florida	Cocoa	Testing mode
Florida	Englewood	Testing mode
Florida	Hillsborough County	Terminated
Florida	Clearwater	Terminated
Florida	Lehigh Acres	Testing mode
Florida	Manatee County	Testing mode
Florida	Oldsmar	Permitting
Florida	Pinellas County	Feasibility, planning
Florida	St. Petersburg	Testing mode
Florida	Tarpon Springs	Feasibility, planning
Florida	Sarasota County	Construction
Kuwait	Sulaibiya	Feasibility, planning
Australia (SA)	Bolivar	Full operation
Australia (SA)	Willunga	Testing mode

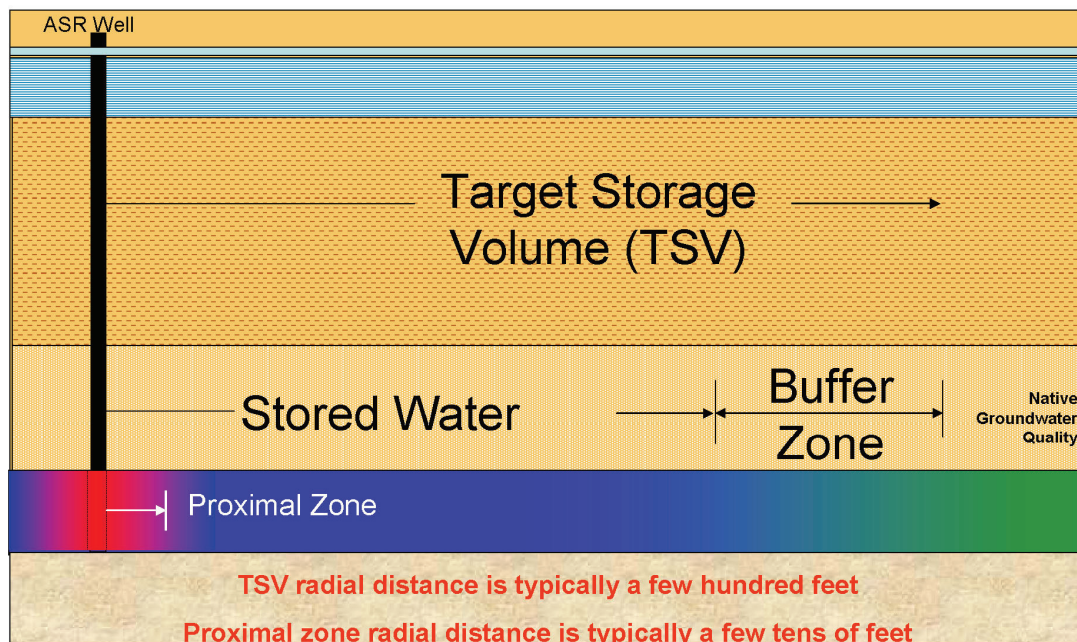


Figure 2.1. ASR well schematic.

As shown in Figure 2.1, immediately surrounding the borehole or screened section of the ASR well is a “proximal” zone, typically within a few feet to a few tens of feet surrounding the well. This is a zone of relatively high geochemical and microbial reactivity, driven primarily by the generally high oxidation–reduction potential (ORP), possibly high nitrate content, and relatively high dissolved organic carbon content of the recharge water, particularly for most reclaimed water sources. Nutrients such as ammonia and phosphate and small but important traces of ferric hydroxide may also be present in the recharge water due to pretreatment processes. Water quality gradients in this zone are potentially high, with ORPs typically dropping from a positive several hundred millivolts to a negative several hundred millivolts during injection (Vanderzalm et al., 2006). pH values also may vary and are typically lower near the well and increase away from the well. Velocities decline as the recharge water moves away from the well into the aquifer, providing some opportunity for settling out of any entrained particulates and sorption of colloids (Skjemstad et al., 2002; Greskiowak et al., 2005). Microbial metabolism products and corrosion and precipitation products accumulate in this zone. Desorption, adsorption, ion exchange, and other processes also occur. Microbial processes contribute to the mobilization and attenuation of metals and other constituents (Lisle, 2005). Specific concentrations for water quality constituents at each of the sites investigated for this project are provided in Appendix C.

The number of pore volume flushes experienced in the proximal zone during a single long ASR recharge period will be at a maximum next to the well, declining with the square of the distance from the well. Some rapid geochemical reactions achieve near-equilibrium within a few pore volume flushes, while others may take hundreds of pore volume flushes to achieve equilibrium. This proximal zone has a capacity to cause significant water quality changes due to a variety of reaction processes during ASR recharge, storage, and recovery.

During extended storage periods, a die-off of microbial biomass occurs due to lack of new dissolved organic matter, carbon, and nutrients. This may result in a negative redox potential at the ASR well (Vanderzalm et al., 2006). Some of this organic material is then backflushed from the ASR well at the beginning of recovery. Depending primarily upon the materials of well construction, backflushing to waste may last from 10 min to 2 h. Some of this same material also may be recovered from the well during the periodic backflushing that is normally scheduled during extended recharge periods at most ASR wells to remove minor particulates that have accumulated in the recharge water.

Once the recharge water leaves the proximal zone during recharge and enters the main portion of the storage zone further away from the well, geochemical and hydraulic gradients are reduced, the number of pore volume flushes during each ASR cycle declines, and water quality changes are less pronounced. During the initial ASR operating cycle, water quality changes are at a maximum. With successive cycles at approximately the same storage and recovery volumes, the storage zone around the well gradually becomes purged of ambient groundwater. Geochemical and microbial reactions tend to be less significant. After the pore volume has been flushed a sufficient number of times, the storage zone approaches a new geochemical and microbial equilibrium. This process is accelerated if a portion of the stored water is left in the aquifer during each of the first few cycles.

At the edge of the storage zone is the beginning of the buffer zone surrounding the well, typically at a radial distance of several hundred feet. However, in layered media, layers with lower hydraulic conductivity may not necessarily be flushed by injectant, and residual native groundwater diffuses slowly into the flushed zone during the storage and recovery phases (Pavelic et al., 2006b). The buffer zone provides some degree of separation between the stored water and the surrounding water in the aquifer. Depending upon the hydrogeologic settings of ASR wellfields in various parts of the world, the differences in water quality between stored water and the ambient groundwater may involve conditions of fresh to brackish, low nitrate to high nitrate, low fluoride to high fluoride, low hydrogen sulfide to high hydrogen sulfide, etc. Water quality changes within the buffer zone may be substantial. It is often important to not recover the buffer zone during extended pumping, since water quality deterioration may tend to occur rapidly, particularly in brackish storage zones. Recovery concentrations of these constituents will reflect normal mixing and dispersion processes and may be augmented by ion exchange, desorption, and other processes, particularly if recovery includes all or part of the buffer zone.

If the buffer zone is formed in one step at the beginning of ASR operations, instead of cumulatively over a period of several operating cycles, a geochemical and microbial quasi-equilibrium may be achieved during the initial operating cycle. Otherwise, equilibrium will eventually be achieved over several cycles at approximately the same volume, typically requiring several years of operation. The sum of the volume in the buffer zone and the volume to be recovered seasonally is called the target storage volume (TSV). The TSV is typically measured in terms of million gallons (MG) of recovery capacity per MG per day (mgd), which converts to a unit of days. Experience to date with ASR wells in brackish aquifers of Florida suggests typical TSV values of 50–350 days. TSV values in excess of 70 days have been associated with attenuation of arsenic, and so arsenic is not present in water recovered from such ASR wells, so long as the buffer zone is maintained.

During ASR recovery, the first flush of water recovered may contain particulates and microbial matter, as discussed above. The duration of the first flush is typically a few minutes to a few hours, dependent upon the length and materials of construction of the well casing, recharge water quality, and other factors. With regular backflushing to remove these

materials, ASR wells have been in sustained operation for over 30 years. Backflushing frequencies typically range from daily to annually, with most backflushing operations being conducted every few weeks. ASR operations are in contrast with injection wells, which are not equipped with pumps and therefore accumulating solids cannot be backflushed from such wells.

After a few operating cycles at approximately the same volume, or after formation of the buffer zone, the water subsequently recovered is usually relatively uniform in quality. Due to the long flow path through the aquifer for water recovered toward the end of an extended recovery period, any opportunity for desorption may lead to steadily increasing concentrations of desorbed compounds in the recovered water along the flow path toward the well, reaching a peak concentration and then decreasing as desorption proceeds to completion. Conversely, microbial processes may augment, inhibit, or override desorption processes. The science has yet to be developed regarding the complex interplay of microbial and geochemical processes occurring during ASR storage. These processes can be inferred from other investigations and research regarding bank filtration, wastewater treatment, and soil aquifer treatment processes; however, there are several unique aspects relating to ASR systems, an understanding of which will facilitate analysis of the WateReuse Foundation (WRF) data.

- Contact time between the stored water and the aquifer matrix is typically weeks to months for ASR wells, compared to hours to days in the unsaturated zone of soil aquifer treatment systems, some bank filtration wells, and wastewater treatment plants.
- Perhaps more importantly, most, but not all, ASR wells are in deep, confined anoxic aquifers under reducing to highly reducing conditions. A few ASR wells are in deep water table aquifers with low-level oxidizing conditions. These sites tend to occur in the southwestern United States.
- Flow in ASR wells is, by definition, in two directions, away from the well during recharge and back toward the well during recovery. The lateral reach of the stored water “bubble” typically does not extend more than a few hundred feet from the ASR well.
- Finally, many ASR wells store water in brackish or saline aquifers or aquifers that have at least one water quality constituent present in the ambient groundwater at concentrations that would require treatment to achieve drinking water standards. Three of the four WRF sampling sites are in brackish aquifers.

This generic ASR conceptual model is adaptable to different site conditions (geology, water quality, operations, etc.), using specific data for each site. For example, where the dissolved organic content of the recharge water is very low, as may occur with advanced pretreatment, subsurface microbial processes may occur at a slower rate, and low redox conditions may develop more slowly or not at all around the ASR well. High dissolved oxygen (DO) levels in the recharge water can also push the proximal zone farther from the well. The persistence of a small chlorine residual for a few weeks instead of hours to days is an indication of slow development of biomass in the proximal zone of an ASR well.

It is possible that water quality changes during reclaimed water ASR operations may be different for storage in fresh water aquifers compared to brackish water aquifers. Sorption and ion exchange processes occurring during recovery of water stored in brackish aquifers would perhaps be more significant compared to similar storage in fresh aquifers, particularly if a portion or all of the buffer zone was recovered. No research of this in an ASR setting has been

conducted; however, brine regeneration of ion exchange reactors for iron and manganese removal has been a standard water treatment process for decades.

2.3 WATER QUALITY FACTORS IMPORTANT FOR RECLAIMED WATER ASR

There are a number of potential contaminants to consider when dealing with the recharge of reclaimed water into ASR wells. A critical question, however, is whether attenuation of these contaminants occurs during periods of storage. If concentrations of contaminants decreased with time due to adsorption, degradation, or die-off, problems resulting from their presence during recharge might be mitigated.

Physical, chemical, and biological processes are responsible for the breakdown of compounds in natural water. Examples of physical processes occurring in aquifers are phase partitioning and adsorption. Chemical processes, which involve breaking or forming bonds, include complexation, oxidation–reduction, and hydrolysis. Biological processes consist of accumulation and transformation processes conducted by living organisms. Studies have indicated that the primary removal processes occurring in aquifers fall into the physical and biological categories (Khan and Rorije, 2002).

2.3.1 Nutrients and Metals

Potential contaminants associated with reclaimed water ASR include conventional wastewater contaminants, such as nutrients and metals. Information describing the potential attenuation of these and other contaminants in the subsurface is limited. Tartakovsky et al. (2002) observed subsurface nitrate removal rates as high as 1.2 mg of nitrogen/L-day when ethanol was injected to serve as the carbon source for in situ biological denitrification. Lin and Puls (2003) studied the subsurface behavior of arsenic species and found that iron minerals tend to oxidize As(III) to As(V), which then adsorbs to iron, clay, or feldspars found in the aquifer. The potential for long-term in situ arsenic attenuation was not addressed in that study.

2.3.2 Microbial Contaminants

Bacteria, viruses, and other pathogens may pose yet another concern for groundwater through reclaimed water ASR. According to a review by David John and Joan Rose (2004), the inactivation rate of viruses, such as coliphage, poliovirus, echovirus, and hepatitis A virus, appeared to increase with increasing temperature, based upon controlled investigations at 5, 22, and 30 °C. This overall trend was not observed with the bacterial data, for which the peak attenuation rate was at 22 °C. Additionally, the rate of inactivation of the hepatitis A virus appeared to be slower than that of the other viruses examined. The authors also observed that the median value for inactivation rates of coliphage, poliovirus, echovirus, and coliform bacteria fell in the range of 0.127–0.251 log₁₀ inactivation/day (i.e., the T₉₀, the time for 90% to be inactivated, is 4–20 days) (Dillon and Toze, 2005).

Ambient temperatures likely to be encountered during ASR storage range widely, from about 1 °C during winter recharge, as recorded for an ASR wellfield at Mannheim, ON, Canada, to 38 °C ambient groundwater temperature, as recorded at the Miami-Dade West wellfield ASR system in Florida. Higher temperatures may occur for some ASR wellfields, such as in Middle East countries.

In general, more field studies with large databases of supporting environmental variables, including information on indigenous microorganisms, are needed to account for variability between investigations and to develop sound conceptual models and greater confidence in trends for the attenuation of microbes. A better balance is needed between controlled experiments under lab conditions and carefully conducted field investigations under more realistic, but therefore less-controlled, field conditions. To date, the ability to conduct such field studies in the United States has been effectively precluded by underground injection control (UIC) regulatory restrictions regarding subsurface testing of microbial attenuation in ASR wells.

2.3.3 Pesticides

Herbicides and pesticides also must be considered when evaluating reclaimed water ASR. Tuxen et al. (2003) reported that in both laboratory and field studies, phenoxy acid herbicides, hormone-like chemicals used to kill broadleaf weeds, undergo both aerobic and anaerobic degradation. Snyder et al. (2004b) found that atrazine, a common herbicide used to control broadleaf and grassy weeds, adsorbed or degraded at a slow to moderate rate in the subsurface, with adsorption most likely being the dominant attenuation mechanism.

2.3.4 Endocrine Disruptors, Pharmaceuticals, and Personal Care Products

While numerous researchers have focused on the development of methods to detect and quantify endocrine-disrupting compounds (EDCs) and pharmaceuticals, relatively little work has been done to evaluate potential attenuation of these substances in the subsurface. In laboratory studies using sediment and groundwater from a reclaimed water ASR site at Bolivar, SA, Australia, Ying et al. (2003) found that 17 β -estradiol (E2), 17 α -ethynylestradiol, and 4-*n*-nonylphenol degraded under aerobic conditions, while bisphenol A and 4-*tert*-octylphenol persisted under both aerobic and anaerobic conditions. Several studies have shown that these compounds can sorb to aquifer material with varying degrees of affinity (Mansell and Drewes, 2004; Snyder et al., 2004b; Ying et al., 2004).

Pharmaceuticals, such as ibuprofen, acetaminophen, sulfamethoxazole, and caffeine, have also been examined for natural attenuation when in contact with aquifer materials. Under the environmental conditions of several field experiments, caffeine, ibuprofen, and other pharmaceuticals were efficiently removed to concentrations near or below the analytical detection limit after retention times of less than 6 months during groundwater recharge (Drewes et al., 2003). Using biologically active sand batch reactors and continuous flow simulated ASR columns, Snyder et al. (2004a) demonstrated that acetaminophen, caffeine, and ibuprofen can be adsorbed and degraded in the subsurface. This study also showed that while sulfamethoxazole adsorbed to the biologically active sand, almost no degradation occurred, a result that has been confirmed by Cordy et al. (2004).

2.3.5 Water Quality Factors Summary

While some research has been conducted on water quality changes applicable to reclaimed water ASR, very few compound-specific trends have been determined. A wide range of water quality parameters, from nutrients to microcontaminants, are of interest in both the stored and ambient water. Bench-scale experiments with sorption and anaerobic biodegradation may prove useful in understanding water quality changes through ASR, but further research at the operational level is needed.

2.4 REGULATIONS

Governance of reclaimed water ASR encompasses the complexity of reclaimed water and the gradual evolution of groundwater regulations. Regulatory frameworks for these water resources are at an early stage of development in most of the countries where ASR is practiced. The following sections describe regulations in the United States and Australia, the two countries where study sites for this project were chosen.

2.4.1 U.S. Federal Regulations

Groundwater management and development in the United States is a right that is typically reserved by the individual states and is not subject to direct control by the federal government. Further complicating ASR regulations, facilities are often permitted by multiple agencies having jurisdiction in different areas, such as groundwater quality protection, water resources management, and water rights. Most ASR systems are used for municipal water supplies, and so drinking water protection agencies are usually involved in the regulatory process.

On the federal level, management and regulation of ASR wells primarily falls under the UIC program authorized by the 1974 Safe Drinking Water Act. In carrying out the mandate of the Safe Drinking Water Act, the UIC regulations provide that “no injection shall be authorized by permit or rule if it results in the movement of fluid containing any contaminant into Underground Sources of Drinking Water, if the presence of that contaminant may cause a violation of any primary drinking water regulation under 40 CFR part 141 or may adversely affect the health of persons.” Aquifers that are not underground sources of drinking water are not exempted aquifers. They simply are not subject to the special protection afforded underground sources of drinking water.

2.4.1.1 UIC Regulations

Federal UIC regulations have been promulgated and are administered by the U.S. Environmental Protection Agency (EPA) under the authority of the Safe Drinking Water Act. The UIC regulations classify injection wells into Classes I to V, based upon their use and other considerations. ASR wells are a subset of Class V, as follows:

Class V. Injection wells not included in Class I, II, III, or IV. Typically, Class V wells are shallow wells used to place a variety of fluids directly below the land surface. However, if the fluids you place in the ground qualify as a hazardous waste under the Resource Conservation and Recovery Act (RCRA), your well is either a Class I or Class IV well, not a Class V well. Examples of Class V wells are described in Sec. 144.81.

Examples of categories of Class V wells cited in a 1999 EPA study included agricultural drainage wells, stormwater drainage wells, large-capacity septic systems, sewage treatment effluent wells, aquifer remediation wells, car wash and laundromat effluent wells, salt water intrusion barrier wells, aquifer recharge and ASR wells, subsidence control wells, and industrial wells (USEPA, 1999). Thus, it is clear that the existing UIC regulations are intended to apply to both ASR wells and other recharge wells used to replenish water in an aquifer, whether recharge is with drinking water, reclaimed water, or stormwater. All such sources are treated as contaminants under the UIC regulatory framework.

All ASR wells are classified as Class V wells under the UIC program. In states with primacy status for Class V well regulation, this program is administered by the state agency rather

than the EPA. State UIC regulations must be at least as restrictive as the federal regulations; they may be more restrictive at the discretion of an individual state. At the present time, 34 states have primacy status.

The sections of the UIC program that address ASR are as follows:

- 40 CFR Part 144, Underground Injection Control Program: general provisions, general program requirements, authorization of underground injection by rule, authorization by permit, permit conditions, and requirements for owners and operators of Class V injection wells
- 40 CFR Part 145, State UIC Program Requirements: requirements for state programs, state program submissions, and program approval, revision, and withdrawal
- 40 CFR Part 146, Underground Injection Control Program, Criteria and Standards: general provisions and criteria and standards applicable to Class V injection wells
- 40 CFR Part 147, State Underground Injection Control Programs

ASR regulations should not be viewed in the same context as groundwater regulations, which have been implemented to varying degrees in different states. UIC programs are either directly implemented by EPA or are specifically delegated to a state agency.

2.4.2 State Regulations

Generally, state groundwater laws are similar to state surface water laws. Western states use a system of water rights permits under a priority system called the prior appropriation doctrine (“first in time, first in right”), while many eastern states use a system in which the right to develop and use water resources is tied to land ownership (typically under the correlative rights doctrine). There are states, however, where prior appropriation water rights are used for surface water but land ownership determines the right to use groundwater. Several states have instituted regional groundwater resources management programs, in which net withdrawals from groundwater are restricted in order to restore groundwater levels, prevent saltwater intrusion, or otherwise protect overtaxed aquifers. Under these programs, ASR often can be used to offset depletions and increase the total withdrawals allowed by a groundwater user. In practice, the regulatory frameworks governing reclaimed water ASR in different states may be characterized more by their differences than by their commonalities. The differences reflect the unique needs, constraints, and opportunities of each state.

ASR regulations have been adopted in at least five states to address both the water quality and water use and water rights aspects of ASR facility permitting, typically with the intent of streamlining and clarifying the regulatory process (Pyne, 2005). These are Colorado, New Jersey, Idaho, California, and Arizona. Three of these are discussed in greater detail below.

2.4.2.1 Arizona Regulations

Arizona does not have primacy for the EPA UIC Class V program. In Arizona, regulations addressing ASR are independent from the State’s water reuse regulations. The use of reclaimed water for ASR is regulated under statutes and administrative rules administered by the Arizona Department of Environmental Quality and the Arizona Department of Water Resources. Several different permits are required by these agencies prior to implementation of a groundwater recharge project. In general, the Arizona Department of Environmental Quality regulates groundwater quality and the Department of Water Resources manages

groundwater supply. All aquifers in Arizona currently are classified for drinking water protected use, and the state has adopted National Primary Drinking Water maximum contaminant levels (MCLs) as aquifer water quality standards. These standards apply to all groundwater in saturated formations that yield more than 20 L/day (5 gal/day) of water. Any groundwater recharge project involving injection of reclaimed water into an aquifer is required to demonstrate compliance with aquifer water quality standards. The point of compliance is a vertical plane downgradient of the recharge facility that extends through the uppermost aquifers underlying that facility. The point of compliance for a pollutant that is a hazardous substance is the limit of the pollutant management area. The pollutant management area is the limit projected in the horizontal plane of the area on which pollutants are or will be placed. An alternative point of compliance may be approved under certain conditions. The alternative point of compliance cannot be further downgradient than any of the following: the property boundary, any point of an existing or reasonably foreseeable future drinking water source, or 750 ft from the edge of the pollutant management area (<http://www.azdeq.gov/environ/water/permits/stats.html>).

Provided below is a summary of Arizona Class A+ standards for reclaimed water:

Class A+ reclaimed water is wastewater that has undergone secondary treatment, filtration, nitrogen removal treatment, and disinfection. Chemical feed facilities to add coagulants or polymers are required to ensure that filtered effluent before disinfection complies with the 24-h average turbidity criterion prescribed in subsection (B)(1). Chemical feed facilities may remain idle if the 24-h average turbidity criterion in (B)(1) is achieved without chemical addition.

An owner of a facility shall ensure that:

The turbidity of Class A+ reclaimed water at a point in the wastewater treatment process after filtration and immediately before disinfection complies with the following:

- a. The 24-h average turbidity of filtered effluent is 2 nephelometric turbidity units (NTU) or less, and
- b. The turbidity of filtered effluent does not exceed 5 NTU at any time.

Class A+ reclaimed water meets the following criteria after disinfection treatment and before discharge to a reclaimed water distribution system:

- a. There are no detectable fecal coliform organisms in four of the last seven daily reclaimed water samples taken, and
- b. The single sample maximum concentration of fecal coliform organisms in a reclaimed water sample is less than 23/100 mL.
- c. If alternative treatment processes or alternative turbidity criteria are used, or reclaimed water is blended with other water to produce Class A+ reclaimed water under subsection (C), there are no detectable enteric viruses in four of the last seven monthly reclaimed water samples taken.

The five-sample geometric mean concentration of total nitrogen in a reclaimed water sample is less than 10 mg/L.

2.4.2.2 California Regulations

Although California does not have primacy for EPA UIC Class V regulations, EPA accepts State standards which equal or exceed federal standards for drinking water protection. The State Water Resources Control Board oversees the nine Regional Water Quality Control Boards (RWQCBs), but the RWQCBs administer the UIC program. Although there are no specific State regulations directed at using reclaimed water for ASR, the California Department of Health Services (DHS) has draft regulations for injecting reclaimed water into potable aquifers (California Department of Health Services, 2004). While DHS has the authority to adopt such criteria, they are implemented through the RWQCBs, who are required to include them in water reuse permits. The RWQCBs may include other water quality requirements in addition to the DHS criteria. It is likely that ASR wells into which reclaimed water is injected into groundwater used as, or suitable for, potable supply would have to comply with the quality requirements in the DHS groundwater recharge regulations. The most recent draft requirements are summarized in Table 2.2 and include some requirements, e.g., retention time underground, distance to withdrawal, and dilution, that would not be applicable for ASR. It is likely that substantial changes will be made prior to adoption of the criteria.

The draft regulations require that reclaimed water comply with the following State drinking water regulations: primary MCLs, inorganic chemicals (except nitrogen), MCLs for disinfection byproducts (DBPs), and action levels for lead and copper. Quarterly monitoring is required, with compliance determined from a running average of the last four samples. The reclaimed water also must be monitored annually for several secondary MCLs. In addition, the reclaimed water must be sampled quarterly for unregulated chemicals, priority toxic pollutants, and chemicals with State notification levels, which DHS specifies based on a review of the project. Each year, the reclaimed water must be monitored for endocrine disruptors and pharmaceuticals that are specified by DHS after review of the project. According to the DHS draft regulations, compliance with reclaimed water standards is measured at the point of recharge into an injection well. How this will be applied for recharge of reclaimed water into an ASR well has not yet been determined. However, for a recent ASR project for the Central Valley RWQCB at Roseville that involved recharging of drinking water, compliance with drinking water standards was allowed to be measured at a monitor well, not at the ASR well during recharge. This is potentially significant to reclaimed ASR projects, since the constituent of concern at Roseville was trihalomethanes (THMs), which are known to attenuate naturally during ASR storage under anaerobic conditions (Pavelic et al, 2006a).

Table 2.2. California Draft Groundwater Recharge Regulations for Injection

Contaminant Type	Requirement(s)
<i>Pathogenic Microorganisms</i>	
Filtration	≤2 NTU
Disinfection	5-log virus inactivation, ^a ≤2.2 total coliforms per 100 mL
Retention time underground	12 mo
Horizontal separation ^b	600 m (2000 ft)
<i>Regulated Contaminants</i>	
Drinking water standards	Meet all drinking water MCLs (except nitrogen) and new federal and state regulations as they are adopted
Total nitrogen	<ul style="list-style-type: none"> Level specified by DHS for existing project with no RWC^c increase ≤5 mg/L for new project or increased RWC at existing project
<i>Unregulated Contaminants</i>	
TOC in filtered wastewater	TOC ≤ 16 mg/L in any portion of the filtered wastewater not subjected to RO ^d treatment
TOC in recycled water	100% RO treatment to achieve: TOC level specified by DHS for existing project with no RWC increase TOC ≤ 0.5 mg/L/RWC (new project or increased RWC at existing project)
RWC	≤50% subject to above requirements 50–100% subject to additional requirements

^aThe virus log reduction requirement may be met by a combination of removal and inactivation.

^bMay be reduced upon demonstration via tracer testing that the required detention time will be met at the proposed alternative distance.

^cRWC, recycled water contribution.

^dRO, reverse osmosis.

Source: Adapted from California Department of Health Services (2004).

The proposed DHS draft regulations specify total organic carbon (TOC) as a surrogate for determining organics removal efficiency. Although TOC is not a measure of specific organic compounds, it is considered to be a suitable measure of the gross organic content of reclaimed water for the purpose of determining organics removal efficiency. The proposed TOC limit is based on increasing concern over unregulated chemical contaminants and the realization that current technology using membranes can readily reduce TOC to 0.2 mg/L or less. The TOC limit applies to TOC of wastewater origin in recharged water. Weekly sampling is required for TOC, with compliance determined monthly from the average of the most recent 20 TOC samples.

Any intentional augmentation of drinking water sources with reclaimed water in California requires two State permits. A waste discharge or water recycling permit is required from a RWQCB, which has the authority to impose more restrictive requirements than those recommended by DHS, and a public drinking water system using an impacted source is required to obtain an amended water supply permit from DHS to address changes to the source water.

2.4.2.3 Florida Regulations

Although Florida has no ASR-specific statutes, it does have primacy for EPA UIC Class V regulations and has developed criteria, standards, and permitting procedures that address underground injection control (Florida Department of Environmental Protection, 2002). Florida also has adopted related rules for groundwater, including groundwater classes, standards, and exemptions (Florida Department of Environmental Protection, 1996) and groundwater permitting and monitoring requirements (Florida Department of Environmental Protection, 2001). ASR wells into which reclaimed water is injected into potable aquifers must comply with the State's requirements for groundwater recharge of reclaimed water via injection, which are summarized in Table 2.3. The reclaimed water injection regulations pertain to G-I, G-II, and F-I groundwaters, all of which are classified as potable aquifers. Typically, reclaimed water must meet G-II groundwater standards prior to injection. G-II groundwater standards are, for the most part, primary and secondary drinking water standards. Exceptions for secondary standards are granted through a Water Quality Criteria Exemption or approved zone of discharge.

Table 2.3. Florida Water Reuse Rules for Groundwater Recharge via Injection

Type of Use	Water Quality Limits	Treatment Required
Groundwater recharge or injection to groundwater having TDS < 3000 mg/L	<ul style="list-style-type: none"> No detectable total coliforms/100 mL 20 mg/LCBOD₅ 5.0 mg/L TSSa^b 3.0 mg/L TOC 0.2 mg/L TOX^b 10 mg/L total N Primary^c and secondary drinking water standards 	<ul style="list-style-type: none"> Secondary Filtration Disinfection Multiple barriers for control of pathogens and organics Pilot testing required
Groundwater recharge or injection to groundwater having TDS 3000–10,000 mg/L	<ul style="list-style-type: none"> No detectable total coliforms/100 mL 20 mg/LCBOD₅ 5.0 mg/L TSS 10 mg/L total N Primary drinking water standards^c 	<ul style="list-style-type: none"> Secondary Filtration Disinfection

^aTSS, total suspended solids.

^bTOX, total organic halogen.

^cExcept for asbestos.

Source: Adapted from Florida Department of Environmental Protection (1999).

The Florida regulations include requirements for planned groundwater recharge by injection into water supply aquifers. Groundwater recharge projects in Florida that involve injection also must comply with the State's UIC regulations (Florida Department of Environmental Regulation, 2002), which include criteria pertaining to ASR wells.

For reclaimed water ASR projects, the Florida Department of Environmental Protection regulations provide for compliance with secondary drinking water standards to be measured at the edge of a zone of discharge, instead of at the ASR well during recharge, thereby taking full advantage of natural treatment and mixing mechanisms occurring in the aquifer.

Currently, no allowance is provided for subsurface treatment relative to primary drinking water standards, for which measurements are conducted at the wellhead prior to recharge.

2.4.2.4 Point-of-Compliance Measurement

As indicated in the discussions above regarding the regulatory framework for reclaimed ASR programs in California, Arizona, and Florida, this is an evolving situation. There is a common commitment to meeting all drinking water standards and evaluating water quality relative to guidance concentrations for those constituents that are not covered by the drinking water standards. The significant differences between the state programs relate to where the point of compliance is measured. This is a particularly important difference for ASR wells, for which continuous long-term recharge into the local aquifer is replaced by seasonal and wet-dry cyclic operations within a small radius around the well, typically a few hundred feet. Where the point of compliance has been established at a monitor well, thereby providing for natural treatment processes occurring close to the ASR well during recharge and storage, it is possible that pretreatment costs may be reduced without adversely threatening public health or groundwater quality. Alternatively, if these pretreatment processes are implemented anyway, the ASR storage will provide an added barrier to further protect public health and groundwater quality. Achieving a better understanding of the natural treatment processes occurring during ASR storage of reclaimed water is one of the key objectives of this WRF project.

2.4.3 Australian Guidelines

Similar to the regulatory structure in the United States, guidelines for ASR and recycled water in Australia are addressed at both the federal and state level. They are also still being developed with respect to both recycled water and ASR. The principles contained in the National Water Quality Management Strategy have been adopted by the Commonwealth and State governments of Australia and provide a unified and coherent platform for managing water quality, including groundwater, rivers, lakes, drinking water, sewage effluent, and stormwater. In 2005, National Water Quality Management Strategy Draft Water Recycling Guidelines, developed with a risk management approach, were issued for public comment. The next phase of the Water Recycling Guidelines to be developed in 2006–7 will specifically include management of aquifer recharge issues and will address ASR (Dillon, 2005). Regarding water rights, there is no systematic state or national policy regarding rights to take reclaimed water or stormwater, to own recharged water, to transfer recharge credits, or to use aquifer storage capacity.

Previous Australian efforts at establishing guidelines included the Australian Water Resources Council (1982) guidelines for the use of reclaimed water for aquifer recharge. More recently, the South Australian Environmental Protection Authority (2004) issued a Code of Practice for Aquifer Storage and Recovery, but this code only applies to stormwater recharge and recovery, not reclaimed water. Dillon, with Pavelic (1996) and with Molloy (2006), proposed technical guidance for ASR with reclaimed water. All proposed guidelines have adopted a multibarrier approach to groundwater quality protection and generally provide a differential protection policy. A differential protection policy protects water for its existing beneficial uses or environmental values, which depend upon ambient water quality and historical use. Examples of environmental values are raw water for drinking water supplies, irrigation, industrial use, and ecosystem support. In all cases, a groundwater attenuation zone concept applies. This concept entails that beyond a certain distance and time since injection, water quality should meet the criteria corresponding at least to its original environmental

value. While all proposed guidelines share the multibarrier approach and protection policy, only the most recent (Dillon and Molloy, 2006) adopts the risk management approach outlined in the Draft Recycling Guidelines.

Localized arrangements are in place in a few locations for water allocations to ASR operators, particularly those addressing groundwater exploitation within catchment water allocation plans. Also site specific, the Code of Practice for Aquifer Storage and Recovery places some restrictions on attenuation zones based on land tenure and aquifer characteristics, namely, fractured rock and karst geology (South Australian Environmental Protection Authority, 2004).

In conclusion, the guidelines in Australia for both ASR and reclaimed water are still being developed and are evolving at the national, regional, and local levels. The most recently proposed guidelines exercise a risk-based approach, a newer paradigm that is also being utilized in drinking water regulations. For reclaimed water ASR guidelines, this approach will likely build upon the multibarrier and use-protective approaches of the National Water Quality Management Strategy.

CHAPTER 3

CONSTITUENTS

3.1 CONSTITUENT SELECTION RATIONALE

The chemical and microbiological parameters monitored in this study were selected to provide guidance regarding the constituents of greatest concern in reclaimed water ASR and to indicate the fate of these compounds in the subsurface environment. A comprehensive list of over 300 compounds was generated from several sources, including the following:

- The U.S. Geological Survey list of 95 organic constituents analyzed during the 1999 and 2000 sampling events at 139 surface water sites nationwide (Barnes et al., 2002); the list includes veterinary and human antibiotics, prescription drugs, nonprescription drugs, steroids, hormones, and other wastewater-related compounds
- A short list of microbiota selected by various state and federal agencies for investigations being conducted by the South Florida Water Management District and the Southwest Florida Water Management District to address the fate of microbiota during ASR storage
- Draft regulations from the California DHS, located at URL <http://www.dhs.ca.gov/ps/ddwem/publications/waterrecycling/rechargeregulationsdraft-12-01-04.pdf>
- The State of Arizona Numeric Aquifer Water Quality Standards

Lists from these studies and regulations were combined for various chemical categories, such as metals, DBPs, pesticides, etc. Due to the infeasibility of testing for so many analytes, the initial list of over 300 compounds was screened using the qualitative selection criteria below, presented in descending order of importance:

- Applicability to water quality standards or guidance
- Availability of analytical methods and their pricing
- Usefulness in aquifer characterization (compounds used to distinguish wastewater from native groundwater)
- Degree of public and/or scientific concern, as determined by the Project Advisory Committee
- Applicability to irrigation water quality, because irrigation is often the end use
- Expected mobility in solution and aquifers
- Frequency of occurrence in the environment
- Grouping with suites of analytes available with single laboratory tests

For the large list of trace organics in the U.S. Geological Survey list, selection criteria also focused on the ability of the compound to indicate removal mechanisms in the aquifer. This selection process is described further in Section 3.10, below.

Table 3.1 presents the selection criteria pertaining to each parameter category chosen for the study. The following sections describe the selection of specific parameters within those categories. Table 3.2 lists the specific parameters and summarizes the rationale for each category in more detail.

Table 3.1. Selection Criteria Pertaining to Each Parameter Category

	General	Nutrients	Metals	DBPs	Radioactivity	Industrial Pollutants	Pesticides	Microbiota	Trace Organics
Existing Standards or Guidance	X	X	X	X	X	X	X	X	
Characterization of Chemical Environment	X	X	X		X				X
Comparison with Background Water	X		X			X	X		X
Public Environmental Concern			X	X	X	X	X	X	X
Irrigation Concern		X							

Table 3.2. Parameter Categories and Rationale

Category	Compound	Rationale
General Parameters	Alkalinity Bicarbonate Boron Calcium Chloride DO Fluoride Magnesium pH Redox potential Sodium Specific conductance TDS Temperature TOC Turbidity	Standard compounds already monitored in most ASR programs; these compounds provide information about the chemical environment
Nutrients	Total nitrogen Ammonia Nitrate Nitrite Total phosphorous Orthophosphate	Of agricultural interest for irrigation reuse
Metals	Arsenic (total) Barium (total) Cadmium (total) Copper (total) Iron (total) Lead (total) Mercury (total) Selenium (total)	Regulated, most can be analyzed as part of one suite; selenium is of environmental interest in some regions
Disinfection Byproducts	Cyanide TTHMs HAA ₅ NDMA	Can be found in wastewater and are toxic to humans
Radioactivity	Gross alpha particle activity Total uranium	Required for Florida reuse permits
Industrial Pollutants	Perchlorate Chlorate Bromate Iodate PBDEs	Perchlorate is newly regulated; the remaining halogenic compounds are part of its analytical suite; PBDEs have been detected in final wastewater effluent and may migrate with particles
Pesticides	Aldrin Atrazine Diazinon Dieldrin Chlorpyrifos Lindane	Some of these pesticides are regulated; all can be analyzed as part of one suite
Pathogen Indicators	Total and fecal coliforms <i>E. coli</i> Enterococci bacteria Coliphage <i>Cryptosporidium</i> <i>Giardia</i> HPC	Coliphage is a viral indicator; heterotrophic plate count (HPC) indicates regrowth potential; the remaining pathogens are regulated for reuse

3.2 GENERAL PARAMETERS

The general parameters category features routinely tested wastewater components. The TDS and electrical conductivity (EC) indicate the ionic strength of solution, which affects the equilibria of all reactions, including sorption. These are also critical parameters for determining irrigation usability.

Bicarbonate, alkalinity, and pH demonstrate much about the chemical nature of the solution. Calcium, magnesium, and sodium are used to discern the sodium adsorption ratio of the injected water, which is of interest in irrigation use. Because some crops are sensitive to boron, it is also of concern when water is to be used for irrigation (Tisdale et al., 1993). Of these ions, calcium, magnesium, sodium, chloride, fluoride, and boron are further expected to act as tracers in distinguishing the injected water from groundwater.

Temperature was included because it is a major factor affecting microbial and chemical kinetics and may also be used as a quasi-conservative tracer to determine the extent and speed of injected water mixing with groundwater.

Redox potential indicates the types of oxidation–reduction reactions that may affect chemical degradation processes. In most confined aquifers, DO falls to levels allowing only anaerobic microbial activity. Aquifers that are unconfined or have sufficient through-flow and hydraulic connection to the atmosphere may have DO at levels sufficient to support aerobic microorganisms and consequently aerobic degradation of introduced organic matter (Lyman et al., 1992). ASR wells in some southwestern states are in deep, water table aquifers, which are aerobic. Redox potential will indicate whether DO is present or if other electron acceptors, such as nitrate, manganese, iron, or sulfate, are being used in redox reactions.

3.3 NUTRIENTS

The selected nutrients are routinely tested in wastewater due to their impact on aquatic environments. Nitrogen and phosphorus are often measured in agricultural runoff, and thus their levels and forms should be known if the water is used for irrigation. Nutrients may accelerate subsurface microbial activity and affect clogging of ASR wells, and their escape from an aquifer to surface water bodies could stimulate undesirable effects, such as eutrophication. Generally, storage zones are chosen to limit such escape. The various forms of nitrogen (total, TKN, NH_4^+ , NO_3^- , and NO_2^-) indicate the bioavailability, mobility, and redox potential of the compounds and therefore reflect their position in the nitrogen cycle. Of the many phosphorus forms, the orthophosphate fraction represents the most plant-available and leachable of phosphorus compounds.

3.4 METALS

Arsenic, copper, lead, and mercury were selected based on their toxicities and prevalence. In addition, these metals are regulated in the United States. While arsenic's ability to cause cancer in humans is still debatable, it has been classified by the U.S. EPA as a carcinogen based on evidence of skin cancer. Arsenic partitions in and out of solution via redox-sensitive reactions, and anaerobic environments such as those expected in aquifer storage often lead to arsenic in its most mobile form. Copper is considered toxic via noncarcinogenic effects. Lead is associated with cancer at very high doses but is primarily associated with neurodevelopmental problems in children. Mercury is also a neurotoxicant and has various toxic pathways (Cohn et al., 2003).

3.5 DISINFECTION BYPRODUCTS

Many DBPs have been identified as toxic to humans, with both carcinogenic and noncarcinogenic effects reported. DBPs are formed during treatment and often occur in concentrations that are orders of magnitude greater than other organic pollutants. The most widely studied of organic DBPs, total THMs (TTHMs), are comprised of chloroform, bromodichloromethane, dibromochloromethane, and bromoform; all are suspected carcinogens. Second to TTHMs in prevalence are the haloacetic acids (HAAs), comprised of nine compounds, including dichloroacetic acid, trichloroacetic acid, and various brominated forms. HAAs are highly water soluble, and various health effects are attributed to them (Cohn et al., 2003).

N-Nitrosodimethylamine (NDMA) has been of rising concern, as it is suspected to be carcinogenic at very low concentrations. It was of interest to this study also because it primarily degrades by photolysis (NTP, 2002), and less is known about its fate in subsurface environments. Cyanide is another common DBP that is toxic in certain forms to humans and aquatic life.

3.6 RADIOACTIVITY

The radioactivity parameters of gross alpha particle count and total uranium were included because they are required for Florida reuse permits. In certain areas, including southwest Florida, these constituents have been noted at concentrations above background in water recovered from ASR wells, particularly during early operating cycles. Uranium concentrations have not exceeded State standards. Gross alpha particle counts and radium activity levels have generally not exceeded standards, with a few exceptions. With successive ASR cycles, radioactivity levels have generally declined. If present in the ambient groundwater, radon will be present in the ASR recovered water at the same activity level, as was determined for Seattle, WA. However, at that site the radon levels were below drinking water standards. Other than the fact that radioactivity is a water quality constituent of concern, the significance of radioactivity for reclaimed ASR is probably small.

3.7 INDUSTRIAL POLLUTANTS

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are persistent, bioaccumulative, and toxic (Betts, 2001). These are strongly hydrophobic compounds, meaning that they do not combine with water molecules. They were included in this study based on a California study that detected PBDEs in wastewater.

3.8 PESTICIDES

Pesticides were selected based on their regulatory significance and the availability of analytical methods and standards. Dieldrin and aldrin are on Florida's watch list, and lindane and atrazine are included in Arizona's Numeric Aquifer Water Quality Standards. Diazinon and chlorpyrifos were included because they are reported at no extra cost as part of the analytical suite for dieldrin, aldrin, lindane, and atrazine.

3.9 PATHOGEN INDICATORS

Further knowledge on pathogen lifespan underground is desired. Pathogens were chosen that represent bacteria (total and fecal coliforms), protozoa (*Cryptosporidium* and *Giardia*), and

viruses (coliphage). These indicators were also chosen based on their having established techniques and common occurrence. While likely to show variable results, heterotrophic plate count (HPC) was chosen because it is an affordable test that reflects microbial growth potential.

3.10 ENDOCRINE DISRUPTORS AND PHARMACEUTICAL AND PERSONAL CARE PRODUCTS

EDCs and pharmaceutical and personal care products (PPCPs) span many chemical properties, categories, and classifications but are grouped here based on their potential effects on human health and their being exclusive to anthropogenic sources. Given the multitude of EDCs and PPCPs that are considered compounds of emerging concern and thus could have been selected for observation in this study, the chemicals in this category were selected to represent various physical characteristics that could reveal removal mechanisms in the aquifer.

EDCs and PPCPs were sorted based on compound class, such as analgesic, antibiotic, or hormone. From each class, compounds representing various molecular weights (MW) and octanol-water partitioning coefficients (K_{ow}) were selected. K_{ow} represents the ratio under controlled conditions at which a constituent is partitioned to octanol versus water. It has a linear empirical relationship with the organic carbon partitioning coefficient, K_{oc} , and thus indicates the tendency of a compound to sorb to particulate matter. Higher log K_{ow} values indicate a greater likelihood that the contaminant will be removed from solution via adsorption to organic particles in the aquifer.

The partitioning behavior of an organic compound depends significantly on whether it exists in an ionized or neutral state. Therefore, the acid dissociation constant (K_a) was considered where available. Measurements of this physical property do not exist for many of the target compounds; however, they can be predicted using modeling software. K_a describes a compound's tendency to donate a proton to solution and thus be charged or neutral at a given pH. The neutral form of an organic acid is expected to sorb to particulate matter to a higher degree than the ionized. Thus, if an organic compound has a pK_a above the range of pH in natural waters, it can be expected to be dissociated and less likely to sorb to particulate matter. The speciation of an organic compound also affects its solubility, toxicity, and oxidation kinetics.

Some compounds that were filtered out based on the property sort were added back to the target EDC and PPCP list to address specific concerns. These include progesterone, testosterone, and androstenedione, which were added because research has indicated that removal efficiencies for ketone hormones differ from those of phenolic hormones (i.e., estradiol, estrone, and ethynylestradiol) (Snyder et al., 2005). DEET was added due to increasing accounts of its occurrence in drinking water (Thacker, 2004). Finally, caffeine was included for its (arguable) use as an anthropogenic marker of wastewater. Caffeine is a challenging marker, since it is ubiquitous in blanks and rapidly or easily removed by wastewater treatment plants, but the ability to analyze it and its frequency of occurrence made it suitable for the target list.

Compounds automatically reported as part of existing analytical suites were also included, as they were available for no extra cost. These included trimethoprim, fluoxetine, pentoxifylline, dilantin, tri(2-chloroethyl) phosphate (TCEP), diazepam, oxybenzone, estriol, ethynylestradiol, naproxen, diclofenac, and gemfibrozil.

Table 3.3 presents the EDCs and PPCPs chosen for study and their associated K_{ow} and molecular weights.

Table 3.3. Selected EDCs and PPCPs in Order of Increasing K_{ow}

Constituent	Use	log K_{ow}	pK _a	MW
Iopromide	X-ray contrast media	-2.05	10.2	791
Caffeine	Stimulant	-0.07	10.4	194
Acetaminophen	Analgesic	0.46	9.4	152
Meprobamate	Antianxiety	0.70	10.9	218
Sulfamethoxazole	Antibiotic	0.89	2.66	253
Hydrocodone	Painkiller	2.16	7.32	299
DEET	Mosquito repellent, industrial	2.18	0.67	191
Carbamazepine	Antiseizure medicine	2.45	0.37	236
Atrazine	Herbicide	2.61	1.7	215
Androstenedione	Androgen hormone	2.75	NA ^a	286
Erythromycin	Antibiotic	3.06	8.88	734
Estrone	Estrogen hormone	3.13	9.43	270
Bisphenol A	Plasticizer	3.32	9.59–11.3	228
Testosterone	Androgen hormone	3.32	NA	288
Progesterone	Estrogen hormone	3.87	NA	314
Ibuprofen	Analgesic, anti-inflammatory	3.97	4.15	206
17 β -Estradiol	Estrogen hormone	4.01	10.4	272
Triclosan	Antimicrobial	4.76	7.98	290
Nonylphenol	Surfactant degradation product	3.28–4.77	10.7	220
Chlorpyrifos	Organochlorine pesticide	4.96	NA	351
Butylated hydroxy toluene	Antioxidant	5.10	NA	220
Fluoranthene	Polycyclic aromatic hydrocarbon	5.16	NA	202

^aNA, not available.

Table 3.4 provides a summary of many of the target compounds' expected degradability characteristics in common wastewater treatment plant and environmental processes. This table shows the potential for attenuation due to chlorine and chloramine oxidation, biodegradation, photolysis, and carbon binding. It is important to note that these predictions are generalities based on previous studies conducted by team members (Snyder et al., 2003, 2004b, 2006; Westerhoff et al., 2005; Yoon et al., 2003a, 2003b). Carbon binding is offered as a preliminary indicator of potential adsorption during ASR storage, based upon experience in other applications above ground. To the extent that these processes are conducted effectively during wastewater treatment, the reclaimed water being recharged subsequently into the ASR wells may be expected to have reduced concentrations of these microcontaminants, assuming their presence in the untreated wastewater flow stream. These may potentially sorb to organic material in the near-well zone and desorb or mobilize on onset of recovery. Sorption helps increase residence time and hence biodegradation in an aquifer but does not necessarily provide a sustainable removal process on its own (Dillon and Pavelic, 1996).

Table 3.4. Removal Potential for Target Compounds

Compound	Biodegradation	Chlorine	Chloramine	Photolysis	Carbon
Androstenedione	NE ^a	Poor	Poor	Poor	Good
BDE #28	Poor	NE	NE	NE	Good
BDE #47	Poor	NE	NE	NE	Good
Bisphenol A	Moderate	Good	Good	Moderate	Moderate
Caffeine	Good	Poor	Poor	Poor	Moderate
Carbamazepine	Moderate	Poor	Poor	Poor	Moderate
Chlorate	Poor	Poor	Poor	Poor	Poor
Chlorpyrifos	NE	NE	NE	NE	NE
DEET	Moderate	Poor	Poor	Poor	Moderate
Dilantin	Moderate	Poor	Poor	Poor	Poor
Erythromycin-H2O	Poor	Good	Poor	Poor	Moderate
Estradiol	Good	Good	Good	Poor	Good
Estrone	Good	Good	Good	Poor	Good
Fluoranthene	NE	Poor	Poor	NE	Good
Gemfibrozil	Good	Moderate	Poor	Poor	Moderate
Hydrocodone	Moderate	Good	Moderate	Poor	Moderate
Ibuprofen	Good	Poor	Poor	Poor	Poor
Meprobamate	Moderate	Poor	Poor	Poor	Poor
Naproxen	Moderate	Good	Poor	Poor	Moderate
NDMA	NE	NE	NE	NE	Moderate
Nonylphenol	Moderate	Good	Good	Moderate	Good
Pentoxifylline	Poor	Moderate	Poor	Poor	Moderate
Perchlorate	Poor	Poor	Poor	Poor	Poor
Sulfamethoxazole	Poor	Good	Poor	Moderate	Poor
TCEP	Moderate	Poor	Poor	Poor	Moderate
Triclosan	Poor	Good	Good	Moderate	Good

^aNE, not evaluated.

Photolysis is included in Table 3.4, even though it would not occur during ASR storage underground. However, at some ASR sites it may be a useful part of the overall treatment process, since a portion of the pretreatment may occur in lagoons or ponds where photolysis would occur.

CHAPTER 4

SAMPLING SITES AND ANALYTICAL PLANS

Four reclaimed water ASR facilities were selected and agreed to participate in this study's sampling program. The study sites were:

- Chandler, AZ, Tumbleweed Recharge Facility
- Englewood, FL, South Regional Wastewater Treatment Plant
- Manatee County, FL, Southwest Water Reclamation Facility
- Bolivar, Australia, Bolivar Water Reclamation Plant

Comprehensive descriptions of these four facilities are provided below. Table 4.1 provides a summary of the site characteristics.

Table 4.1. Summary of Site Characteristics

ASR Site Attribute	Chandler, AZ	Englewood, FL	Manatee, FL	Bolivar, Australia
Redox Status	Undetermined	Probably reduced	Probably reduced	Denitrifying
Mineralogy	Alluvium	Carbonate	Carbonate	Calcite, quartz
Confinement	Confined	Confined	Confined	Confined
Salinity, TDS, mg/L	1000	20,000	2000	2100
Groundwater Temp, °C	NA ^a	NA	26	22–26
Recharge Water Temp, °C	24	26–28	24	7–18
Pretreatment before ASR	NdeN, extended aeration, tertiary filters, UV	Aeration, filtration, chlorination	Aeration, filtration, chlorination	Activated sludge, aeration lagoons, DAF/F, ^b chlorination
TOC in Injectant, mg/L	7.4	9.6	10.6	12–20
Residence Time in Aquifer, mo	0.5–5	0.5–2	0.5	0–11
Prior Use of ASR Site	2004–present	2001–present	None	1999–present
Storage Volume, MG	300	700	10	50
Travel Time to Observation Wells, days	14	Not applicable	Not applicable	1–2 and 90–120

^aNA, not available.

^bDAF/F, dissolved air flotation filtration.

4.1 SAMPLING SITES

4.1.1 Chandler, AZ, Tumbleweed Recharge Facility

4.1.1.1 Background

In 1996, the City of Chandler constructed the Tumbleweed Recharge Facility in Tumbleweed Park to conserve 100% of the reclaimed water. Initially, vadose zone wells were used to inject reclaimed water into the ground above the water table. The reclaimed water was then treated further by ground filtration in the vadose zone before it reached the upper aquifer water table. Ultimately, the vadose wells were found to be inadequate due to clogging of pores and the occurrence of fungal growth in the cloth materials of the wells. This technology was abandoned due to these challenges, and ASR technology was adopted due to its ability to allow the facility to purge the system three times a day for 20 min each.

4.1.1.2 Reclaimed Water Source

Reclaimed water injected into these wells originates from the Airport Reclamation Facility, a 5-mgd water reclamation plant built in 1999 and expanded to 10 mgd in 2003. Specific water reclamation facility processes include influent pumping and screening, biological nitrogen removal (NdeN) with extended aeration basins, secondary clarifiers, tertiary filters, UV disinfection (low intensity, low pressure, open channel type), and effluent pumping. The plant, currently rated at 10 mgd and being expanded to 15 mgd, is designed to meet Arizona Class A+ reclaimed water quality standards. The 2004 operating data showed plant effluent average turbidity was 0.5 NTU, and average TSS was 1.67 mg/L. The average effluent nitrate was 1.6 mg/L with a minimum nitrate concentration of 0.4 mg/L. Note that for the current expansion, it is anticipated that the UV system will be replaced with hypochlorite, likely the on-site generation type.

4.1.1.3 Wells

The Tumbleweed Facility consists of five wells drilled to a depth of 350 ft and has an annual average permitted recharge capacity of 5 mgd of tertiary treated effluent. Tumbleweed ASR well nos. 4 and 5 consist of a 30-in. carbon steel surface casing extending to a depth of 39 ft below the surface and a 20-in. stainless steel inner casing extending to a depth 350 ft. A 2 3/8-in. sounding tube extends from the ground surface to 140 ft below grade, with the lower 80 ft perforated with 0.020-in. slots. At 45 ft, a bentonite seal extends to 50 ft below the ground surface. At 60 ft below the surface, a Colorado silica sand filter pack begins and extends to 350 ft. The surface casing is cemented to 45 ft. At 350 ft, a stainless steel bottom plate terminates the borehole. Observation well 2A is screened from 100–300 ft. The ASR well has a louvered stainless steel screen, and the observation well has a carbon steel casing and screen.

During the summer months, recharge flow currently is about 2–5 mgd into all five wells. During winter months, recharge flow is 7–10 mgd. Local demand for reuse water is increasing each year, and so the amount of water available for recharge is declining each year; the amount required to meet system demands during summer months is approaching a point where previously stored water will need to be recovered from the ASR wellfield. It is anticipated that all reclaimed water stored will be recovered. The permitted annual storage volume is 5600 acre-ft, which is equivalent to an average of 5.0 mgd.

4.1.1.4 ASR Storage Zone

The ASR storage zone is in an upper alluvial unit (UAU) and is recharged through both vadose zone wells and ASR wells. Underlying the UAU is the middle alluvial unit (MAU), which is used as a drinking water supply in Chandler. The UAU is comprised of sand, silt, and clay, with distinct lenses of gravel, cobbles, and boulders, and is unconsolidated. The MAU is finer grained and contains more clay than the UAU. The clay is sticky and harder than in the UAU. Gravel, cobbles, and boulders are not typically present in the MAU; however, a calcium carbonate crust is present. The contact between the two units is uncomformable and occurs at depths between 300 and 490 ft, varying over the surrounding area.

Horizontal hydraulic conductivity of the UAU is estimated at 150 ft/day based on pumping tests conducted at ASR wells 1, 2, and 3. Transmissivity is about 251,000 gal/day/ft (gpd/ft). The UAU has been subdivided vertically into three layers, based on differences in head indicating changes in aquifer hydraulics characteristics. For all three layers, the specific yield is estimated at 0.08 and the porosity is estimated at 0.15. The upper and lower layers are about 150 ft thick, while the middle layer is about 20 ft. The upper and lower layers have an estimated vertical hydraulic conductivity of 7.5 ft/day, while the middle layer vertical hydraulic conductivity is estimated at 0.0085 ft/day.

Plugging has been observed in the ASR wells and has been attributed to a variety of causes. These include entrained air and gas binding, TSS, biological growth, geochemical reactions, and particle rearrangement of soils adjacent to the well. To control such plugging, each well is backflushed to waste for 30 min, three times daily, at a rate of 2 mgd. Relative to other operating ASR sites, this backflushing frequency is considered quite high.

4.1.1.5 Monitoring

Compliance monitoring is required at two points: the first point is located 500 ft west of the northwest property boundary, and the second is situated on the northeast corner of the property boundary. Permitting for these wells is provided through the Arizona Department of Water Resources and the Arizona Department of Environmental Quality. In addition to daily measurements of flow, monthly measurements of nitrogen species, major cations, and anions are required. Annual measurements are required for metals and volatile organic compounds.

4.1.2 Englewood, FL, South Regional Wastewater Treatment Plant

4.1.2.1 Background

The South Regional Wastewater Treatment Plant, owned and operated by the Englewood Water District, is located in northwest Charlotte County, FL. This facility, consisting of twin advanced secondary treatment units, produces 2.2 mgd of reclaimed water and is currently being expanded to 3 mgd of production capacity. Reclaimed water was initially stored in on-site reuse ponds before being distributed for nonagricultural irrigation of city property and golf courses. The Englewood Water District began investigating the feasibility of aquifer storage and recovery in December 1997 and applied to the Florida Department of Environmental Protection (FDEP) and the Southwest Florida Water Management District (SWFWMD) for their ASR test well construction permits in March 1998. An ASR test well construction permit was issued by FDEP in June 1999, and well construction permits were issued by SWFWMD in January 2000. Construction of the ASR test well system and monitoring network was initiated in January 2000 and was completed in April 2000. A comprehensive engineering report was submitted to FDEP in July 2000 requesting

authorization to commence ASR cycle testing. Englewood Water District received authorization to cycle test, which was initiated in July 2001 and is currently ongoing.

4.1.2.2 Reclaimed Water Source

The South Regional Wastewater Treatment Plant is a 3.0-mgd complete mix activated sludge process domestic wastewater treatment plant. The facility consists of flow equalization, influent screening, aeration, secondary clarification, filtration, chlorination, and aerobic holding and dewatering of residuals with centrifuges.

4.1.2.3 Wells

Facilities include one ASR well, cased with carbon steel casing, and three adjacent observation wells, one of which is in the storage zone, one in an overlying aquifer, and one in the surficial aquifer. The storage zone observation well is 400 ft from the ASR well and is cased with polyvinyl chloride. An additional off-site observation well is located at a distance of approximately 2200 ft and monitors a shallower producing interval at a depth of 280–320 ft.

In June 1999, Englewood Water District received a permit for the construction of the following facilities at the South Regional Wastewater Treatment Plant: one Class V ASR test injection well (ASRTP-1), one 6-in. storage zone monitoring well (approximately 400 ft from the ASR well), one 6-in. intermediate monitoring well (approximately 2200 ft from the ASR well), and one 6-in. shallow monitoring well (approximately 150 ft from the ASR well). The basic well design consisted of a 16-in. diameter injection well cased to a depth of 512 ft and an open hole to 700 ft. This ASR well was designed to inject a maximum of 1 mgd of reclaimed water.

During testing, the native water quality in the storage zone was found to be saline. Below 300 ft in depth, the concentration of background TDS was estimated to be greater than 10,000 mg/L. The background TDS concentration in the reclaimed water ASR well (storage zone) was determined to be approximately 19,000 mg/L. The exceptionally poor water quality led to problems during drilling (i.e., no acceptable location was available to discharge the saltwater produced from the borehole), resulting in closed-circulation drilling throughout most of the process.

ASR cycle testing was initiated in July 2001 at recharge rates ranging from 0.25–1.0 mgd. All water recharged met primary and secondary drinking water standards with the exception of color, which required a Water Quality Criteria Exemption from FDEP. Recharge of the well is continuing on an as-needed basis. Additional recharge and recovery cycles are scheduled for the end of 2006, followed by application for a reclaimed water ASR well operating permit.

At least 650 MG have been recharged to date, with limited recovery due to low demand for reclaimed water plus extended wet weather conditions. This is a net recharge volume, including reductions in storage occurring during recovery periods. Four ASR test cycles were conducted between 2001 and 2003, recovering a total of about 120 MG. Recharge then continued from 2003 until 2004. As demand for reclaimed water increases in the Englewood Water District service area, it is anticipated that less water will flow to the ASR well and more water will be recovered.

4.1.2.4 ASR Storage Zone

The ASR storage zone is constructed in the upper Floridan Aquifer system, which is a limestone, artesian aquifer. The ambient groundwater quality in this aquifer is brackish, with

a TDS concentration of about 19,350 mg/L in the ASR well and 22,100 mg/L in the storage zone monitor well 400 ft away, as measured upon completion of well construction and baseline testing. Aquifer transmissivity, based on step-drawdown pumping tests, is estimated at 35,000 gpd/ft. The static water level is 5 ft above land surface.

4.1.3 Manatee County, FL, Southwest Water Reclamation Facility

4.1.3.1 Background

The Manatee Southwest Water Reclamation Facility provides secondary treatment, filtration, and disinfection of reclaimed water without any volume restrictions. However, land limitations prevent the construction of additional lakes to store reclaimed water for use during the dry season. Reclaimed water produced by this facility is used for residential and agricultural irrigation through the Manatee Agricultural Reuse System.

Manatee County is attempting to meet high residential and agricultural demands for reclaimed water. In order to provide sufficient water for agricultural and residential irrigation in the service area, water must be saved during the wet season for use in the dry season. Presently, storage lakes in the system are not sufficient to provide enough reuse water in the dry season. The County anticipates that reclaimed water ASR will provide an increase in irrigation water supplies. Cycle testing was stopped in July 2005 by FDEP due to operational issues.

4.1.3.2 Reclaimed Water Source

This ASR facility was under construction for several years at the Manatee County Southwest Wastewater Treatment Plant but has encountered several prolonged delays prior to and during cycle testing. The plant has a 3-month average daily flow of 18 mgd and is an activated sludge domestic advanced secondary wastewater treatment plant. Treatment processes at this facility include a headworks structure, degritting system, primary clarifiers, aeration basins, secondary clarifiers, traveling bridge filter units, and chlorine contact basins with a gaseous chlorine feed system. The plant also includes a pump station for the deep well injection and the reuse systems and a refiltration system for the stored reclaimed water.

4.1.3.3 Wells

The ASR system consists of three individual wells, including one ASR well and two observation wells, one of which is a storage zone observation well and the other at an overlying producing interval. The ASR test production well consists of a 16-in. carbon steel casing set to a depth of 510 ft with the open hole section extending to a depth of 690 ft. This open hole interval reflects the ASR storage zone at the Manatee County Southwest ASR test site. Two monitoring wells were constructed at the project site. The first was constructed to reach the storage zone, and the second was constructed to reach the first overlying intermediate aquifer system (350–400 ft below land surface). The storage zone monitor well also penetrates the storage zone and is completed with an 8-in.-diameter carbon steel casing, also set to 510 ft with open hole extending to 690 ft. The overlying shallower monitor well consists of an 8-in. black steel casing set to 350 ft with open hole extending to approximately 400 ft.

4.1.3.4 ASR Storage Zone

This is an artesian aquifer with an ambient TDS concentration of 2000 mg/L. The storage zone is the Suwannee Limestone of the upper Floridan Aquifer. Both TDS and chloride concentrations would normally be utilized as natural tracers for differentiating reclaimed water from ambient groundwater; however, as discussed below, this was complicated by the high and variable salinity of the reclaimed water. Transmissivity of this aquifer is about 60,000 gpd/ft. The distance from the ASR well to the storage zone observation well is 200 ft. The estimated theoretical travel time to the observation well is about 21 days at a flow rate of 2 mgd.

4.1.4 Bolivar, SA, Australia, Bolivar Water Reclamation Plant

4.1.4.1 Background

In 1999, the Bolivar Water Reclamation Plant, which serves the Adelaide metropolitan area and the Virginia Reclaimed Water Pipeline, was commissioned to provide the reuse of up to 15.9 mgd (60 million L [ML]/day) of reclaimed water for irrigation and horticulture on the Northern Adelaide Plains. As a result, crop irrigation expanded, the stress on overexploited groundwater supplies decreased, and the discharge of nutrient-rich effluent to sensitive marine environments was reduced. Reclaimed water ASR is being considered as a means of expanding the existing reuse capabilities of the Bolivar Water Reclamation Plant.

The Bolivar site, near Adelaide, Australia, includes 1 ASR well and 16 observation wells, 2 of which were utilized for the WRF sampling program in addition to the ASR well.

4.1.4.2 Reclaimed Water Source

Reclaimed water used in the testing program is treated by the Bolivar Wastewater Treatment Plant (initially with trickling filters and, since 2001, activated sludge) and stored in aeration lagoons and then reclaimed via dissolved air flotation and filtration followed by chlorination prior to injection. At this plant, activated sludge reactors were installed in January 2001 to replace secondary treatment by trickling filters. The treated water was stored in stabilization ponds before treatment in a water reclamation plant involving coagulation and dissolved air flotation filtration followed by disinfection (chlorination). Water was then discharged to an open balancing storage before being pumped to the ASR site via the Virginia Pipeline Scheme, which supplies reclaimed water for horticulture on the northern Adelaide Plains (Kracman et al., 2000).

4.1.4.3 Wells

The ASR well is cased to 103 m and is a completed open hole to 160 m. Samples were also collected at an observation well located 4 m from the ASR well, fully penetrating the storage zone between 102 and 160 m, and at a second observation well located 50 m from the ASR well which penetrated a discrete layer of higher hydraulic conductivity within the aquifer (134–139 m). The ASR well is cased with fiber-reinforced plastic, and the 4-m (no. 19450) and 50-m (no. 19181) wells are cased with polyvinyl chloride.

4.1.4.4 ASR Storage Zone

The ASR storage zone is a confined limestone aquifer containing primarily calcite and quartz. The ambient groundwater TDS concentration is 2100 mg/L. In the first three ASR cycles, 137 MG (519 ML) of reclaimed water from the Bolivar Water Reclamation Plant was injected into the anaerobic, calcareous aquifer at the Bolivar ASR research site, and 98 MG (370 ML) was recovered. The reclaimed water used for this work contained relatively high concentrations of organic carbon (~16 mg of dissolved organic carbon/L), which presents a

unique opportunity to evaluate subsurface, microbially mediated attenuation of contaminants. The dominant water quality reactions observed to occur during storage of the reclaimed water ASR included the reduction of dissolved oxygen and nitrate coupled with the oxidation of organic matter. These reactions generated biomass and caused the dissolution of the calcite matrix.

4.2 SAMPLING PLANS

This study was designed to investigate the variables of aquifer characteristics, storage time, travel distance, recharge water quality, and operational history. A sampling plan was developed for each of the four testing sites to capture unique environmental and operational conditions. The plans designated the time and location of sampling with respect to recharge, storage, and recovery practice. Sampling events were integrated with planned operating and monitoring activities where possible. Table 4.2 summarizes the sampling plans for all sites. The specific dates and volumes of flow occurring in or out of the well at the time of sampling are available in the raw data set in Appendix C.

Table 4.2. Sampling Plans

Location	Event	Sampling Location ^a	Underground Residence Time ^b	Estimated Travel Distance	Parameters
Chandler	Recharge	ASRW MW	NA ^c	NA	Full suite
	Recovery	ASRW	2 mo	Negligible	Full suite
	Recovery	ASRW MW	3 mo	200 ft	Previous detects
	Recovery	ASRW	5 mo	500 ft	Previous detects
Englewood	Recharge	ASRW	NA	NA	Full suite
	Recovery	ASRW	2 wks	Negligible	Full suite
	Recovery	ASRW	1 mo	Negligible	Full suite
Manatee	Background	ASRW	NA	NA	Full suite
	Recharge	ASRW	NA	NA	Full suite
	Recovery	ASRW	2 wks	Negligible	Full suite
Bolivar	Recharge	ASRW	NA	NA	Full suite
	Storage	ASRW	4 mo	Negligible	Full suite
		4-m MW	4 mo	13 ft (4 m)	Full suite
		50-m MW	7 mo	164 ft (50 m)	Full suite
	Recovery	ASRW	13 mo	70 ft (21 m)	Full suite
		4-m MW	13 mo	70 ft (21 m)	Full suite
		50-m MW	16 mo	170 ft (54 m)	Full suite
	Recovery	ASRW	17 mo	150 ft (45 m)	Full suite
		4-m MW	17 mo	150 ft (45 m)	Full suite
		50-m MW	>19 mo	220 ft (67 m).	Full suite

^aASRW, aquifer storage recovery well; MW, monitoring well.

^bApproximated assuming minimal mixing in aquifer, i.e., first water injected was last water recovered.

^cNA, not applicable.

4.2.1 Chandler, AZ, Tumbleweed Recharge Facility

Sampling for the Chandler study was conducted at ASR well 5, which began operations in early 2004, and also at observation well 2A. The direction of regional groundwater flow is to the northwest, and so the monitor well is immediately downgradient of the ASR well. The lateral distance between the two wells is about 300 ft, and travel time during recharge has been estimated by Chandler operations staff at about 14 days.

In an effort to confirm this travel time, a tracer study was conducted between ASR well 5 and observation well 2A. At the final stages of several months of recharge, 2000 gal of a 15,000-mg/L CaCl₂ solution was added to ASR well 5. Daily conductivity readings were then taken at the observation well for 1 month to estimate the rate of movement of the recharge water

between the two wells. The conductivity at the observation well did not increase within the 4 weeks in which daily measurements were taken. These data can be found in Appendix C.

Following the tracer study, six samples were collected and analyzed for the full parameter list during four sampling events. On May 3, 2005, a sample was collected from well 5 while it was recharging at a rate of 1.3 mgd. A total of 310 MG of reclaimed water had been recharged into the well by this date, which was at the end of a recharge period. A sample was collected at the same time from the observation well. Comparison of water quality data from the two wells on this date was intended to provide an indication of any changes in water quality due to flow through the aquifer and due to 2 weeks' travel time. ASR well 5 (and the remaining ASR wells) then sat idle for 2 months. On July 6, 2005, recovery commenced from ASR well 5, and a sample was collected from that well on day 1. This sample represents water that sat in the aquifer around the well for 2 months but had not traveled any significant distance underground. Two weeks later, on July 22, 2005, samples were collected from both the ASR well and the observation well. On Aug. 17, 2005, after 6 weeks of recovery, a final sample was collected from the ASR well. The final sample represents water that had been underground for about 5 months and had traveled through the aquifer, on average, more than 500 ft.

4.2.2 Englewood Water District, FL, South Regional Wastewater Treatment Plant

For the WRF sampling program, three samples were to have been collected during three sampling events. The WRF sampling plans had to be modified at the last minute due to operational constraints. The planned 1-week storage period between recharge and recovery was reduced to 1 day. The recharge water sample was collected on May 18 from a representative reclaimed water flow stream at the wastewater treatment plant, 2 days after the end of recharge. The first and second recovered water samples were collected after 1 and 2 weeks of recovery, as planned. Operations were as follows:

Date	Recharge, MG	Recovery, MG
3/25–5/9	0	0
5/10–5/16	4	0
5/17–5/31	0	6
6/1–6/30	0	12

One sample was collected from the ASR well on May 25 at the end of 1 week of recovery. A second sample was collected from the ASR well on May 31 after 2 weeks of recovery. The recovery flow rate averaged 0.43 mgd. Cumulative storage was 639 MG on June 30.

Independent of the WRF sampling program, a sample was collected by Englewood Water District on June 22 for analysis of primary and secondary drinking water standards. Those analytical results have been provided to the Carollo project team. At the time of sampling, the TDS and chloride concentrations of the recovered water were 704 and 244 mg/L, respectively, indicating continued recovery of fresh water with insignificant blending with surrounding ambient brackish water in the aquifer.

The short storage and recovery period was originally selected based on some concern that extended storage duration or recovery pumping might cause increased salinity due to density

stratification between the fresh recharge water and the brackish ambient water in the aquifer, as well as the considerable thickness of the storage zone. For the same reason, sampling was conducted only in the ASR well, not in the storage zone observation well. Conservative constituents, such as chloride and TDS, indicated that water quality remained fresh during the short period sampled for this program.

The first sample collected during recovery (May 25) represented water that had traveled in the aquifer adjacent to the ASR well for about 2 weeks, initially away from the well during recharge and then back toward the well during recovery. The second sample represented water that had been in the aquifer for probably about 2 months and had traveled a short distance away from and then back towards the ASR well. Considering the 188-ft thickness of the storage zone and the low recharge rate, it is probable that the travel distance was quite small, probably a few tens of feet.

4.2.3 Manatee County, FL, Southwest Water Reclamation Facility

WRF sampling included a background sample pumped from the storage zone. This was obtained on Dec. 1, 2004, prior to any recharge activities. Cycle 1 included recharge of 10 MG during 5 days of recharge at 2 mgd, followed by 1 day of storage, followed by 10 MG of recovery. For the WRF program, a sample was collected from the ASR well on Dec. 14, 2004, during cycle 1 recharge and also on Dec. 28, 2004, during cycle 1 recovery. These were midpoints of recharge and recovery, each at flow rates of 2 mgd. Cumulative volumes stored and recovered for each sample were 5 MG. During cycle 1, no samples were collected from the observation well.

The background sample from the aquifer was obtained only at this site, since the other three WRF sites had already experienced some recharge activities. The purpose of obtaining this sample was to verify, for at least one site, whether any of the reclaimed water constituents of interest for the WRF project were present in the ambient groundwater. The remaining two samples would be representative of recharge water and water recovered after 2 weeks of subsurface storage.

Planned sampling for the WRF sampling program included 10 samples collected during seven sampling events in cycles 1 and 3. However, an extended delay occurred following completion of cycle 2. Due to time constraints of the WRF sampling program, the decision was made to complete the data analysis without the cycle 3 data from the ASR well and the storage zone observation well. Resumption of cycle testing is anticipated during April 2006; however, there are currently no plans to obtain and analyze the WRF samples.

4.2.4 Bolivar, SA, Australia, Bolivar Water Reclamation Plant

Prior to the WRF sampling program, two ASR test cycles had been completed at this site and recharge for a third cycle was almost completed, recharging 519,000 m³ (137 MG) between Oct. 11, 1999, and May 28, 2004. Of this total recharge volume, about 243,000 m³ (64 MG) had been recovered prior to the start of the WRF sampling program, leaving 276,000 m³ (73 MG) in storage. The WRF sampling program occurred during the third cycle.

The third cycle included recharge of 154,500 m³ (41 MG) during 169 days (Dec. 11, 2003, to May 28, 2004). This was followed by storage for 319 days (May 28, 2004, to April 22, 2005) and then by recovery of 123,400 m³ (33 MG) during 90 days (Apr. 22, 2005, to July 21, 2005).

A sample of the recharge water was collected on May 6, 2004. This was 22 days prior to the end of cycle 3 recharge. On Sept. 28, 2004, after 4 months of storage, samples were collected from the ASR well and both observation wells. On May 12, 2005, 20 days into recovery, another set of samples was collected from all three wells. On July 21, 2005, at the end of the recovery period, another set of samples was collected. This was after 90 days of recovery.

The Bolivar data set provides the opportunity to evaluate water quality changes during long storage periods, namely 4 months and up to 13 and 17 months. Comparison of the data from all three wells for each sampling event provides the opportunity to evaluate changes in water quality due to subsurface movement, as opposed to just storage time.

Table 4.2, above, summarizes the sampling plan for all sites. The specific dates and amount of flow occurring in or out of the well at the time of sampling are available in the raw data set in Appendix C.

4.3 ANALYTICAL METHODS

All samples collected were grab samples taken directly from the liquids flow stream into or out of the ASR well and from the sampling tap at the monitoring wells. These were contained in the appropriate bottle, sometimes containing preservatives, for each analytical test. Where possible, dissolved oxygen and ORP were measured with field probes at the sampling point. Remaining general parameters, such as alkalinity, were measured by each facility's own lab or regularly contracted lab. The nearest laboratory capable of *Cryptosporidium* and *Giardia* analyses was contracted for each site for the microbiological parameters.

All samples being analyzed for PPCPs and EDCs were sent to the Southern Nevada Water Authority. Travel blanks were included with the first shipment of these samples from each site for the Englewood, Manatee, and Chandler sites. Travel blanks were included with all shipments from the Bolivar, Australia, site due to the longer shipping distance.

Laboratories used EPA Standard Method techniques or similar standard methods in Australia. The specific method used by each site for each parameter is listed in Appendix B. All nondetects were recorded in the raw data set (Appendix C) as being less than the specific method detection limit (MDL). The Southern Nevada Water Authority used novel analytical techniques with substantial quality assurance—quality control. Information on the development, validation, and implementation of these methods can be found in Appendix B.

CHAPTER 5

SAMPLING RESULTS

5.1 INTRODUCTION

This chapter presents the results of the sampling program for each parameter category by site. Appendix C contains the water quality data for each site and for each constituent. Changes were observed with respect to both storage time and travel distance in the cases where monitoring wells were available. Comments are included for those constituents where at least a 20% change in concentration occurred. Changes less than 20% were considered not significant. Constituents that were not detected or not found to have any experimental significance at a particular site are not discussed for that site.

In general, insufficient data were obtained to justify standard statistical analysis for each site. Instead, a broad survey was conducted that compared limited data from four sites. This reflected the planned scope and budget of the project. Many of the conclusions may, therefore, be considered qualitative, based upon best judgment. Patterns evident in the data, or lack thereof, are noted and provide a basis for future comparisons with data from other comparable site investigations and also for planning subsequent research activities. Future projects may elect to focus data collection at a single reclaimed water ASR site, obtaining a sufficient number of samples at that site to support statistically valid conclusions but thereby foregoing the opportunity to compare data from different sites with a variety of hydrogeologic and water quality considerations. Of particular importance is the observation from this study that numerous samples would probably be needed to document the absence or presence of short-term (hourly) variability in reclaimed water quality prior to recharge at a particular site. This would entail great expense; however, until such a study is completed there would be no way to definitively characterize changes in recovered water quality occurring during ASR storage compared to a single grab sample of recharge water obtained during recharge. Obtaining statistically significant results for the slate of constituents developed for this project will probably require focusing a large budget at a single, hopefully representative site, augmented by passive (adsorption) samplers, such as those employed by Komarova et al. (2006), and laboratory column studies using spiked influent (e.g., Ying et al., 2003).

The following unique site features were considered throughout the analysis.

The Chandler, AZ, site underwent a salt tracer study at the beginning of sampling. Salt was injected into the ASR well to measure its travel time to the nearby monitoring well. While conductivity at the monitoring well never increased, spikes in conductivity, TDS, and chloride were observed in the final sample of recovered water from the ASR well. This suggested that the salt traveled in a different direction from the monitoring well but was later recovered after sufficient pumping.

The Englewood, FL, site's recharge water sample may not have been representative of the water recovered after storage. The recovered water was stored during mid-March, slightly more than 2 months prior to the recharge water sample. While the recharge water came from the same source in both instances, seasonal factors may have resulted in different effluent quality. For this site, greater weight is placed upon comparisons of the two recovered water

samples, which represent a known 2-week storage period of similar source water. Key distinguishing features of this data set are (1) the relatively short storage period available to drive geochemical and microbial subsurface processes (2 weeks and 2 months, respectively, for the two samples obtained during recovery), and (2) a very large cumulative volume of reclaimed wastewater (651 MG) has been stored at this site since 2001, greater than at any other sites. Any significant changes in water quality need to be considered with this in mind. It is also pertinent that the storage zone is highly brackish, with an ambient TDS concentration of around 20,000 mg/L.

The Manatee, FL, site was sampled during its first-ever injection phase. Prior to injection, a sample was taken of native groundwater. Because there would be known mixing of injected water and groundwater for at least the first few cycles of recharge, concentrations in recovered water were interpreted with respect to a mixing ratio established by TDS and boron concentrations. The recovered water sample was estimated to be a blend of 64–76% native groundwater and 24–36% reclaimed water, reflecting the relatively small volume of water recharged and the consequent substantial mixing in the aquifer.

At the Bolivar, Australia, site poorer quality, secondary wastewater previously had been injected into its aquifer. Thus, the recharge water sample collected at the start of the study period does not reflect the residual water characteristics, which included higher organic and nitrogen concentrations. Yet, the recharge water quality was more likely to be stable and representative at this site than the others, since the treated effluent has a long detention time in oxidation ponds prior to further treatment at the water reclamation plant. Mixing ratios with native groundwater were calculated for each sample by using chloride as a tracer, and mixing corrections were made for concentrations of other species for use in inferring degradation. It should also be noted that the storage period between the end of recharge and the beginning of recovery at Bolivar was much longer than at the other sites.

5.2 GENERAL CONSTITUENTS

As described in Chapter 3, the “general” constituents category refers to those compounds that describe the basic water chemistry (pH, redox potential, temperature, etc.) as well as prevalent natural water components, such as calcium and sodium. The trends described below are summarized in Table 5.1. Actual data for each constituent and for each site are provided in Appendix C. For some constituents, similar water quality responses were common to all four sites, while for others notable differences were evident. The same general format is followed for other classes of constituents in Tables 5.2 through 5.6.

5.2.1 Chandler, AZ

DO at the ASR well during recharge (8.3 mg/L) declined, but not as much as was expected during either 2 months of storage or movement through the aquifer to the monitoring well. The DO concentrations leveled out at approximately 5 mg/L, suggesting minimal microbial or geochemical activity or, perhaps more likely, a faulty measurement. Field measurements of DO were made with an Orion portable meter. It is not known whether a flow cell was used or whether the equipment had been calibrated. ORP measurements were made in the lab using method SM 2580, not in the field, and so the values were undoubtedly inaccurate and were dismissed from consideration.

pH values changed moderately, buffered by the high alkalinity. Of some interest is that the lowest pH (7.2) occurred at the beginning of recovery from the ASR well, consistent with microbial and/or geochemical activity around the well.

Table 5.1. Water Quality Changes Observed: General Constituents

Constituent	Chandler, AZ	Englewood, FL	Manatee, FL	Bolivar, Australia
Bicarbonate	Increased	Increased	No change	Increased
Calcium	Increased	Increased	No change	Increased
Chloride	No change	No change	No change	No change
Dissolved oxygen	Decreased	No change	Decreased	Decreased
Fluoride	Ambiguous	Increased	No data	Ambiguous
Magnesium	Increased	Ambiguous	No change	Ambiguous
pH	Decreased	No change	Increased	Ambiguous
Redox Potential	Data dismissed	Data dismissed	Decreased	Ambiguous
Sodium	Decreased	No change	No change	No change
TDS	No change	No change	No change	No change
Temperature	Seasonal variability	No change	No change	Seasonal variability
TOC	Decreased	Decreased	Decreased	Decreased
Turbidity	Ambiguous	Increased	Increased	Ambiguous

Bicarbonate in the recharge water increased from 132–204 mg/L during movement of the water from the ASR well to the monitoring well. It also increased from 132–164 mg/L during 2 months of storage at the ASR well. No significant change in bicarbonate occurred during 6 weeks of recovery at the ASR well. Calcium also increased at the ASR well during the recovery period, from 71–110 mg/L. It appears that some carbonate may be present in the storage zone mineralogy.

Chloride was detected in the range of 410–464 mg/L at the ASR and monitoring well except for the last sample during recovery (936 mg/L). This peak may have been a result of the salt slug that was added 3 months earlier that appeared to have migrated outside of the monitoring zone until sufficient recovery efforts drew it back in.

Fluoride showed some reduction in concentration due to storage, declining from 1.21–0.75 mg/L in 2 months, possibly due to adsorption onto calcium minerals in the aquifer. An increase in fluoride concentration after 6 weeks of recovery may have been due to desorption along the flow path back to the well during recovery or associated with the sodium chloride tracer, given that reclaimed water was used to create the salt solution.

Magnesium concentrations increased from 17–25 mg/L during movement of water from the ASR well to the monitoring well during recharge. They also varied with storage time, increasing from 17–26 mg/L at the ASR well during 2 months of storage.

The sodium concentration at the beginning of recovery from the ASR well was very high (550 mg/L), declining during recovery to 210 mg/L after 6 weeks. Considering the sodium chloride tracer addition at the monitoring well and the elevated chloride concentration, a higher sodium concentration might have been expected at the end of recovery at the ASR well. Possibly cation exchange occurred, exchanging sodium for calcium.

Varying between 21 and 28 °C, temperature showed seasonal variability, serving as a crude tracer. Water recovered during early summer after 6 weeks of storage was cooler than reclaimed water produced at the same time during early summer.

TOC in the recharge water (7.36 mg/L) declined from 7.36–1.85 mg/L during movement to the monitoring well and also declined to 2.94 mg/L at the ASR well during 2 months of storage. Subsequent declines in TOC were smaller, reaching 1.97 mg/L after 6 weeks. Such a TOC reduction, combined with the slight pH reduction at the beginning of recovery, suggests microbial activity near the well.

Turbidity values in the recharge water (0.42 NTU) may be compared with lower values (0.108–0.18 NTU) in the recovered water. The ASR well is constructed of a stainless steel louvered screen and therefore should generate little or no rust. Monitoring well values were elevated (1.86 and 0.873 NTU), probably reflecting their carbon steel construction and associated generation of rust.

5.2.2 Englewood, FL

While the DO measurements were taken in the field, the ORP analyses were conducted in a laboratory. Given exposure of the sample to oxygen during travel, the ORP results are invalid.

Bicarbonate increased slightly during 2 weeks of storage, from 158–180 mg/L, but did not increase further after 2 months of storage. During the same time period, the calcium concentration increased from 44–58 mg/L and then to 77 mg/L, suggesting some dissolution of limestone.

The TOC of the reclaimed water declined substantially. It was initially 9.58 mg/L, declining to 7.89 mg/L in 2 weeks and to 2.58 after 2 months. The decline of TOC and nutrients, combined with the strong indications of microbial activity, suggest that the ORP should have been reduced, along with the DO concentration.

5.2.3 Manatee, FL

Potential natural tracers for this site included chloride, TDS, and boron. However, chloride in the aquifer was 514 mg/L, while in the recharge water background sample it was 401 mg/L, which does not provide much difference on which to base conclusions regarding mixing. The boron concentration was measured at 0.06 mg/L in the groundwater and 0.27 mg/L in the recharge water. No supplemental data were available from the County regarding typical boron concentrations in the reclaimed water.

Considering TDS and boron as reasonable tracers, it appears that the recovery sample (12/28/04) represented a blend of between 64–76% ambient groundwater with 24–36% reclaimed water. Changes in water quality that varied significantly from this blend ratio would be indicative of subsurface microbial or geochemical reactions. For those constituents measured at nondetect levels, the blend ratio was calculated as a zero. This would introduce a small amount of bias into the resulting conclusions.

Significant departures from predicted concentrations in recovered water based upon the blend ratio were that pH, turbidity, and conductivity were higher than expected and DO and TOC were lower than expected, given mixing alone.

5.2.4 Bolivar, Australia

Chloride was considered the best natural tracer for this site, to distinguish changes in water quality due to blending with groundwater from those due to geochemical and microbial reactions. Calculations are shown in Appendix A, Table A3. In this suite of samples taken after 11 months storage and 3 months of recovery, chloride concentrations of 611, 715, and 502 mg/L were detected at the ASR, 4-m, and 50-m well, respectively. These indicated the percentages of reclaimed water in the final recovered water samples had fallen to 60%, 40%, and 80%, respectively. Note that the 50-m piezometer was screened over a 5-m interval, which was in a high-permeability layer that connected with the ASR well. The 4-m well, like the ASR well, fully penetrates the aquifer and is exposed to high- and low-permeability layers that increase the proportion of native groundwater diffusing from low-flow zones and accelerated by induced vertical flow of water in this well. A full explanation of the hydraulic behavior has been given by Pavelic et al. (2006b).

DO was 11.9 mg/L in the recharge water and at low levels in the ambient groundwater. At the ASR well after 4 months, the DO reading was 2.7 mg/L, which reflected entry of air into the sample. At the 4-m and 50-m monitoring wells, DO levels were at background levels in this denitrifying environment. After 11 months of storage, DO levels remained consistently low.

Redox potential averaged 389 mV in the recharge water. Ambient groundwater redox potential averaged 29 mV. At the ASR well after 4 months of storage, the redox potential was expected to be strongly reducing (Vanderzalm et al., 2006), but the 112 mV recorded also suggested air entry to this sample. At the 4-m monitoring well, the redox potential had declined from +389 mV to -32 mV. After 11 months of storage and 3 weeks of recovery, redox potential values were 9, -36, and 21 mV at the ASR well and 4-m and 50-m monitoring wells, respectively. After 11 months of storage and 3 months of recovery, redox potential values were -41, -62, and 9 mV, all significantly lower than the previous sample set and below ambient groundwater values. This indicates continuing microbial and geochemical activities close to the well during extended ASR recovery.

During the 4-month storage period, average bicarbonate concentration at the ASR well increased substantially from 162 mg/L in the recharge water and 265 mg/L in the ambient groundwater to 391 mg/L during the storage phase, due to organic carbon oxidation and dissolution of calcite. At the 4-m and 50-m monitoring wells, bicarbonate values were similar to those in the ambient groundwater. Similarly, the calcium concentration at the ASR well increased during the storage period from 37 mg/L in the recharge water to 78 mg/L, compared to 155 mg/L in the ambient groundwater.

Fluoride was 0.98 mg/L in the recharge water, and its concentration in the ambient groundwater was 0.24 mg/L. At the ASR well after 5 months of storage, the fluoride concentration had declined slightly to 0.87 mg/L. At the 4-m and 50-m monitoring wells it was present at 0.86 and 0.37 mg/L, respectively, suggesting a combination of blending and possible precipitation by ion exchange with calcite. Fluoride remained within a range of 0.3–0.76 mg/L in later samples.

The temperature was 15–18 °C in the recharge water during winter months; however, the ambient groundwater temperature was 25–27 °C. At the end of the 4-month storage period, temperatures at the ASR well and the 4-m monitoring well were 15.1 and 15.8 °C, respectively, while water at the 50-m monitoring well was 20.6 °C. These values increased to 17, 21, and 20 °C after 11 months of storage and 3 weeks of pumping and 23, 21, and 21 °C

after 11 months of storage and 3 months of pumping. A relatively substantial annual temperature variation occurs in the ASR storage zone at this site.

TOC values in the recharge water were quite high compared to those at the other three WRF ASR sites, averaging 12.6 mg/L, compared to a range of 7–11 mg/L for the other three sites. TOC was 0.3 mg/L in the ambient groundwater at the Bolivar site. After 4 months of storage, TOC at the ASR well was 31.8 mg/L, probably representing organic matter accumulating in and adjacent to the borehole during the recharge period (Le Gal La Salle et al., 2005; Vanderzalm et al., 2006). The sample was collected prior to complete purging of particulates from the near-well zone, as indicated by the high turbidity of this sample, 32.6 NTU. After 11 months of storage and 3 weeks of recovery, TOC values were relatively steady at all three wells, with values between 7.4–8.6 mg/L. However, when the associated chloride dilution ratios are applied, it is apparent that no further reduction in TOC actually occurred except by dilution with ambient groundwater; this remaining TOC was recalcitrant, as identified in an earlier study of apparent molecular weight and functional groups from ¹³C nuclear magnetic resonance (Skjemstad et al., 2002).

5.3 NUTRIENTS

5.3.1 Chandler, AZ

Total nitrogen increased during ASR storage, from 1.7–2.4 mg/L, and increased further to 6.4 mg/L during recovery. This may reflect desorption and release of nitrogen from organic metabolism, which would tend to lead to biofilm formation on the aquifer matrix surrounding the ASR well. Nitrate concentrations during this same period increased from 0.9–3.9 mg/L, which is opposite what would be expected under reducing conditions. Desorption may have occurred along the flow path to the ASR well, overriding any decrease in nitrate concentrations resulting from denitrification.

Total phosphorus declined from 4.1 mg/L in the recharge water to 1.5 mg/L after 2 months of storage and then declined further to 0.42 mg/L after 6 weeks of recovery. Orthophosphate behaved similarly, declining from 1.9–1.47 mg/L during storage and to 0.97 mg/L after 6 weeks of recovery. Of some interest is that phosphate was never detected at the monitoring well. These changes in nutrient concentrations, combined with a TOC reduction, suggest microbial activity and sorption–desorption processes occurring in the storage zone.

5.3.2 Englewood, FL

Total nitrogen and most of the nitrogen species fluctuated in the Englewood, FL, samples, with the exception of nitrate, which consistently declined from 1.09 mg/L in the recharge water to 0.103 mg/L in the first recovered sample and 0.029 mg/L in the final sample. The reduction of nitrate is consistent with the expected microbial activity and low-oxygen conditions. Phosphorus levels increased from 2.5 mg/L in the recharge water to 4.3 mg/L in the final recovered sample, and orthophosphates remained the same.

5.3.3 Manatee, FL

Concentrations of all compounds at the Manatee site were interpreted with respect to mixing ratios determined from boron and TDS as tracers, because sampling occurred during Manatee's first injection into this aquifer and thus there was no buffer zone preventing direct mixing with native groundwater. After accounting for an estimated 70% groundwater and

30% recharge water mix, nitrite was higher than expected, at 0.36 mg/L versus the 0.20 mg/L expected. Nitrate, total phosphorus, and orthophosphate appeared to have decreased over the 2-week storage period with respect to the estimated mixing ratio. Nitrate was measured at 0.76 mg/L versus an expected 1.2 mg/L, total phosphorus was measured at 0.22 mg/L versus an expected 0.82 mg/L, and orthophosphate was measured at 0.14 mg/L versus an expected 0.41 mg/L.

5.3.4 Bolivar, Australia

Total nitrogen in the recharge water at the Bolivar site was variable, and 3 weeks before the end of injection it was 8.2 mg/L. At the ASR well after 5 months of storage, the total nitrogen was 9.4 mg/L, while at the 4-m monitoring well it was 1.3 mg/L, a considerable reduction. However, at the 50-m monitoring well it was 7.2 mg/L. This is believed to be the result of mixing with previously stored nitrogen-rich injectant. After 11 months of storage and 3 weeks of recovery, total nitrogen values at the ASR well and 4-m and 50-m monitoring wells were 0.7, 1.0, and 5.2 mg/L, respectively (mostly ammonia). After 11 months of storage and 3 months of recovery, total nitrogen values increased from 0.5 mg/L at the ASR well (mostly organic N) to 11.3 mg/L at the 50-m well (mostly ammonia). The increases are believed to reflect mixing with residual, nitrogen-rich injectant stored in previous cycles. Total phosphorus (TP) was 1.58 mg/L in the WRF recharge water sample. In the ASR well after 4 months of storage the TP concentration was 2.64 mg/L, possibly due to enrichment by organic particulates that accumulated in the well. At the 4-m monitoring well the TP value was 0.85 mg/L, while at the 50-m monitoring well it was only 0.04 mg/L. The orthophosphate and TP concentrations after 11 months of storage and 3 months of recovery were similar to those after 3 weeks of pumping, with all levels markedly lower than concentrations after 4 months of storage. Thus, phosphorus in both total and ortho forms typically decreased with distance from the well and with storage time. This substantial reduction in TP is likely due to sorption, precipitation, and microbial activity in the proximal zone.

The water quality changes observed for nutrients at all sites are summarized in Table 5.2.

Table 5.2. Water Quality Changes Observed: Nutrients

Nutrient	Chandler	Englewood	Manatee	Bolivar
Total Nitrogen	Increased	Ambiguous	No change	Ambiguous
Total Kjeldahl Nitrogen	Ambiguous	Ambiguous	No change	Ambiguous
Nitrate	Increased	Decreased	Decreased	Decreased
Nitrite	Ambiguous	Decreased	Increased	Ambiguous
Ammonia	Ambiguous	Ambiguous	No change	Ambiguous
Total Phosphorus	Decreased	Increased	Decreased	Decreased
Orthophosphate	Decreased	No change	Decreased	Decreased

5.4 METALS

5.4.1 Chandler, AZ

Arsenic was initially detected at 0.0033 mg/L in the recharge water at the Chandler site and 0.0042 mg/L in the monitoring well sample. It was not detected in subsequent samples except for the final recovery sample, in which it was found at 0.0029 mg/L. A slight increase in barium occurred during ASR storage and recovery, from 0.017–0.063 mg/L, possibly due to the presence of barium minerals in the storage zone. Iron concentrations in the monitoring well were high, corresponding perhaps to the relatively high turbidity values. The monitoring well is constructed of carbon steel casing, which could have contributed to the iron levels. The WWTP process does not include coagulation, which could otherwise add iron to the reclaimed water.

5.4.2 Englewood, FL

Barium initially declined from 0.003 mg/L in the recharge water to 0.001 mg/L after 1 week of storage and then increased to 0.012 mg/L in a sample collected after 2 weeks storage. Iron increased from 0.11–1.18 mg/L during 2 weeks of storage. Remaining metals concentrations were essentially unchanged. Since the casing material is carbon steel, the increase in iron was not unexpected. A corresponding increase in turbidity, from 0.8–1.7 NTU, was also noted, and probably represented rust in the recovered water.

5.4.3 Manatee, FL

Arsenic was detected at 0.008 mg/L in the background water, was not detected at an MDL of 0.007 mg/L in the recharge water, and was found at 0.024 mg/L in the recovered water. This probably reflects mobilization triggered by the injection of recharge water containing oxygen. Iron and barium concentrations were higher in the background sample than in the recharge water at Manatee. These concentrations in the recovered water were consistent with expected mixing ratios, given no evidence for transformation other than mixing.

5.4.4 Bolivar, Australia

Analysis of the metals data indicates mobilization of arsenic close to the ASR well, with concentrations increasing from 2 µg/L in the recharge water to 75 µg/L in the ASR well after 4 months of storage. At the 4-m and 50-m monitoring wells, the concentrations were 20 and <2 µg/L, respectively. After 11 months of storage, arsenic concentrations were 20, 7, and 1 µg/L after 3 weeks of pumping and 11, 7, and <1 µg/L after 3 months of pumping at the ASR well and 4-m and 50-m monitoring wells, respectively.

A relatively high concentration of barium was noted at the 50-m monitoring well. In the recharge water at the ASR well it was 3 µg/L, increasing to 4 µg/L after 4 months. At the 4-m and 50-m monitoring wells, it was 3 and 33 µg/L, respectively. Barium minerals are known to be present in the storage zone at concentrations up to 80 ppm. Copper decreased from 0.009 mg/L in the recharge water to consistently below the MDL for recovered and monitoring well samples. Selenium was detected in all samples at 5–7 µg/L on the last sampling occasion, whereas it had not exceeded the 3-µg/L detection limit in injectant or previous groundwater samples.

Iron concentrations were variable. The ambient groundwater iron content was 1.0 mg/L. The recharge water contained <0.03 mg/L. After 4 months of storage, however, the iron concentration at the ASR well was 6.9 mg/L. This increase possibly reflects dissolution of ferric iron under low-redox conditions. During recovery and at other wells, iron concentrations were lower than in the native groundwater.

The water quality changes observed for metals at all sites are summarized in Table 5.3.

Table 5.3. Water Quality Changes Observed: Metals

Metal	Chandler	Englewood	Manatee	Bolivar
Arsenic	Ambiguous	Decreased	Increased	Ambiguous
Barium	Increased	Ambiguous	No change	Increased
Cadmium	Not detected	Not detected	Not detected	Not detected
Copper	Not detected	No change	Not detected	Decreased
Iron	Ambiguous	Increased	No change	Ambiguous
Lead	Not detected	Not detected	Not detected	No change
Mercury	Not detected	Not detected	Not detected	Not detected
Selenium	Not detected	Not detected	Not detected	Increased

5.5 RADIONUCLIDES

5.5.1 Chandler, AZ

A small but significant increase occurred in gross alpha radioactivity, from 0.5 mBq/L in the recharge water to 1.7 mBq/L after 2 months of storage and increasing to 5.4 mBq/L after 6 weeks of recovery. Total uranium was not detected in the recharge water but was found in the monitoring well samples at up to 4.5 pCi/L and increased to 4.2 pCi/L in the final recovered water sample. The values are below drinking water action levels but suggest baseline radioactivity in area sediments.

5.5.2 Englewood, FL

Neither gross alpha particle activity nor total uranium was detected in any of the Englewood samples.

5.5.3 Manatee, FL

Manatee's background sample contained 4.8 ± 5.9 mBq/L of gross alpha particle activity and 0.3 ± 0.4 µg/L total uranium. Neither constituent was detected in the recharge water, and the recovered water contained 4.8 ± 4.4 mBq/L gross alpha particle activity and 9.0 ± 0.4 µg of total uranium/L. Given the known dilution effect, these values suggest an unexpected increase in radionuclides in the recovered water, but the measurements are reported with a high level of uncertainty.

5.5.4 Bolivar, Australia

Gross alpha particle activity decreased and then increased over the course of storage, with a peak value of 110 mBq/L found at the ASR well after 11 months of storage and 3 months of pumping. Total uranium increased slightly over time at the ASR and 4-m monitoring well, reaching an overall peak of 3.8 µg/L at the 4-m well after 4 months of storage. Uranium was never found above the 0.5-µg/L detection limit at the 50-m monitoring well.

The water quality changes observed for radionuclides at all sites are summarized in Table 5.4.

Table 5.4. Water Quality Changes Observed: Radionuclides

Radionuclide	Chandler	Englewood	Manatee	Bolivar
Gross alpha	Increased	Not detected	Increased	Ambiguous
Uranium	Increased	Not detected	Increased	Ambiguous

5.6 DISINFECTION BYPRODUCTS

5.6.1 Chandler, AZ

TTHMs declined in the ASR well from 0.17–0.019 µg/L during 2 months of storage and declined further to 0.014 µg/L during 6 weeks of recovery. Haloacetic acids (HAA5) declined similarly, from 0.096 to <0.02 µg/L during 2 months of storage, probably all of which occurred during the first few days.

5.6.2 Englewood, FL

A significant reduction in TTHMs and HAA5 occurred during 2 weeks of storage, from 8.4 to <0.5 µg/L and from 12–1.3 µg/L, respectively. All are very low values. This is a strong indication of microbial activity.

5.6.3 Manatee, FL

TTHMs were not detected in the background water but were found at 12.27 µg/L in the recharge water and at 4.24 µg/L in the recovered water. Given a mixing ratio of up to three parts native groundwater to one part recharge water, these values do not indicate a reduction in TTHMs beyond dilution over the 2-week storage period. HAA5 was not measured in the background or recharge water but was found at 0.6 µg/L in the recovered water.

5.6.4 Bolivar, Australia

TTHM concentrations were 234 µg/L in the recharge water. At the ASR well after 4 months of storage, THMs had declined to 18 µg/L, while at the 4-m and 50-m monitoring wells they had declined to 80 and <4 µg/L, respectively. HAA5 concentrations declined from 71 µg/L in the recharge water to <9 µg/L in all monitoring well samples after 5 months.

The water quality changes observed for DBPs at all sites are summarized in Table 5.5.

Table 5.5. Water Quality Changes Observed: DBPs

DBP	Chandler	Englewood	Manatee	Bolivar
Cyanide	Not detected	Not detected	Not detected	Not detected
TTHM	Decreased	Decreased	No change	Decreased
HAA5	Decreased	Decreased	No data	Decreased

5.7 MICROBIOTA

5.7.1 Chandler, AZ

HPC for the recharge water was 8/mL, increasing to 500/mL at the monitoring well. However, pathogenic microbiota and protozoa were not detected at the method limits in either well. Following 2 months of storage, HPC values were essentially unchanged and very low in the ASR well and had declined to 26/mL in the monitoring well. After 6 weeks of recovery, HPC values in the recovered water had increased to 146/mL.

5.7.2 Englewood, FL

After 2 weeks of storage, total coliforms were too numerous to count and the HPC increased from 7 to 850/mL. However, fecal coliforms, *E. coli*, enterococci, and coliphage were not detected at the method limits.

5.7.3 Manatee, FL

The only microbial parameter detected in the background sample was an HPC of 8.5 counts/mL. The recharge water showed 71/mL, and the recovered water contained 3/mL, a decrease beyond that expected from mixing. The only other microbiological detect at Manatee was 4 CFU of total coliforms/100 mL in the recovered sample.

5.7.4 Bolivar, Australia

Total coliform bacteria declined during the storage period from 110 CFU/100 mL in the recharge water to 68 in the ASR well after 4 months of storage, to 15 in the 4-m monitoring well, and were not detected in the 50-m monitoring well nor in water from the ASR well during recovery. Fecal coliforms and *E. coli* bacteria were found at 6 CFU/100 mL in the recharge water but were 0 in all subsequent samples at all wells. Enterococci were not detected in the recharge water or in any recovered samples but were found twice at the 50-m monitoring well. Coliphage, *Cryptosporidium*, and *Giardia* were analyzed but not detected in any samples.

The water quality changes observed for microbiota at all sites are summarized in Table 5.6.

Table 5.6. Water Quality Changes Observed: Microbiota

Parameter	Chandler	Englewood	Manatee	Bolivar
Total coliforms	Not detected	Increased	Increased	Decreased
Fecal coliforms	Not detected	Not detected	Not detected	Decreased
<i>E. coli</i>	Not detected	Not detected	Not detected	Decreased
Enterococci	Not detected	Not detected	Not detected	Ambiguous
Coliphage	Not detected	Not detected	Not detected	Not detected
<i>Cryptosporidium</i>	Not detected	Ambiguous	Not detected	Not detected
<i>Giardia</i>	Not detected	Decreased	Not detected	Not detected
HPC	Ambiguous	Increased	Decreased	No data

5.8 MICROCONTAMINANTS

Microcontaminant concentrations exceeding 5 times the MDL were considered significant to support analysis regarding trends and stability of the data. Microcontaminants that were present at concentrations below 5 times the MDL were noted for each site but were not used to determine trends. Data tables are presented for each site as part of the analysis.

5.8.1 Travel and Laboratory Blanks

When considering microcontaminant data, it is especially important to consider blank contamination. In this study, both travel and laboratory blanks were analyzed. Travel blanks were obtained from reagent water systems at the ASR site by utility personnel in bottles sent by the Southern Nevada Water Authority (SNWA) along with sample bottles. Laboratory blanks were performed by filling a sample bottle with reagent water (Nanopure) at SNWA and processing with samples. Both travel and laboratory blanks were handled and processed in the same manner as samples. Microcontaminant data for the travel and laboratory blanks can be found in Appendix A.

Bisphenol A was detected only in the travel blank on the first sampling event at Bolivar, while DEET was detected in four of the six travel blanks collected. Oddly, estradiol was detected in two travel blanks, both at 11 ng/L, negating the results for this parameter. NDMA was detected in two travel blanks. Unfortunately, both detections were greater than 20 ng/L. It is possible that this NDMA originated from ion-exchange media used in reagent-grade water purification. Nonylphenol was detected in all travel blanks and varied greatly in concentration. In two Bolivar travel blanks, conducted at two different time periods, the nonylphenol concentration exceeded 10,000 ng/L and likely came from contamination with a detergent. Triclosan was only detected in one travel blank, at 3.4 ng/L. Nonylphenol was detected in seven of nine laboratory blanks, with a mean concentration of 174 ng/L. DEET and fluoranthene were each detected in one of the nine laboratory blanks, at 2.4 and 5.1 ng/L, respectively.

Based on detections in the travel and laboratory blanks, results for butylated hydroxytoluene (BHT), DEET, estradiol, NDMA, and nonylphenol were dismissed from the data set.

5.8.2 Trendable Microcontaminant Data

Several microcontaminants were not measured above the MDL in any sample from any site. These were aldrin, several BDE congeners, bromate, diazinon, dieldrin, iodate, and progesterone. Given the objective of reporting increases or reductions in microcontaminant concentrations during ASR storage, a minimum detection criterion was established that would eliminate bias from measured values below the MDL. A trend of increasing or decreasing concentration was only noted if it included a measurement that was at or above 5 times the MDL. A 20% change in concentration, the same criterion used in analysis of the other parameters, was considered an indication of a notable increase or decrease. Thus, a compound needed to appear at least once at a site at 5 times the MDL and to be increased or decreased more than 20% (after mixing was taken into account) to be considered indicative of a noteworthy change in concentration. Table 5.7 shows the progressive reduction of the original microcontaminant constituent list to compounds potentially usable for noting trends in the individual site data sets.

5.8.3 Recharge Water Quality

A significant issue for microcontaminant data analysis is the potential variability in concentrations of microcontaminants in the reclaimed water. Only one recharge water sample was collected at each ASR site due to budgetary restrictions. This grab sample represents one moment in time and does not provide an integrated view of the water entering the ASR well. For the Bolivar data set, reclaimed water variability is probably subdued due to extended storage in oxidation ponds during pretreatment of the wastewater. For the other three sites, less storage is provided at the treatment plant, and so variability in microcontaminant concentrations is probably more pronounced. Previous data from team members have shown that concentrations of these target compounds can vary diurnally in typical wastewater treatment plants that do not have extended storage to attenuate variability in influent water quality. Recharge samples for the four sites are shown in Table 5.8.

5.8.4 Analytical Approaches

Given the variability in recharge water microcontaminant concentrations discussed above, comparison of recharge water quality to recovered water quality involves an inherent degree of uncertainty. This was evidenced by the frequent occurrence of higher microcontaminant concentrations in recovered water than in recharge water. Conclusions that are more defensible may be obtained by comparing successive recovered water samples from the same well and comparing water quality data at adjacent wells obtained at the same time. However, the latter approach fails to address water quality changes occurring during storage periods between the end of recharge and the beginning of recovery.

Table 5.7. Reduced Microcontaminant Constituent List for Trend Analysis

Original List	Less Rejected Data ^a	Less Nondetects ^b	Less Nondetects >5× MDL ^c
Acetaminophen	Acetaminophen	Acetaminophen	Acetaminophen
Aldrin	Aldrin	Aldrin	Aldrin
Androstenedione	Androstenedione	Androstenedione	Androstenedione
Atrazine	Atrazine	Atrazine	Atrazine
BDE # 100	BDE # 100	BDE # 100	BDE # 100
BDE #153	BDE #153	BDE #153	BDE #153
BDE #154	BDE #154	BDE #154	BDE #154
BDE #28	BDE #28	BDE #28	BDE #28
BDE #47	BDE #47	BDE #47	BDE #47
BDE #99	BDE #99	BDE #99	BDE #99
α-BHC	α-BHC	α-BHC	α-BHC
β-BHC	β-BHC	β-BHC	β-BHC
δ-BHC	δ-BHC	δ-BHC	δ-BHC
γ-BHC	γ-BHC	γ-BHC	γ-BHC
BHT	BHT	BHT	BHT
Bisphenol A	Bisphenol A	Bisphenol A	Bisphenol A
Bromate	Bromate	Bromate	Bromate
Caffeine	Caffeine	Caffeine	Caffeine
Carbamazepine	Carbamazepine	Carbamazepine	Carbamazepine
Chlorate	Chlorate	Chlorate	Chlorate
Chlorpyrifos	Chlorpyrifos	Chlorpyrifos	Chlorpyrifos
DEET	DEET	DEET	DEET
Diazepam	Diazepam	Diazepam	Diazepam
Diazinon	Diazinon	Diazinon	Diazinon
Diclofenac	Diclofenac	Diclofenac	Diclofenac
Dieldrin	Dieldrin	Dieldrin	Dieldrin
Dilantin	Dilantin	Dilantin	Dilantin
Erythromycin-H2O	Erythromycin-H2O	Erythromycin-H2O	Erythromycin-H2O
Estradiol	Estradiol	Estradiol	Estradiol
Estriol	Estriol	Estriol	Estriol
Estrone	Estrone	Estrone	Estrone
Ethinylestradiol	Ethinylestradiol	Ethinylestradiol	Ethinylestradiol
Fluoranthene	Fluoranthene	Fluoranthene	Fluoranthene
Fluoxetine	Fluoxetine	Fluoxetine	Fluoxetine
Gemfibrozil	Gemfibrozil	Gemfibrozil	Gemfibrozil
Hydrocodone	Hydrocodone	Hydrocodone	Hydrocodone
Ibuprofen	Ibuprofen	Ibuprofen	Ibuprofen
Iodate	Iodate	Iodate	Iodate
Iopromide	Iopromide	Iopromide	Iopromide
Meprobamate	Meprobamate	Meprobamate	Meprobamate
Naproxen	Naproxen	Naproxen	Naproxen
NDMA	NDMA	NDMA	NDMA
Nonylphenol (sum)	Nonylphenol (sum)	Nonylphenol (sum)	Nonylphenol (sum)
Oxybenzone	Oxybenzone	Oxybenzone	Oxybenzone
Pentoxifylline	Pentoxifylline	Pentoxifylline	Pentoxifylline
Perchlorate	Perchlorate	Perchlorate	Perchlorate
Progesterone	Progesterone	Progesterone	Progesterone
Sulfamethoxazole	Sulfamethoxazole	Sulfamethoxazole	Sulfamethoxazole
TCEP	TCEP	TCEP	TCEP
Testosterone	Testosterone	Testosterone	Testosterone
Triclosan	Triclosan	Triclosan	Triclosan
Trimethoprim	Trimethoprim	Trimethoprim	Trimethoprim

^aConstituents crossed out were removed from analysis due to repeat presence in lab and/or travel blanks.

^bConstituents crossed out were not measured above the MDL in any sample.

^cConstituents crossed out were not measured at 5 times the MDL in any sample.

Table 5.8. Recharge Water Concentrations of Trendable Microcontaminants

Compound	log K _{ow}	pK _a	MW	MDL, ng/L	Microcontaminant Concn, ng/L			
					Englewood	Manatee	Chandler	Bolivar
Acetaminophen	0.46	9.4	151	1	<1.0	<10	<1.0	<1.0
Androstenedione	2.75	NA ^a	286	1	4.5	<10	3.1	7.9
Atrazine	2.61	1.7	215	1	601	72	<1.0	9.2
Caffeine	-0.07	10.4	194	1	<10	<100	<10	13
Carbamazepine	2.45	0.37	236	1	433	190	92	125
Chlorate	NA	NA	83	100	350	480,000	97,000	NA
Diazepam	2.82	8.33	284	1	1.9	<10	1.2	2.4
Diclofenac	4.51	NA	296	1	<1.0	<10	<1.0	<1.0
Dilantin	2.47	9.13	252	1	685	308	50	32
Erythromycin-H ₂ O	3.06	8.88	734	1	39	120	<1.0	<1.0
Estriol	2.45	9.43	288	5	<5.0	<50	<5.0	177
Estrone	3.13	9.43	270	1	7.9	<10	3.4	32
Ethinylestradiol	3.67	9.43	296	1	<1.0	<10	<1.0	27
Fluoranthene	5.16	NA	202	5	24	10	26	<5.0
Fluoxetine	4.05	8.7	309	1	52	<10	11	<1.0
Gemfibrozil	4.77	4.42	250	1	<1.0	845	<1.0	<1.0
Hydrocodone	2.16	7.32	299	1	83	60	<1.0	<1.0
Ibuprofen	3.97	4.15	206	1	103	126	38	80
Iopromide	-2.05	10.2	791	1	4.9	842	292	183
Meprobamate	0.7	10.9	218	1	444	1170	677	<1.0
Naproxen	3.18	0.37	230	1	<1.0	94	<1.0	<1.0
Pentoxifylline	0.29	0.97	278	1	15	32	1.8	<1.0
Perchlorate	-5.8	NA	99	50	<50	84	550	NA
Sulfamethoxazole	0.89	2.66	253	1	24	139	<1.0	<1.0
TCEP	1.44	NA	286	1	213	223	401	151
Triclosan	4.76	7.98	290	1	<1.0	<10	<1.0	<1.0
Trimethoprim	0.91	7.12	290	1	1	34	<1.0	<1.0

^aNA, not available.

To account for these issues, two analytical approaches were utilized. The first, Approach A, considers all water quality data as being equally representative, even though reasonable concern exists that recharge water quality is quite variable with respect to microcontaminants. Consequently, observations based upon comparisons to recharge water quality have an inherent degree of uncertainty. The second, Approach B, ignores recharge water quality data and focuses upon comparison of recovered water samples at the same well and also recovery samples collected at the same time from different wells. By not comparing changes from the

start of storage, however, changes occurring over longer time periods may not be detected with the second analytical approach.

For each of the four sites, comments are provided for microcontaminants that were detected at concentrations sufficient to support analysis of increasing or decreasing trends. These microcontaminants are highlighted in bold in the discussions below. All other microcontaminants were either not detected or were present at concentrations too low to support analysis of increasing or decreasing trends or stability. Those are included with the full data set in Appendix C. A parallel analysis that considered the same constituents for each site would not be applicable due to the differences between sites.

5.8.5 Chandler, AZ

Although many target compounds were nondetectable or were present at very low levels in the recharge and recovered water, several microcontaminants were detectable well above the MDL. The compounds occurring at the greatest concentration (>5 times the MDL) included iopromide, meprobamate, TCEP, carbamazepine, dilantin, erythromycin, ibuprofen, naproxen, triclosan, and gemfibrozil. The occurrence of these microcontaminants in wastewater is well documented (Stumm-Zollinger and Fair, 1965; Tabak and Bunch, 1970; Garrison et al., 1976; Hignite and Azarnoff, 1977; Tabak et al., 1981; Buser et al., 1998; Snyder et al., 1999, 2001; Ternes et al., 1999, 2001; Kolpin et al., 2002; Anderson et al., 2004). Team members have found these compounds to occur in wastewater effluents at concentrations similar to those found here (Snyder et al., 1999, 2001a, 2001b, 2004b, 2005, 2006; Vanderford et al., 2003); however, the actual occurrence in recharge (reclaimed) water is highly dependent upon the wastewater treatment processes employed.

Caffeine was not detected in the recharge water, yet it was detectable in two of the recovery samples at the ASR well at increasing concentrations as recovery progressed for 2 weeks and then declining to nondetect levels after 6 weeks of recovery. However, no caffeine was ever detected at the observation well. This is possibly due to variability in recharge water quality; however, it is more likely due to desorption from the aquifer matrix during recovery. As shown in Table 5.8, caffeine is easily biodegraded and has a moderate affinity to carbon, and so subsurface microbial activity and sorption–desorption processes are probably involved.

Carbamazepine also increased during ASR storage, from 92 ng/L in the recharge water at the end of recharge to 358 ng/L at the beginning of recovery. Subsequent samples declined slightly during recovery. At the monitor well, no attenuation was evident, due to lateral movement of the water through the aquifer, although some attenuation may have occurred during the storage and recovery period. Alternatively, variability in recharge water quality may account for all of the variability in carbamazepine concentrations. No attenuation was evident.

Dilantin concentrations increased during storage and recovery and showed no significant attenuation.

Erythromycin-H₂O was not found in the recharge water, with a method detection limit of 1 ng/L; however, 2 months later at the beginning of recovery it was found at 44 ng/L, decreasing to 34 and 21 ng/L after 2 and 6 weeks of recovery, respectively. None was detected at the observation well. The removal of erythromycin is most likely due to sorption–desorption, as biodegradation of this compound is generally poor.

Fluoranthene was relatively stable, showing no initial increase in concentration between the end of recharge and beginning of recovery. However, some attenuation may have occurred during the recovery period, from 26–13 ng/L, and some attenuation also may have occurred by the time the water reached the monitor well, at which values of 5.2 and 10 ng/L were recorded during recharge and recovery. Variability in recharge water quality could also have accounted for these changes.

Fluoxetine was present at 11 ng/L in the recharge water at the ASR well but was not detected at any other time or location, suggesting complete subsurface attenuation with time, distance, or both.

Hydrocodone was present at a concentration of 2.6 ng/L in the recovered water at the ASR well after 2 months of storage, increasing to 3.6 ng/L after 2 weeks of recovery and then declining to 3.0 ng/L after 6 weeks of recovery. Concentrations were at nondetectable levels in the ASR well during recharge and also in the observation well. A similar pattern was observed for trimethoprim, which increased from nondetect to 3.3 ng/L after 2 months of storage at the ASR well and then to 7.5 and 6.6 ng/L after 2 and 6 weeks of storage, respectively, with nothing detected at the observation well. Both of these constituents are relatively stable; however, neither was detected at the observation well, implying reactivity close to the ASR well.

Iopromide concentrations at Chandler appeared to rapidly decrease postinjection, from 292 ng/L in the recharge water to concentrations varying from 14–24 ng/L in the ASR well and the monitor well during the recovery period. However, iopromide concentrations in the ASR well and associated monitoring wells are relatively constant, despite a small decrease during recovery. Degradation in the subsurface is not expected for iopromide, as it has a low potential for biodegradation and a low affinity for organic carbon. The rapid decrease during the storage period would therefore suggest possible variability in recharge water quality. Alternatively, subsurface processes may be more effective than expected at removing this microcontaminant during ASR storage.

Pentoxifylline behaved similarly to caffeine. It was detected in the recharge water at 1.8 ng/L, increasing to 3.0 ng/L in the recovered water and then declining to 2.1 ng/L after 6 weeks of recovery. Concentrations were relatively steady. This would be expected, as it is poorly biodegraded and only moderately bound to carbon. It was not detected at the monitor well.

Perchlorate was present at 0.55 µg/L in the recharge water at the end of recharge but was <0.05 µg/L 2 months later in the recovered water at the beginning of recovery. In the observation well it was initially present at 0.45 µg/L at the end of recharge, but 2 months later it had declined to <0.05 µg/L. Perchlorate is known to be extremely stable in groundwater under aerobic conditions but is also known to attenuate rapidly under reducing conditions typically associated with ASR storage. The detection of perchlorate in the ASR well and monitoring well at different concentrations suggests possible variability in the low recharge concentrations of this oxyhalide. Chlorate and perchlorate are known to form in hypochlorite during chlorine disinfection and can be detected depending on the holding time of the hypochlorite and dose applied. However, at the Chandler site disinfection is currently achieved through UV, not chlorination. Another plausible explanation is the presence of perchlorate and chlorate in Central Arizona Project water, which is the regional imported water supply source for the Chandler area. The same pattern followed for chlorate, which declined from 97 to <0.1 µg/L in the ASR well during the storage period and from 78 to <0.1

µg/L in the observation well. An alternate, more plausible hypothesis is that both perchlorate and chlorate were attenuated under reducing conditions that probably occurred during ASR storage. Other research investigations have demonstrated such attenuation, including under oxidizing conditions whenever a carbon source and nutrient source are present to support anaerobic microbial activity in the biofilms coating the aquifer matrix around the ASR well (Brown et al., 1997; Hatzinger, 2005; Herman and Frankenburger, 1998; Wallace et al., 1998). Careful measurements to verify ORP and DO levels in the aquifer at this site during extended storage periods would be very helpful. Since perchlorate is widely recognized for its stability in groundwater, its significant attenuation during ASR storage would be quite an important finding, implying that similar reduction and microbial processes may also attenuate other microcontaminants in reclaimed water during ASR storage.

Sulfamethoxazole was not detected in the recharge water but was present at 385 ng/L in the observation well at the end of recharge. Table 5.8 shows that this compound has relatively poor biodegradation potential and poor affinity for carbon, and so little subsurface attenuation would be expected. Ten weeks after the end of recharge, the observation well concentration had declined to 299 ng/L after 2 weeks of recovery, while at the ASR well the concentration had increased to 229 ng/L. After 6 weeks of recovery, the concentration at the ASR well had increased to 251 ng/L. The data set is consistent with a hypothesized slug of this constituent recharged during winter 2005 and then recovered during the sampling period, with little if any subsurface attenuation. However, it is striking that the concentration in the ASR well at the beginning of recovery, after 2 months of storage, increased from <1 to 214 ng/L.

The analysis of general constituents suggests the possibility that the initial recovery sample at Chandler was collected prior to complete flushing of particulate and microbiological debris from the well. The extent that this constituent might be attached to or otherwise associated with the solid material might account for the initial relatively high concentration. Several other microcontaminants showed a similar pattern of initial increase between the end of recharge and the beginning of recovery and then attenuation. These included meprobamate, TCEP, ibuprofen, naproxen, triclosan, and gemfibrozil.

Table 5.9 shows microcontaminants in bins based upon percent removal or accumulation during ASR recovery (Approach B) for the Chandler site. The percent removal was calculated based on the degree of removal from the initial ASR recovery sample to the final sample. This information is presented only for the Chandler and Englewood sites, because it relies on a direct comparison from an early recovered water sample to a later recovered water sample, assuming no dilution. Because there was only one recovered water sample at Manatee and Bolivar's samples were known to include mixing with previously stored water and ambient groundwater, these sites were not included in the bin comparison. These removal percentages are generalities based upon a very limited data set ($n = 3$). Additionally, in some cases, compounds detected in the initial sample were no longer detectable in the final sample (i.e., caffeine). In this case, percent removal is reported based on the MDL and likely underestimates actual removal. Ibuprofen was well removed during ASR recovery (81%), which can be attributed to biodegradation. The moderate removal of several compounds was most likely due to both biodegradation and adsorption. Reduction may also have contributed; however, this would most likely have occurred prior to the beginning of recovery and would therefore not be a significant factor for the second analytical approach.

5.8.6 Englewood, FL

As discussed previously, uncertainty exists regarding the Englewood recharge water quality, which was determined from a sample collected several days after the recharge period. Interpretation of the data with Approach A indicates that many constituents increased in concentration between recharge and the first recovered sample. This water had been in storage underground for about 2 weeks. These constituents that were found at increased concentrations included **acetaminophen** (<1–2.3 ng/L), **carbamazepine** (433–606 ng/L), **diclofenac** (<1.0–62 ng/L), **erythromycin-H₂O** (39–180 ng/L), **estrone** (7.9–10 ng/L), **fluoxetine** (52–97 ng/L), **gemfibrozil** (<1.0–875 ng/L), **hydrocodone** (83–103 ng/L), **ibuprofen** (103–126 ng/L), **iopromide** (4.9–83 ng/L), **pentoxifylline** (15–20 ng/L), **sulfamethoxazole** (24–1410 ng/L), **triclosan** (<1.0–42 ng/L), and **trimethoprim** (111 ng/L). Pesticides were generally at nondetect levels in all samples, with the exception of fluoranthene, which remained stable at 24–27 ng/L.

The simplest explanation for the increase in concentration for so many constituents during 2 weeks of ASR storage is short-term variability in recharge water quality. An alternate hypothesis, however, is that during 7 days of recovery there occurred desorption of microcontaminants that had sorbed onto the limestone aquifer matrix and associated microbial biofilms close to the well during the previous extended recharge period from 2001, during which a very large volume of water (net, 651 MG) had been recharged. It is hypothesized that during this 4-year period extensive biofilm formation would have occurred around the well, probably within a radial distance of a few feet to a few tens of feet. This accumulation of carbon would tend to sorb microcontaminants that are more amenable to carbon adsorption. Microcontaminants would sorb on both the biofilm and the aquifer matrix during recharge, with the highest concentrations closest to the well. Desorption would tend to be cumulative along the recovery flow path so that concentrations in the recovered water from the well would initially be high, reaching a peak and then gradually declining as recovery approached the total volume recharged. For Englewood, this high-volume recovery is not likely to ever occur, due to practical constraints associated with increasing salinity in the recovered water. Consequently, the potential for recovery of elevated concentrations of microcontaminants, desorbed from the aquifer matrix and from biofilms close to the ASR well, would therefore be relatively high. Furthermore, the opportunity for microbial assimilation of these organic compounds under low-redox conditions would be minimal during short storage periods.

The principal difference between the two recovery samples is that the second sample would be from water stored for the previous 2 months, whereas the first sample would have been stored for only about 2 weeks. The second sample would also have traveled a slightly longer flow path in the aquifer, initially away from and then back toward the ASR well.

Based on Approach B, Table 5.10 provides removal bins for compounds detected in the recovery water from Englewood. Compounds were generally removed to a lesser extent during the 1-week time period between samples compared to Chandler, even though the differential in subsurface storage time (2 weeks to 2 months) is greater. It is impossible to draw any firm conclusions on the fate of these microcontaminants during ASR storage at Englewood from this limited data set. The most notable difference between Englewood microcontaminants and those from Chandler was the moderate decrease in sulfamethoxazole at Englewood, while the concentration appeared to increase at Chandler (Table 5.9). Similarly, trimethoprim declined by 62% at Englewood while doubling at Chandler.

Table 5.9. Changes in Microcontaminant Concentrations of Recovered Samples: Chandler

	Reduction		Formation				Rise or Fall	Stable
	0–30%	31–69%	70–100%	0–30%	31–69%	70–100%		
Pentoxifylline		Erythromycin	Ibuprofen	Chlorate		Trimethoprim	Chlorate	Hydrocodone
Caffeine		Fluoranthene	Chlorate	Sulfamethoxazole			Sulfamethoxazole	
Carbamazepine		Meprobamate	Perchlorate					
Chlorate		Naproxen						
Dilantin		TCEP						
Gemfibrozil								
Hydrocodone								
Iopromide								
Sulfamethoxazole								

Table 5.10. Changes in Microcontaminant Concentrations of Recovered Samples: Englewood

Reduction		Formation			Rise or Fall	Stable
0–30%	31–69%	70–100%	0–30%	31–69%	70–100%	
TCEP	Acetaminophen		Estrone	Erythromycin-H2O		Hydrocodone
Carbamazepine	Hydrocodone		Sulfamethoxazole	Naproxen		Fluoxetine
Atrazine	Sulfamethoxazole		Chlorate	Gemfibrozil		Fluoranthene
Ibuprofen	Trimethoprim					Diclofenac
						Triclosan
						Iopromide
						Pentoxifylline
						Meprobamate
						Dilantin
						Diazepam

5.8.7 Manatee, FL

The background sample from the storage zone at Manatee contained nondetect concentrations of all microcontaminants. That no microcontaminants were found was not unexpected for a confined, artesian limestone aquifer over 500 ft deep. Regarding the recharge to recovery water quality changes and taking the mixing ratio into consideration, the following comparisons were noted.

Compounds found at concentrations higher than expected were **gemfibrozil, iopromide, naproxen, sulfamethoxazole, and trimethoprim**. Compounds found at concentrations lower than expected were **atrazine** and **chlorate**. Compounds observed to be at the same concentrations less dilution were **carbamazepine, dilantin, erythromycin, hydrocodone, ibuprofen, and meprobamate**.

5.8.8 Bolivar, Australia

It appears that the Bolivar reclaimed water contained fewer microcontaminants than the other three WRF ASR sites. This is either due to an absence of these contaminants in the wastewater or the relatively advanced capability of the wastewater treatment processes at Bolivar to remove them.

Several microcontaminants were not found in the WRF sample of reclaimed water but were found at significant concentrations in one or more samples of the recovered water. These included acetaminophen, androstenedione, erythromycin, estriol, gemfibrozil, and ibuprofen, each discussed below.

Several microcontaminants were found in lower concentrations during recovery than in the recharge water sample. These included atrazine, caffeine, and dilantin, which are discussed below. Processes such as variability in recharge water quality and both biotic and abiotic processes of attenuation may have contributed to the reductions in concentrations of these compounds.

Acetaminophen was present at the ASR well sample at the end of a 5-month storage period at a concentration of 3.9 ng/L. It was also present in the ASR well at the end of recovery, after 18 months of storage, at 2.4 ng/L. At the 4-m observation well at the end of recovery it was present at 179 ng/L.

Atrazine was present at 9.2 ng/L in the recharge water. Concentrations were 1.8, 8.2, and 3.4 ng/L in the three wells after 4 months of storage. After 13 months of storage, including 3 weeks of recovery, the concentrations for the same three wells were 5, 3.8, and 1.7 ng/L, respectively. After 18 months of storage, including 3 months of recovery, the concentrations were 2.2, 1.9, and 2.0 ng/L, respectively. When these last values are adjusted according to the chloride dilution ratio, it is possible that slow attenuation is occurring.

Caffeine was found at 13 ng/L in the reclaimed water. After 4 months of storage, a sample pumped from the ASR well had a caffeine concentration of 112 ng/L, while at the 4-m and 50-m observation wells it was present at 13 and <10 ng/L. Based upon analysis of general constituent data, it appears that the caffeine present in the ASR well sample may have been associated with particulates in that sample. Caffeine was not detected in samples from any of the three wells that were collected 3 weeks after the start of recovery. However, at the end of recovery after 18 months of storage the sample results were 17, 141, and 17 ng/L at the ASR well and 4-m and 50-m observation wells, respectively. Caffeine is derived from previously

recharged reclaimed water with higher organic content, possibly including higher concentrations of caffeine. Degradation of caffeine is ambiguous, and it is frequently found in blanks around the 10-ng/L level.

Carbamazepine was present at 125 ng/L in the recharge water. It was present at concentrations of 319, 373, and 284 ng/L in the three wells after 4 months of storage. After 13 months of storage, including 3 weeks of recovery, the concentrations for the same three wells were 81, 438, and 356 ng/L, respectively. After 18 months of storage, including 3 months of recovery, the concentrations were 173, 131, and 64 ng/L, respectively. After adjusting these last values according to the chloride dilution ratio, it appears that no significant attenuation is occurring. Conversely, concentrations were higher than anticipated. Possibly, sorption–desorption is occurring or, alternatively, the recharge water quality is highly variable. Most likely, extended recovery is pulling in poorer quality water from earlier cycles. Carbamazepine is considered to be relatively persistent in groundwater, and so it would be surprising to see it drop substantially.

Chlorate was present at insignificant concentrations at the ASR well during all three samples and also at the 50-m monitor well; however, at the 4-m monitor well it was found at significant but slowly declining concentrations after 4 months of storage, at 3 weeks into recovery and 13 weeks into recovery. No recharge water quality data were available for chlorate.

Diazepam is present at 2.4 ng/L in the recharge water. It was present at concentrations of 4.9, 2.5, and 1.4 in the three wells after 4 months of storage. After 13 months of storage, including 3 weeks of recovery, the concentrations for the same three wells were 1.6, 1.4, and 1.4 ng/L, respectively. After 18 months of storage, including 3 months of recovery, the concentrations were 2.1, 1.8, and 1.6 ng/L, respectively. Adjusting these last values according to the chloride dilution ratio, it appears that no significant attenuation is occurring. Conversely, concentrations are higher than anticipated. Most likely, extended recovery is pulling in poorer quality water through longer flow paths from earlier cycles.

Dilantin was found at 32 ng/L in the recharge water. It appears to be attenuated slowly in the subsurface. The first set of samples after 4 months of storage showed concentrations of 110, 126, and 82 ng/L in the ASR well and 4-m and 50-m observation wells, respectively. After 13 months of storage (and 3 weeks of recovery), corresponding concentrations were 104, 91, and 85 ng/L. After 18 months of storage and 3 months of recovery, concentrations were 32, 26, and 18 ng/L, respectively. After adjusting for the chloride dilution ratio, these last concentrations would be higher but still below concentrations for the second set of samples.

Erythromycin-H₂O in the three samples from the ASR well was present at 484, 14, and 26 ng/L after 5, 13, and 18 months of storage, respectively. In the 4-m observation well it was present at 8.6, 14, and 29 ng/L, respectively. In the 50-m observation well it was present at <1, 1.6, and <1 ng/L, respectively. It appears that this compound is sorbed and desorbed close to the ASR well.

Estriol was present at <5, 56, and 95 ng/L in the ASR well after 5 months, 13 months (3 weeks into recovery), and 18 months (3 months into recovery) of storage, respectively. At the 4-m observation well it was present at 73, 49, and 96 ng/L, respectively. At the 50-m observation well it was present at 98, 96, and 81 ng/L, respectively. This compound appears to persist in the subsurface at the Bolivar site. Androstenedione was found at 1.2, 1.5, and 3.5 ng/L concentrations in the ASR well after 5 months, 13 months (3 weeks into recovery), and

18 months (3 months into recovery) of stored water, respectively. At the 4-m observation well, corresponding concentrations were 1.0, 1.5, and 2.3 ng/L, respectively. At the 50-m observation well, corresponding concentrations were 20, 18, and 14 ng/L, respectively. It appears that toward the end of recovery the compound was at much higher concentrations in the 50-m observation well. This was probably due to recovery of a blend with previously stored, poorer quality water from earlier cycles.

Ethinylestradiol concentrations were initially low during the storage period at all three wells; however, once recovery started the concentrations increased, showing no attenuation or an increase compared to the recharge concentration at the ASR well (27 ng/L).

Ethinylestradiol is a persistent compound, especially in an anaerobic environment (Ying et al., 2004). Considering the anoxic nature of the Bolivar aquifer, it is not surprising that ethinylestradiol did not dissipate during the ASR period.

Ibuprofen was found at 11, 28, and 19 ng/L in the ASR well after 5 months, 13 months (3 weeks into recovery), and 18 months (3 months into recovery) of storage, respectively. At the 4-m observation well, corresponding concentrations were <1, 87, and 18 ng/L, respectively. At the 50-m observation well, corresponding concentrations were 32, 182, and 23 ng/L, respectively. Increasing concentrations at the farthest monitor well suggest possible recovery of poorer quality water stored in earlier cycles.

Iopromide climbed steadily during recovery from the ASR well, after initially dropping from 183 ng/L in the recharge water to 7.3 ng/L after 4 months of storage at the ASR well. Higher concentrations were observed with increasing distance from the ASR well and also with increasing time during recovery. This compound has poor biodegradation, oxidation, and sorption characteristics. The increasing concentrations suggest blending during recovery with previously stored water of poorer quality.

Gemfibrozil was found at concentrations of 3.9, 95, and 44 ng/L in the ASR well after 5 months, 13 months (3 weeks into recovery), and 18 months (3 months into recovery) of stored water, respectively. At the 4-m observation well, corresponding concentrations were <1, 109, and 44 ng/L, respectively. At the 50-m observation well, corresponding concentrations were 756, 836, and 151 ng/L, respectively. Once again, concentrations increased with distance from the ASR well and peaked soon after the beginning of recovery, suggesting recovery of previously stored water with higher concentrations of this compound.

Several microcontaminants were found in similar concentrations in the recharge and recovered water samples. **TCEP** was found at 151 ng/L in the recharge water. It was found at concentrations of 219, 293, and 184 ng/L in the three wells after 5 months of storage. After 13 months of storage, including 3 weeks of recovery, the concentrations for the same three wells were 258, 222, and 156 ng/L, respectively. After 18 months of storage, including 3 months of recovery, the concentrations were 78, 74, and 46 ng/L, respectively. After adjusting these last values according to the chloride dilution ratio, it appears that no significant attenuation is occurring. Possibly, sorption–desorption is occurring or, alternatively, the recharge water quality is highly variable.

A summary of the overall trends observed for both analytical approaches is presented in Table 5.11. In some cases Approach A gives an opposite result to Approach B. As described previously, Approach A compares recovered water quality to recharge water quality, implying that the recharge water sample is representative of all recharge water quality at that general time and shows no hourly variability. Approach B accepts that hourly variability in recharge water quality may, in fact, be occurring, and so the recharge water quality analysis is discounted. Instead, a comparison is made between successive recovered water samples at the same well or between recovered water quality samples at adjacent monitor wells. Further research will be required to ascertain the reasons for the different conclusions based upon the two analytical approaches. One interpretation may be that recharge water quality is highly variable for many of the microcontaminants. Another interpretation is that subsurface physical, microbial, and geochemical processes occurring during ASR storage are not well understood. A plausible hypothesis is that both of these interpretations are correct.

Table 5.11. Microcontaminant Trends Observed by Data Analysis Approaches A and B^a

Microcontaminant	Chandler	Englewood	Manatee ^b	Bolivar
Acetaminophen		A – increased B – decreased		A – increased B – increased
Androstenedione				A – ambiguous B – ambiguous
Atrazine		A – decreased B – decreased	A – decreased	A – decreased B – decreased
Caffeine	A – ambiguous B – decreased			A – ambiguous B – ambiguous
Carbamazepine	A – ambiguous B – decreased	A – increased B – decreased	A – no change	A – increased B – decreased
Chlorate	A – decreased B – decreased	A – decreased B – no change	A – decreased	A – ambiguous B – ambiguous
Diazepam		A – decreased B – no change		A – ambiguous B – ambiguous
Diclofenac		A – increased B – no change		
Dilantin	A – increased B – decreased	A – decreased B – no change	A – no change	A – ambiguous B – decreased
Erythromycin-H2O	A – ambiguous B – decreased	A – increased B – increased	A – no change	A – increased B – ambiguous
Estriol				A – decreased B – ambiguous
Estrone		A – increased B – increased		A – decreased B – decreased
Ethinylestradiol				A – ambiguous B – ambiguous
Fluoranthene	A – decreased B – decreased	A – no change B – no change		
Fluoxetine	A – decreased B – N/A	A – increased B – no change		
Gemfibrozil	A – increased B – decreased	A – increased B – increased	A – increased	A – increased B – ambiguous
Hydrocodone	A – ambiguous B – ambiguous	A – no change B – decreased	A – no change	
Ibuprofen	A – increased B – decreased	A – ambiguous B – decreased	A – no change	A – ambiguous B – ambiguous
Iopromide	A – decreased B – decreased	A – increased B – no change	A – increased	A – ambiguous B – ambiguous
Meprobamate	A – increased B – decreased	A – no change B – no change	A – no change	
Naproxen	A – increased B – decreased	A – increased B – increased	A – increased	
Pentoxifylline	A – ambiguous B – decreased	A – increased B – no change		
Perchlorate	A – decreased B – decreased			
Sulfamethoxazole	A – increased B – ambiguous	A – increased B – decreased	A – increased	
TCEP	A – increased B – decreased	A – decreased B – decreased		A – ambiguous B – decreased
Triclosan		A – increased B – no change		
Trimethoprim	A – increased B – increased	A – increased B – decreased	A – increased	

^aResults from data analysis Approaches A and B are presented where applicable.

^bAnalytical Approach B was not applicable to Manatee data because only one recovery sample was collected.

CHAPTER 6

DISCUSSION AND CONCLUSIONS

6.1 GENERAL FINDINGS

By observing changes in concentrations of over 90 compounds at four ASR sites with many variables, this study intentionally took a broad assessment of water quality changes in reclaimed water ASR storage. Four operating reclaimed water ASR sites were investigated to determine the changes in water quality occurring during ASR storage. Conditions at each site covered a broad range of conditions, including the following:

- Lithologies (consolidated carbonates and unconsolidated alluvium)
- Salinities (fresh, slightly brackish, or very brackish)
- Aquifer redox states
- Temperatures
- Nutrient status of injected water
- Storage periods (from 2 weeks up to 18 months)
- Locations and possibly different patterns of microcontaminant usage (Arizona, Florida, and South Australia)
- Operational histories (no prior use of the well, many years of prior recharge of high-quality reclaimed water, prior recharge of irrigation-quality reclaimed water)
- Range of sampling points, with some sites sampling ASR wells alone and others sampling ASR wells and also monitoring wells

6.1.1 Redox State

The study found that the accuracies of field measurements of DO and ORP were generally poor and suggests that in the future efforts should be made to improve the characterization of redox conditions. This is especially important given that these conditions have been found to have an important influence on degradation of some organics in aquifers, for several EDCs (Ying et al., 2003, 2004) and for trihalomethanes (Pavelic et al., 2005, 2006a). While anoxic and low-redox conditions are reasonably expected to occur in the storage zone at all four reclaimed ASR sites due to the abundance of carbon and nutrients and the aquifer confinement, the field data fail to show this, probably due to the sampling methods that were utilized at some sites for these two field measurements.

6.1.2 Proximal Zone Activity

TOC, pH, and nutrient reductions observed in this study generally supported the theory that notable microbial and chemical activities occur in the proximal zone. It is therefore recommended that further study focus on an improved definition of redox state, and also the sorption–desorption and biodegradation reactions occurring close to the ASR well, within a radius of 30 m as a typical range for the enhanced activity (proximal) zone. It is also recommended that microbiological expertise be brought into these experiments to characterize the activities of microbial assemblages capable of degrading these microorganisms and to test the adaptation of indigenous communities exposed to

microcontaminants, even exploring the motility of these, and whether this is a further barrier to the zone in which degradation occurs.

There is some evidence that certain pollutants degrade in anaerobic aquifers between recharge and recovery, such as TTHMs and HAA5. While these disinfection byproducts were not the subject of the present study, their attenuation during ASR storage is well documented (Dillon et al., 2005; Pyne et al., 1996). These species may be contained close to an ASR well, and their concentrations may be reduced or eliminated before they have an opportunity to migrate away from the ASR site. For this group, ASR may be considered as part of a treatment train, in addition to providing seasonal and long-term storage.

6.2 MICROCONTAMINANTS

A large emphasis was placed on the microcontaminant portion of this study, which attempted to use the physical characteristics of a strategically selected group of contaminants to inform removal mechanisms in the aquifer. The sampling and analysis program quantified concentrations of trace organics in recharge water, recovered water, and monitoring well samples based on a minimum number of samples. The number of samples required at any one site to statistically support attenuation rates and condition correlations would have been 1 to 2 orders of magnitude higher than could be supported by the scope of the current project.

6.2.1 Recharge Water Variability

Recharge water variability presented a challenge in data interpretation. Six of 39 microcontaminants were not found in a single sample of source water at 5 times the detection limit; however, of these six, four were detected at >5 times the detection limit on recovery. (Only chlorpyrifos and estradiol were undetected in recharged or recovered water.) Of detections in recovered water, 46% showed an increase in concentration of more than 30%, 27% of detections showed a decrease of more than 30%, 13% were considered stable, and for 13% the trend was not easily categorized.

It is considered highly unlikely that these specific analytes are degradation byproducts of each other or of other effluent-derived organic matter. The findings more likely indicate highly variable concentrations of EDCs and PPCPs in reclaimed water and that the four single samples of recharge water may have been atypical of the recharge that was subsequently recovered during periods of sampling of recovered water, even though the timing of samples was designed to maximize the possibility of correlating recharge and recovered analyte concentrations. Monitoring well data at sites where these were sampled were also inconsistent with source water and recovered water concentrations, which indicated variability of input concentrations as the largest factor affecting measured concentrations in monitoring wells and in recovered water. The increased concentrations in recovered water may have resulted from compounds that were present at intermittent concentrations in the recharge water accumulating near the well and desorbed during recovery.

6.2.2 Observed Microcontaminant Trends

The atrazine concentration decreased at the three sites where it was detected. Chlorate was reduced at three sites compared to recharge concentrations but exhibited ambiguous results at the Bolivar site, over the longest storage period. Discounting recharge concentrations and comparing recovered water samples only (Approach B), TCEP decreased at the three sites where it was detected.

For at least two sites, six microcontaminants had concentrations in recovered water that were 30% higher than in recharge water: carbamazepine, gemfibrozil, ibuprofen, iopromide, NDMA, and sulfamethoxazole. Possible causes of temporary increases in microcontaminant concentrations in recovered water have been speculated. These include recovery of colloidal organic material entrapped in the aquifer close to the ASR well, where microcontaminants sorb to these organic colloids and to the biofilm in the aquifer in the vicinity of the ASR well during the injection cycle. Another possibility is desorption, i.e., mobilization of microcontaminants from the immobile phase to the soluble phase as a result of pH, Eh, or temperature change in water that is returning to the injection well as the result of a radial gradient in the aquifer. However, it is expected that the first mechanism (colloid recovery) would occur only very early in the onset of the recovery cycle (i.e., a spike), as we expect particulates to have accumulated very near the well. The first recovered water samples were taken at least 5 days after the start of recovery, and so it is highly unlikely that this first mechanism would be responsible for the increases observed. The second mechanism (desorption) is also likely to occur primarily early in the recovery cycle, as we don't expect strong pH gradients to occur and persist through the storage phase at any distance from an injection well. Three of the four ASR wells have storage zones in carbonate aquifers where pH buffering occurs, and desorption due to pH change is therefore less probable at such sites. Temperature gradients may be quite persistent in aquifers following ASR (Pavelic et al., 2006b), but it is doubtful that these could be sufficient to cause enough change in the adsorption isotherm to facilitate measurable desorption. The times of sampling of recovered water in the recharge and recovery cycles also suggest that temperature gradients were unlikely to influence microcontaminant concentrations in recovered water samples.

6.3 RECOMMENDATIONS FOR FUTURE RESEARCH PROJECTS

The data compilation shows that residence times and degradation rates in the aquifers were insufficient to support a claim of biodegradation of trace organics to a degree that would eclipse source concentration variability at the four sites. A substantially larger database would be required to establish degradation rates of microcontaminants within the aquifers in field experimental programs.

Field investigations should focus on an improved definition of the redox state and sorption-desorption and biodegradation reactions occurring close to the ASR well, within a radius of 30 m. Monitor wells, cores, microbial diffusion chambers, and other tools will be needed to document reactions occurring in the field. Performance of these field investigations at existing ASR sites that have been in operation for several years may be quite useful. Field investigations should include intensive, frequent water quality sampling during short pumping tests, after extended storage periods, so that the water sampled is representative of that stored in the aquifer close to the well. Changes in pH, Eh, turbidity, and other constituents during this period can shed light on conditions occurring close to the well in the aquifer.

It is recommended that microbiological expertise be brought into these experiments with a view to characterizing the activity of microbial assemblages capable of degrading these microorganisms and to test the adaptation of indigenous communities exposed to microcontaminants, even exploring the motility of these, and whether this is a further barrier to the zone in which degradation occurs.

Degradation studies by necessity involve time series of water analyses. That is, costs will be significantly higher than the current broad-suite snapshot sampling and analysis program.

While it is desirable to conduct this type of testing at several field sites, it is strongly recommended that these studies be done in parallel with laboratory experiments using aquifer materials, with inoculation and acclimation of indigenous microorganisms taken from an ASR well and maintaining environmental conditions exactly as in the aquifer. The first step is to derive adsorption and biodegradation rates for the range of aquifer conditions, in the presence of reclaimed water, which may provide a cometabolism pathway for trace organics degradation. To simplify experiments, it is recommended that several of these be run in nanogram per liter and microgram per liter concentration ranges in order to differentiate and relate effects at these contrasting levels. If suitable constructs emerged, then a much wider array of experiments could be performed at the higher concentration range with reduced analytical difficulty. Use of passive samplers, e.g., the methods of Komarova et al. (2006), may facilitate measurement of mass fluxes of trace organics but would need validation of their effectiveness in integrating fluxes in temporally variable concentrations.

6.4 FEASIBILITY OF RECLAIMED WATER ASR

For indirect potable reuse via ASR, even though this report does not provide a sufficient justification of credit for micropollutant attenuation in ASR, there is strong evidence of TOC reduction, and this may be a major advantage for subsequent GAC or reverse osmosis treatment. This is an additional benefit to the initial purpose of ASR in providing storage to minimize variability in supply and demand.

For anticipated uses of recovered reclaimed water in landscape and agricultural irrigation, microcontaminants in recovered water are expected to be of relatively limited interest. Of more importance will be the quality of stored reclaimed water moving away from the ASR well that leaves the ASR system and becomes part of the available groundwater resource. It is therefore appropriate to address the quality and quantity of this recharge water that may ultimately be recovered at another distant well.

6.4.1 Effects on Groundwater

For the fewer than 5% of ASR wells that store reclaimed water, experience to date in Arizona, Florida, Texas, and Australia suggests that, for most wells, a greater volume has been stored than has been recovered. For Arizona, this reflects the water rights regulatory framework, which promotes aquifer recharge by providing credits for long-term storage. For Texas, the objective is aquifer recharge and subsurface water treatment during aquifer conveyance to distant water supply wells, and so local recovery is limited to that occurring during periodic backflushing operations. In Florida, the objective has been both seasonal and long-term storage in brackish aquifers. Demand for reclaimed water typically lags behind the supply for several years, requiring long-term storage. For Australia, the Bolivar ASR demonstration program has recovered approximately one-half of the reclaimed water that it has stored to date. These sites are all early in their long-term operational development, moving in the direction of recovering essentially all of the stored water. Nevertheless, a small percentage of the stored water will remain underground and will therefore move with the natural subsurface hydraulic gradient.

The quantity of this locally “unrecovered” water will depend upon the design and operation of each individual ASR well. In general, most ASR wells store and recover approximately the same volume of water on each operating cycle. For some ASR wells in brackish aquifers, or other aquifers containing poor water quality, this point may be reached after a few years of early operations during which a buffer zone is steadily formed around the well, separating the

stored water from the surrounding poor quality water. Once the buffer zone is formed, by leaving a percentage of the stored water underground during each operating cycle, then subsequent operations are typically at approximately 100% recovery. This has been the historic approach to ASR development. For other ASR wellfields, the buffer zone is formed at one time, prior to the beginning of operations, so that full recovery efficiency occurs from the beginning. This is the preferred and recommended approach to ASR development. At a small number of sites, no buffer zone is required, since the difference between the stored water quality and the ambient groundwater quality is negligible.

Probably at least 80% of ASR wells tend to utilize deep, confined, or semiconfined aquifers for storage, in which typical groundwater velocities are on the order of a few feet to a few tens of feet per year. For these ASR wells, the quantity of stored water that is not recovered is typically insignificant. Some ASR wells, particularly in southwestern states, use unconfined aquifers for ASR storage. In these aquifers groundwater velocities tend to be more rapid. For long-term storage extending over several years, subsurface movement of the stored water may carry it away from the ASR well a sufficient distance that it cannot be recovered, except to another downgradient production well. Whether due to mixing, dispersion, or advective movement of the regional groundwater flow, some of the stored reclaimed water will become part of the available groundwater resource. The time required for this to occur will typically be months to years, during which natural mobilization and attenuation processes will occur in the subsurface, as discussed in this report.

6.4.2 ASR as an Additional Treatment Process

Although ASR is primarily a storage option, the data obtained during this investigation suggest that, for some microcontaminants, additional natural treatment may occur during ASR storage. The available data are too limited to support statistically valid conclusions regarding the range and effectiveness of this natural subsurface treatment; however, with further research, it will be possible to better define the subsurface processes and associated treatment effectiveness. For almost all reclaimed ASR sites, the eventual recovery of any recharge water from a distant production well, instead of from the ASR well, will be accompanied by above-ground treatment that will be required if the water is to be used for drinking. In brackish and many other aquifers, this process may include membrane treatment. In fresh aquifers where no treatment, other than disinfection, may be provided prior to potable water use, it is appropriate to focus attention and further research upon the fate of microcontaminants of wastewater origin upon groundwater quality and the role of ASR, among several other barriers, to protect public health and groundwater quality, in addition to its role of providing water storage.

If ASR is considered when designing water reclamation treatment facilities, it may be possible to optimize the treatment design, taking into account the effectiveness of treatment in the subsurface. For example, pathogen removal has been demonstrated, and avoidance of chlorination will avoid formation of disinfection byproducts, some of which are very persistent in aerobic aquifers. In the case of microcontaminants, it is likely that there is no single set of aquifer conditions that will remove all species of interest; however, a redox zone contrast within the aquifer may broaden the number of microcontaminants that can be removed during ASR. Relying on the ASR to treat those contaminants that are readily degraded in aquifers will allow tailoring of engineered pretreatments to remove the contaminants that are recalcitrant in aquifers and may provide a better planned approach to the use of ASR for both storage and treatment in water reuse, without adversely affecting

public health or groundwater quality at short distances from the ASR well, outside the attenuation zone.

Finally, the opportunity exists to compare the results of this research project with the results from a parallel, similar project recently completed by Kiwa in the Netherlands. Such a comparison may shed light on the complex interrelationship of subsurface physical, geochemical, and microbial processes during ASR storage, as well as on the variability in recharge water quality, particularly for trace constituents.

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APPENDIX A

SUPPLEMENTAL INFORMATION ON RECLAIMED WATER ASR PROJECTS

Profiles of Reclaimed Water ASR Operations

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FOUNTAIN HILLS, AZ

Background

The Fountain Hills Recharge Facility consists of a wastewater treatment plant, an advanced water treatment plant (AWTP), four ASR wells (three operational and one waiting for permitting), monitoring wells, and a storage lake. The wastewater treatment plant is permitted by the Arizona Department of Environmental Quality to produce an annual average of 2.6 mgd but currently produces only 1.85 mgd on an annual average basis. Water is treated to Arizona Class A+ standards and transported to an underground storage tank before being pumped to the AWTP for further treatment by microfiltration. Subsequently, this water is stored in a below-grade holding tank prior to use as injection source water for the ASR wellfield.

Project Purpose

In Fountain Hills, most of the 14.5 in. of average rain each year falls during July and August, with lesser amounts falling in late spring and early summer. In this semiarid climate, conservation of water resources is a priority. Additionally, difficulties in disposing of the volume of reclaimed water produced by the Fountain Hills Sanitary District (FHSD) led to the exploration of alternative uses of this resource. Initially, excess reclaimed water was dispersed to vacant lands seeded with desert grasses. Another option considered was to create a reclaimed water recharge facility to store water during the winter (when the population increases due to seasonal residents) for use in the summer months to irrigate recreational areas, such as golf courses. After successful preliminary testing of a retrofitted production well, FHSD proceeded to test a pilot-scale recharge facility that consisted of an AWTP and an injection wellfield.

Project Description

The complex geology in the Fountain Hills area is a result of the transition zone between the Basin, Range, and Central Highlands physiographic provinces. The subsurface geology of the area includes a succession of tertiary sedimentary deposits, with a thin unconsolidated basin fill deposit primarily comprised of silt, sand, and gravel, the Pemberton Ranch Formation, consisting of up to 400 ft of clay, and a fractured conglomerate, all of which comprise the regional aquifer.

From November 1999 to March 2002, FHSD constructed four ASR wells and five monitoring wells for the Fountain Hills Recharge Facility along with three exploration or test wells. Two of the test wells were constructed by modifying dormant production wells. Three of the ASR wells are operational, and the fourth is currently in the process of being permitted. Each well is approximately 750 ft deep and constructed with 14-in. stainless steel casings, including about 200 ft of full-flow louvered casing, which opens to the aquifer. All control and metering devices are housed in a large vault system above the well. Each well has a submersible pump and a downhole control valve for injection. Each well also has remote control access from the AWTP.

Injection rates for these wells range from approximately 150 gal per min (gpm) to 400 gpm. During summer months, well production ranges from 500–600 gpm.

Planned Expansions

Individual well performance testing, increased monitoring of well plugging through periodic monitoring of water levels, flow rates, and water quality are being considered to improve the longevity of the ASR wells and to maximize their recharge capacities. Two additional wells are proposed in order to meet the maximum scheduled recharge allowance of 3.2 mgd. Existing production wells will be modified to provide these new ASR wells.

Source

Huber, R.; Geiger, K. E.; Bushner, G. *Fountain Hills Sanitary District: from Disposal to Recharge, a Long Term Solution for the Town of Fountain Hills*; 11th Biennial Symposium on Groundwater Recharge, Phoenix, AZ, 2003.

SCOTTSDALE, AZ

Background

Due to the heavy demand on groundwater resources in Arizona, the State enacted the Groundwater Management Act in 1980, which required high-volume users of groundwater to balance groundwater withdrawal and recharge by the year 2025. In response, the City of Scottsdale, a rapidly growing desert community with limited surface water supply, began construction of its Water Campus in October 1998.

The water and wastewater treatment complex includes a 54-mgd surface water treatment plant, a 12-mgd reclamation plant, and a 10-mgd advanced water treatment plant. There is also a 21-mgd recharge facility that consists of a permeate stabilization process and 27 vadose zone injection wells. Six monitoring wells have also been constructed. The complex was designed to operate at a capacity of 24 mgd (based on flow projections through the year 2040).

The treatment scheme at the water reclamation plant includes preliminary screens, primary clarification, secondary biological treatment, filtration through deep bed monomedia (anthracite), and disinfection with chlorine gas. Effluent from the plant is distributed to 17 golf courses in the North Scottsdale area. The advanced wastewater treatment plant was designed to further treat excess effluent from the reclamation plant during the wet season. During the dry season, water is taken from the Colorado River, treated, and recharged into the wells. The advanced wastewater treatment plant employs microfiltration followed by reverse osmosis. Water from the advanced wastewater treatment plant is chemically stabilized and discharged first to a pumping station and then into the vadose wells.

Project Purpose

The goal of this project was to use aquifer recharge to prevent regional aquifer depletion.

Project Description

There are 27 standard and 28 emergency vadose injection wells on the property. Emergency wells are used during the wet season, when the reclamation plant is hydraulically overloaded. For each well, a 4-ft-diameter hole was bored into the ground to a depth of 180 ft. A fiber “sock” was then inserted into the hole and filled with 1/2–3/4 in. of gravel. The fiber provides

a barrier between the gravel and the soil. A 6-in. PVC inductor penetrates the gravel pack to a depth of 20 ft. Additionally, three PVC vent tubes, which reach to a depth of 140 ft, release trapped air from the gravel pack.

The standard wells are designed to have more control and monitoring capabilities. The 6-in. inductor pipe is made of steel and is enclosed in a 10-in. PVC line. The inductor and PVC line travel to 180 ft below land surface, where the water is disposed into the vadose zone. Each standard well has a flow meter, pressure transducer for level and line pressure, and an automatic valve actuator on the feed line. Twenty-two of the 27 wells have a fixed orifice plate at the bottom of the inductor. The remaining wells have a variable orifice valve that can be automatically controlled to maintain line pressure in the manifold system to the wellfield. The design intent was to maintain a constant flow rate of 450 gpm with a water level of 80 ft below land surface.

Planned Expansions

The Water Campus is ready to upgrade their reclamation facility from 12 mgd to 20 mgd. During this expansion, disk filters will replace anthracite filters, backup power will be added, and process treatment trains will be converted to unit processes to better utilize equipment and capacity.

The associated master plan also calls for additional recharge wells, though no initiative has yet been taken to begin this expansion. There are no future construction plans at this point.

Source

Nunez, A., Water and Wastewater Treatment Manager for the City of Scottsdale.

EL PASO, TX

Background

The Fred Hervey Water Reclamation Plant (FHWRP), part of the Public Service Board's Water Resource Management Plan, is owned and operated by El Paso Water Utilities. The facility began operations in 1985 to recycle wastewater from the northeast area of El Paso for recharge of the Hueco Bolson aquifer. This project was the first reclaimed ASR project in the United States. The facility was designed to treat approximately 10 mgd of tertiary treated reclaimed water. Currently, this facility produces 5.2 mgd. The treatment process includes lime treatment, filtration, ozone disinfection, and anaerobic digestion. In 2003, reclaimed water was injected into wells (501 MG) and distributed to spreading basins (317 MG), power plants (817 MG), and a golf course (235 MG).

Project Purpose

The City of El Paso depends on the El Paso River for about 40% of its drinking water and relies on the Hueco Bolson aquifer for the remainder. Given that El Paso uses approximately 100 MG of fresh water per day, it was critical to find a water source that allowed for the preservation of the aquifer (which supplies both El Paso, TX, and Juarez, Mexico) without introducing water shortage issues. The FHWRP reclaimed water ASR project will aid in satisfying this requirement. It is estimated that for every 10 years that the FHWRP operates, the life of the Hueco Bolson Aquifer is extended by 1 year.

Project Description

Overall, the recharge system includes an advanced wastewater treatment plant, a pipeline system to the injection site, and 10 injection wells that reach the area's deep water table, which lies approximately 350 ft below the ground surface. Following injection, the recharge water travels approximately 3/4 of a mi through the aquifer to production wells for municipal water supply.

Initial problems with this project did occur. Corrosion and plugging of the injection wells were experienced but resolved by redrilling the wells. Additionally, the pipeline leading from the treatment plant to the ASR wells corroded from electric fields emitted by cathodic protectors associated with natural gas lines in the area. To mitigate this problem, the pipeline was replaced with PVC.

Planned Expansions

Expansions are being planned for the future of this plant, and additional reclaimed water customers are being sought.

Source

Ornelas, D., Environmental Compliance Manager, El Paso Water Utilities.

COCOA, FL

Background

The City of Cocoa's Advanced Wastewater Treatment Facility uses chlorine disinfection and produces 2.5 mgd of reclaimed water. The primary end use of the reclaimed water is irrigation, mainly at individual residences in Cocoa. Similar to many areas in the state of Florida, seasonal droughts are experienced and supplemental sources, such as stormwater ponds, are used during peak demand days. A drawback of stormwater ponds is the tendency for water to drain into surrounding surface waters, inhibiting storage for later use. The City of Cocoa chose reclaimed water ASR as an alternative for storage of reclaimed water during peak water supply days.

Project Purpose

The goal of this project was to provide additional storage of reclaimed water for future use during droughts.

Project Description

A Phase I feasibility study has been completed for the City of Cocoa. This extensive study included site selection for the ASR well and monitoring wells, preliminary well construction specifications, preliminary modeling of reclaimed water injection and recovery, and recommendations for an alternative storage and recovery system.

Phase II, which includes drilling an exploratory deep monitoring well to evaluate aquifer and groundwater characteristics, was scheduled to begin during late summer 2004. This exploratory well will be designed to reach approximately 1700 ft below sea level. The well

will be approximately 8 in. in diameter and cased to a depth of 100 ft. The exploratory well likely will be converted to a monitoring well for the lower Floridan Aquifer following Phase II.

Planned Expansions

If current permitted capacity of reclaimed water production is not reached with the initial ASR well, then plans for expansion will be developed.

Sources

Marty Sullivan, Andreyev Engineering, Inc.

Steve Harrell, Superintendent, City of Cocoa Water Reclamation Facility

NORTHWEST HILLSBOROUGH COUNTY, FL

Background

The Northwest Hillsborough County reclaimed water program is comprised of four wastewater treatment facilities: the Northwest Regional Water Reclamation Facility, River Oaks Wastewater Treatment Plant, Dale Mabry Wastewater Treatment Plant, and Van Dyke Wastewater Treatment Plant. All treatment facilities, with the exception of Van Dyke, are advanced wastewater treatment plants (i.e., biological nutrient removal plus sand filtration and extended disinfection processes). Reclaimed water from these facilities is sent to storage tanks until distribution. The Van Dyke Wastewater Treatment Plant utilizes standard wastewater treatment (i.e., advanced secondary treatment plus disinfection). Additionally, effluent from River Oaks Wastewater Treatment Plant and the Northwest Regional Water Reclamation Facility is sent to a dechlorination facility prior to distribution. A proposal to connect all treatment facilities has been developed.

End users of reclaimed water in Northwest Hillsborough County include residential, recreational, and industrial customers. Excess water, amounting to 7–8 mgd depending on the season, is discharged to an adjacent channel at the County's Northwest Dechlorination Facility. Since it is anticipated that demand will exceed supply during a typical dry season by the year 2005, a solution needs to be developed to capture excess water usually discharged.

Project Purpose

The goal of this project is to maximize the use of reclaimed water and minimize groundwater withdrawals in addition to minimizing the discharge of excess reclaimed water to Tampa Bay.

Project Description

Northwest Hillsborough County completed a feasibility assessment in 1996 and applied for a permit to drill a Class V, Group III test injection well in February 1997. The test production well was completed in 1998 and was located at the dechlorination facility. The test production well consisted of casing to a depth of 305 ft below sea level with an open hole interval to a depth of 415 ft below sea level. The storage capacity of this well was 0.75–1.5 mgd. The proposed storage zone, which is in the Upper Floridan Aquifer system (Lower Suwannee Limestone, located 300–400 ft below sea level), is a brackish aquifer containing

groundwater with an estimated 1200–1500 mg of TDS/L. Five monitoring wells were also constructed, three on-site and two off-site. The on-site storage zone monitoring well, shallow monitoring well, and water table monitoring well were drilled to depths of 415, 170, and 30 ft below land surface, respectively. The off-site deep monitoring well and water table monitoring well were drilled to depths of 430 and 30 ft below land surface, respectively.

In October 2001, Cycle 1 testing of the test production well was completed. The purpose of this testing was to evaluate the ability of the well to store reclaimed water in the aquifer and recover a substantial percentage of it for beneficial reuse. Initially, 30 MG of reclaimed water was recharged into the well in July 2001. Thirty million gallons was then recovered in August 2001. Data were collected weekly from the test production well, and the only trend observed was a rapid increase in conductivity (low recovery efficiency), suggesting that unforeseen geologic conditions and close proximity of the saltwater interface may have impacted recovery efficiencies due to upconing of salt water from beneath the ASR storage zone, through the underlying confining layer. Data were also collected at the monitoring wells. Reclaimed water was not detected in any of the monitoring wells. All primary drinking water standards were met at the wells prior to recharge.

Three additional cycle tests were completed by May 2003 to further define the system response in addition to providing criteria for cycle testing modification. The Southwest Florida Water Management District and the FDEP have requested that more cycle testing be performed and that two additional monitor wells be constructed on-site.

Planned Expansions

Eight additional wells were proposed in Northwest Hillsborough County, depending on the outcome of additional testing on the first well. However, results of preliminary cycle tests indicated that saline encroachment from below the storage zone impeded recovery efficiencies. Subsequently, the County submitted a plugging and abandonment request to FDEP and have received approval to abandon the ASR test well at the NW Regional WRF. These new wells will not be located at the dechlorination facility due to space limitations. Other county properties along Channel A have been listed as potential sites.

Source

Ed Fox, Hillsborough County

SOUTH/CENTRAL HILLSBOROUGH COUNTY, FL

Background

The South/Central Hillsborough County area consists of three advanced wastewater treatment facilities: Valrico, Falkenburg, and South County. The South County facility also houses a dechlorination facility. Due to high water demand, surface discharge of excess reclaimed water rarely occurs at the South County facility. Excess reclaimed water from the Falkenburg facility may be discharged into an adjacent river or pumped to the dechlorination facility at the South County facility. Reclaimed water from the Valrico facility is discharged into an adjacent creek when not needed. Estimates show that by the year 2020, these facilities will generate approximately 26 mgd of reclaimed water. The concept of interconnecting the treatment facilities and developing a successful reclaimed water ASR program is estimated to result in 100% reuse.

Project Purpose

The goal of this project is to achieve 100% reclaimed water reuse throughout the entire year and to minimize or eliminate discharge of reclaimed water to surface water bodies.

Project Description

Feasibility assessments were completed in 1995. During that time, it was proposed that the test production ASR well be constructed in the Big Bend area (dechlorination facility at the South County Advanced Wastewater Treatment Plant). The target ASR zone is brackish, with an estimated TDS concentration of 1000 mg/L to 3000 mg/L.

In 2000, Hillsborough County applied for and received a construction permit. Since then, the test production well (Class V, Group 3) and associated monitoring wells have been constructed. The total depth of the test production well is 500 ft below land surface, with a 16-in. steel casing to a depth of 400 ft. Currently, details on the construction of the wellhead facility are being developed which, when complete, will allow for the inception of cycle testing. During cycle testing, water from the Falkenburg facility will be pumped to the Big Bend area for use.

The County has currently placed the project on hold pending discussions with regulatory agencies regarding public concerns, testing programs, and monitoring criteria.

Planned Expansions

It is proposed that seven additional ASR wells be built at the dechlorination facility along with six wells at a different location, providing 14 mgd of total capacity. The expansion program will be contingent upon the success of the initial ASR testing program and resolution of public and regulatory concerns.

Source

Ed Fox, Hillsborough County

CLEARWATER, FL

Background

The initial proposed ASR project was a joint venture between the municipalities of Largo and Clearwater, FL, as well as the Southwest Florida Water Management District, who provides funding. The intention was to create reclaimed water storage capacity by providing each city with ASR wells using piping networks to interconnect the various wastewater treatment plants and ASR wells in the cities to facilitate subregional management of reclaimed water. Subsequent to the completion of the feasibility study completed for both cities, the City of Largo elected not to continue with the joint venture ASR program; therefore, the city of Clearwater will be the only municipality pursuing the construction of a reclaimed water ASR test well. The ultimate goal is to ensure sufficient annual supply to meet demands, facilitate expansion of the reuse system, and minimize or eliminate surface water discharge of treated wastewater. In addition, the project investigated options for extending a reclaimed water main to Pasco County for the development of a true regional reclaimed water and ASR system.

Project Purpose

Year-round availability of reclaimed water is the primary factor driving the City's exploration of ASR technology. By metering reclaimed water use, imposing watering restrictions, and building ASR wells, the City hopes to expand its residential reclaimed water customer base to 10,000 homes.

Project Description

The feasibility study for the City of Clearwater has been completed, and an appropriate test well site has been identified based on regional hydrogeology, ambient ground water quality, reclaimed water availability, reclaimed water demands, reclaimed water quality, competing groundwater users, and constraints for a test well site. Two sites were initially recommended as potential locations for an ASR test well: one at the City's Northwest Wastewater Reclamation Facility and the other near a 3-MG above-ground storage tank. At both sites, the targeted storage zone is the water-producing Lower A zone of the Suwannee Limestone, which is situated within the Upper Florida aquifer. The ambient water quality of this storage zone is brackish with acceptable levels of TDS for permitting and operations. Competing groundwater users were identified within a 1-mi radius of both potential test sites. No potable wells were identified within 500 ft of either site, though each site has a heavy concentration of shallow wells (i.e., <150 ft) nearby. Based on the study criteria, the City's Northwest Wastewater Reclamation Facility site was identified as the most appropriate, since it allows greater operational control over the ASR test well system and allows greater flexibility for adjusting the treatment system to produce reclaimed water that meets all primary drinking water standards. It has been recommended that the next phase of the project begin soon, which will include developing a conceptual design and submitting a permit application for a Class V ASR test well system.

The drilling program was completed. The site was found unsuitable for reclaimed water ASR due to sharp increases in TDS concentrations within a 100-ft interval.

Planned Expansions

The project was terminated based on drilling program test results.

Sources

John Milligan, Clearwater Wastewater Treatment Plant Superintendent
Tom Farkas, P.G., Project Manager, PBS&J

LEHIGH ACRES, FL

Background

The Lehigh Acres Wastewater Treatment Plant currently utilizes approximately 20% of its reclaimed water, mainly for irrigation of citrus groves and golf courses. The remaining 80% is reused through a system of rapid infiltration basins. Florida Water Services (FWS), who initially owned the Lehigh Acres Wastewater Treatment Plant when feasibility and permitting occurred for reclaimed aquifer storage and recovery, identified the increasing need for reclaimed water in the area. As a result, FWS planned an expansion to provide service to more customers. Additionally, FWS identified the need for increased levels of reclaimed

water management and banking for future use, which they hoped to achieve through reclaimed water ASR. The Lehigh Acres Wastewater Treatment plant has subsequently been purchased by the Florida Government Utility Authority (FGUA).

Project Purpose

The goal of this project is to maximize the capacity and reliability of the reuse system by providing seasonal storage that will allow for 100% use of reclaimed water in the future. The ASR technology will also promote banking of reclaimed water to facilitate reclaimed water expansion.

Project Description

Phase 1 feasibility studies were completed in April 1999, and the FDEP ASR test well construction permit was issued in March 2001. Nothing has been built to date, due primarily to the fact that the FGUA bought the Lehigh Acres Wastewater Treatment Plant. FGUA is currently reviewing wastewater practices at the Lehigh Acres Wastewater Treatment Plant to determine how best to proceed with the project. Approximately 2 years remain on the FDEP construction permit.

The basic design for the ASR facility includes a 16-in. ASR test well that will reach a depth of 800 ft below land surface. This well is designed to be cased to approximately 520 ft below land surface. Additionally, one 6-in. storage zone monitoring well was designed to be drilled to a depth of 750 ft below land surface, with casing to 520 ft below land surface. In addition, one 6-in. shallow monitoring well was designed to be drilled to a depth of 270 ft below land surface, with casing to 230 ft below land surface. The test well is expected to have a capacity of 2.5 mgd. The target aquifer is the Lower Hawthorn aquifer or Upper Suwannee aquifer. Although the Upper Suwannee is a brackish aquifer, it may be utilized successfully for ASR provided mixing within the aquifer is not excessive and adequate reclaimed water quantities are available.

It was decided that the first test well would be constructed at the Lehigh Acres Wastewater Treatment Plant. Treated water from this plant will meet primary and secondary drinking water standards and will serve as the water for recharge.

Planned Expansions

The permit, received in 2001, is for four wells, two at the Lehigh Acres Wastewater Treatment Plant and two at an additional site approximately 4.5 mi from the plant. The ultimate strategy is to see how the construction of the first well progresses prior to moving forward with the remaining three wells.

Sources

Charles Sweat, P.E., Director of Operations, FGUA
Mike Micheau, P.G., PBS&J

OLDSMAR, FL

Background

The Water Reclamation Facility in Oldsmar, FL, currently produces 1.8 mgd of reclaimed water. This facility utilizes a five-stage Bardenpho process for advanced wastewater treatment and biological nutrient removal, secondary clarification, filtration, and chlorine disinfection. End users of the reclaimed water are residential and commercial customers. During the wet season in Florida, 50–100% of reclaimed water is discharged into Old Tampa Bay. Discharge of excess reclaimed water into surface waters rarely occurs during the dry season. The reclaimed water system currently supplies about 1300 customers, including one major industrial customer. At build-out this is expected to reach 1800 customers.

Project Purpose

The goals of this project are to provide unrestricted public access to reuse water, to reduce potable water use for irrigation, to eliminate or minimize discharge of reclaimed water to Old Tampa Bay during the wet season, to recharge local aquifers, and to provide reclaimed water to adjacent water users.

Project Description

The Phase I feasibility assessment and preliminary design for a reclaimed ASR well at the Water Reclamation Facility were scheduled to begin in December 2004 and to be completed by August 2005. The FDEP serves as the lead permitting agency for this project. The ASR storage zone is expected to be a brackish limestone artesian aquifer at a depth of approximately 75–130 ft. Key regulatory issues are expected to include recovery efficiency, arsenic solution and attenuation, and fate of disinfection byproducts during ASR storage.

Planned Expansions

Results of the Phase I feasibility study and demonstration program will determine whether additional reclaimed water ASR capacity will be considered.

Sources

Tom Friedrich, Jones Edmunds & Associates, Inc.
John Mulvihill, Director of Public Works, City of Oldsmar

PINELLAS COUNTY, FL

Background

The Pinellas County South Cross Bayou Water Reclamation Facility, an advanced wastewater treatment facility, provides South Pinellas County with reclaimed water for industrial, recreational, and residential uses. Influent is treated with sand filters to remove TSS, and chlorine is used for final disinfection. Effluent consistently meets FDEP's standards, including the "5-5-3-1" Grizzle-Fig requirements (5 mg of biochemical oxygen demand/L, 5 mg of TSS/L, 3 mg of nitrogen/L, and 1 mg of phosphorus/L).

Project Purpose

Pinellas County's goal is to utilize ASR wells to supplement their current above-ground storage tanks to eliminate surface discharge of reclaimed water.

Project Description

Pinellas County proposes to use (convert) three Class I injection wells which extend to the Avon Park formation (1080 ft) and have a combined injection capacity of 24–26 mgd. The initial permitting allows the County to back-plug their injection wells and store water for short periods (1 day to several weeks). This is due to the high transmissivity of the Avon Park Formation water. (With further testing, they may even find that they can store water longer). Once the initial operational testing is complete, ensuring that the wells are functional, the County will apply for a permit to convert the injection wells into ASR wells. This approach will offset losses if they have to plug and abandon the wells permanently and will eliminate the need to construct new ASR wells.

Planned Expansions

Since Pinellas County does not have a critical need for additional water storage options, they plan to implement the initial three wells and then explore drilling new ASR wells when they have a better understanding of what water reuse demands might be in the future.

Sources

Dave Slonena, P.G., Pinellas County Utilities
FDEP website (www.dep.state.fl.us)

ST. PETERSBURG, FL

Background

The City of St. Petersburg is currently assessing the viability of using reclaimed water ASR to supplement their reclaimed water systems. Currently, one test ASR well, with a storage capacity of 1–2 mgd, has been constructed at the Southwest Water Reclamation Facility. Wastewater at this facility is treated using filtration and high-level disinfection, and effluent water is used for irrigation by industrial and residential customers. This facility was permitted in 2004 under permit no. 036855-005-UC/MN, which authorized cycle testing.

Project Purpose

The purpose of this project is to develop a supplemental supply using ASR for the City's current reclaimed water system that will prevent dry season shortages and provide wet weather storage.

Project Description

The ASR test well, which consists of a 16-in. steel casing, reaches approximately 550 ft below the land surface into the Lower Suwannee Limestone of the Upper Floridan aquifer system and has an open hole interval extending to 650 ft. Two monitoring wells, one at 538–

548 ft and one at 319–329 ft, have also been built, and the construction of a third monitoring well to 340–350 ft has been permitted.

Planned Expansions

Additional ASR test wells are being considered for installation at other St. Petersburg facilities by 2008. The preliminary conceptual design of the ASR system includes up to seven 1.5-mgd ASR wells to provide a 90–100-day supply of reclaimed water.

Source

Ralph Craig, Plant Manager, Southwest Water Reclamation Facility, City of St. Petersburg

TARPON SPRINGS, FL

Background

The City of Tarpon Springs is currently in the feasibility stage of planning an ASR well at the Tarpon Springs AWTP. This facility is permitted for an annual average capacity of 4 mgd. The system includes the Master Public Access Reuse System and a 2-mgd above-ground storage tank. Currently, 2.4 mgd of reclaimed water is distributed through the Master Public Access System. The balance of the water is used to irrigate Tarpon Springs Golf Course Lake Number One or is discharged to the Anclote River. The City currently uses approximately 60% of its reclaimed water.

Before choosing ASR, other alternatives were explored by the City of Tarpon Springs. The City considered above-ground storage tanks, ground storage reservoirs or lakes, dual-use reclaimed water–storm water ponds, interconnections with adjacent counties, and combinations of the options listed above. It was determined that ASR wells would provide longer-term storage options and therefore minimize surface discharge. ASR also provides the advantages of reducing evaporative water losses and allowing the City to better track and control its resources.

Project Purpose

The purpose of this project is to allow for expansion of the City's reclaimed water system for residential and commercial customers, improve the reclaimed water system reliability, supply, and management, reduce and/or ultimately eliminate reclaimed water surface discharge, reduce costs of purchasing water, conserve fresh water resources, and reduce required capacity and costs of proposed potable water facilities.

Project Description

Because this project is still in the feasibility stage, no designs have been completed at this time.

Planned Expansion

Expansion plans have not been developed, as the site is in the planning feasibility stage.

Sources

Paul Smith, P.E., City Engineer

Raymond Page, Superintendent, Tarpon Springs Advanced Wastewater Treatment Plant

SARASOTA COUNTY, FL

Background

The Central County Water Reclamation Facility (CCWRF) is owned and operated by Sarasota County Utility and is situated in the central portion of Sarasota County, FL. This facility, consisting of advanced secondary treatment with deep bed filtration and high-level disinfection (chlorination), currently produces approximately 4 mgd of reclaimed water. The plant is currently being expanded to a 6-mgd treatment capacity to accommodate the rapid growth being experienced in the north central portion of the county. The CCWRF is one of several WRFs located in the northern portion of the County that are interconnected to provide reclaimed water through an extensive reclaimed water distribution network in the northern reclaimed water service area. Reclaimed water is initially stored at on-site and off-site reuse ponds before being distributed for irrigation of nonagricultural County properties, golf courses, and selected residential communities. Wet weather storage and meeting peak demands during the dry season have hampered expansion of the County's reuse system. In order to address these issues, the County considered the use of ASR technology to remedy the problems.

In July of 1998, the County completed a Reclaimed Water ASR feasibility study, which concluded that reclaimed water ASR was feasible in the north portion of the county and identified an optimum ASR test site at the CCWRF. The County has completed the preliminary design and permitting of a Class V ASR test well at the CCWRF site. A Class V ASR test well construction permit was filed with FDEP in September 1999. Permitting was completed, and a notice of intent to issue was provided by FDEP in July 2001. Following the publication of the notice of intent to issue, a petition in opposition to the issuance of the permit was submitted to FDEP by the Legal Environmental Assistance Foundation (LEAF) and the City of Venice in August 2001. Several meetings were held with both entities in an attempt to address and resolve issues. Following the meetings, the City of Venice withdrew their petition; however, LEAF moved forward with the petition and requested an administrative hearing. An administrative hearing was conducted in August 2002. The result of the administrative hearing was rendered in April 2004 and determined that the County had met all permitting requirements. Several appeals were submitted by LEAF without success. A Class V ASR test well construction permit was issued by FDEP on June 9, 2004 (UIC permit no. 160882-001). Final design and technical specifications have been completed and are currently out for bid. Bids were received and a contract was awarded. Drilling and testing of the ASR test well system is ongoing.

Project Purpose

The purpose of this project was to provide wet weather storage and maximize the use of reclaimed water due to its value as an alternate water supply for irrigation in addition to reducing potable water usage for irrigation. The use of ASR technology will also enhance the overall management of the County's reclaimed water system.

Project Description

Sarasota County received their ASR test well construction permit in June 2004 for construction of the Class V ASR test well system. The proposed ASR test well system consists of one 16-in. ASR test well with a UV disinfection system, one 6-in. storage zone or ZOD monitor well, and two additional 6-in. monitor wells that monitor the zone immediately above the storage zone (lower zone monitor well) and a shallower aquifer unit (upper zone monitor well). The total depth of the ASR test well will be 700 ft and will consist of a 16-in. casing set to a depth of 500 ft below land surface with an open hole extending to a total depth of 700 ft. The storage zone and ZOD monitor well is located approximately 400 ft from the ASR test well and consists of a 6-in. casing set to a depth of 500 ft with an open borehole extending to 550 ft. It should be noted that this well acts not only as the storage zone monitor well but also as a ZOD compliance monitoring point. In lieu of requesting a WQCE for secondary standards that may not reliably meet MCLs, the County and their consultant petitioned FDEP for a ZOD at the CCWRF. The ZOD essentially establishes the compliance of secondary standards at the ZOD well rather than the wellhead, allowing some level of aquifer treatment to occur.

The remaining two monitor wells are located approximately 150 ft from the ASR well. The lower zone monitor well consists of a 6-in. casing set to a depth of 400 ft with an open borehole extending to 450 ft. The upper zone monitor well consists of a 6-in. casing set to a depth of 100 ft with an open hole extending total depth of 180 ft.

Planned Expansion

Following successful completion and demonstration of the ASR test well, the County proposes to install two additional reclaimed water ASR wells at the CCWRF to facilitate further expansion of the reuse system and enhance overall reliability of the North County Reuse System.

Sources

Lori Carroll, Sarasota County
Jim Brown, Sarasota County
Mike Micheau, P.G., PBS&J
Tom Farkas, P.G., PBS&J

SULAIBIYA, KUWAIT

Background

In the late 1980s, field experiments utilizing three production wells were conducted to determine the feasibility of ASR in the east central portion of Kuwait near the city of Sulaibiya. Due to the low transmissivity of the receiving aquifer (40–50 m²/day) and the shallow depth to the potentiometric head (30–40 m below ground surface), it was determined that this site was not suitable for artificial recharge. Additionally, due to a lack of an adequate volume of fresh water to be used for injection, no progress has been made in implementing a project since that study.

Project Purpose

The purpose of this project is to determine the suitability of selected aquifers for ASR using high-quality reclaimed water.

Project Description

An advanced wastewater treatment plant is currently under construction in Sulaibiya, Kuwait, under the direction of the Ministry of Public Works (MPW). This facility will utilize reverse osmosis to further purify tertiary treated wastewater and is scheduled for completion in late 2004. This facility was designed to produce an effluent water quality similar to that of desalinated seawater, including less than 2 mg of total organic carbon/L, less than 5 most probable number of infectious units of enteric viruses/10 L, and less than 2.2 colonies of total coliform bacteria/100 mL.

With the prospect of having high-quality reclaimed water from this wastewater treatment plant, interests in ASR have recently revived. Since the work in the late 1980s, the Ministry of Energy (MOE) has selected another potential site in Kabd, located in the central portion of Kuwait, where reclaimed water could be injected. Currently, the MPW plans to construct a pipeline to transport the treated reclaimed water from the Sulaibiya facility to the Wafra Farm area in southeastern Kuwait for irrigation. However, the MOE may request that the pipeline course be adjusted slightly and a portion of this flow be diverted to the Kabd area for reclaimed water ASR injection. Once the pipeline is constructed and if water is available for recharge, the Kuwait Institute for Scientific Research, MOE, MPW, and an engineering consulting firm will collaborate to conduct a pilot-scale ASR study to determine the feasibility of reclaimed water ASR wells in this area.

Planned Expansions

Since the proposed reclaimed water ASR project is still in a preliminary stage, no planned expansions are foreseen at this time.

Source

Mukhopadhyay, A.; Al-Rashed, M.; Al-Otaibi, M.; Abdel-Jawad, M. Status update report, Kuwait Institute for Scientific Research

WILLUNGA, SA, AUSTRALIA

Background

In 1999, the Willunga Pipeline Scheme was commissioned to transport secondary treated water from the Christies Beach wastewater treatment plant, which serves the southern part of the Adelaide metropolitan area, to irrigate vineyards in the McLaren Vale area. As a result, irrigation in the grape-growing area was expanded, the stress on overexploited groundwater supplies decreased, and the discharge of nutrient-rich effluent to sensitive marine environments was reduced. Reclaimed water ASR is being considered as a means of expanding the reuse capacity of the scheme.

Project Purpose

Drawing upon the success of the Bolivar project described elsewhere in this report, an ASR trial was conducted at Willunga in a similar limestone aquifer and within the Adelaide region to establish the feasibility of storing excess reclaimed water to meet peak demand for irrigation. The trial was intended to provide information necessary to design and operate a full-scale scheme in the McLaren Vale area.

Project Description

The ASR trial site was located immediately east of the Aldinga airport near the township of Willunga, approximately 50 km south of the center of Adelaide in South Australia (Sibenaler et al., 2002). The target aquifer consists of 30 to 60 m of limestone and calcareous sands with varying shell and fossil content. Within a 50-m radius of the ASR well, the aquifer has dual porosity characteristics. Most of the flow is transported through a 2–4-m-thick high-permeability layer. Beyond 50 m, the hydraulic behavior is more typical of a porous flow system, with pump test-derived transmissivities of 70–80 m²/day.

The ASR well was completed as an open hole (i.e., without a screen) between the depths of 56 and 73 m below ground surface. Observation wells were established at radial distances of 8, 26, and 55 m from the ASR well. During the initial cycle testing, the rate of movement of injected water appeared to be much greater than originally anticipated, and two observation wells were subsequently drilled at distances of 200 m and 500 m from the ASR well.

A pilot treatment plant was established at the trial site, and the secondary treated wastewater was filtered with a continuous backwashing sand filter and rechlorinated to meet the South Australian Reclaimed Water Guidelines for Class A water (suitable for unrestricted irrigation).

Five cycles of ASR were conducted between July 31, 2001, and Feb. 26, 2002. For precautionary purposes, a staged program of ASR cycling was carried out. The time scale was progressively increased in each successive cycle from a 2-h injection, 2.8-h storage, and 1.3-h recovery in the first cycle through to a 56-day injection, 13-day storage, 58-day recovery in the last cycle. A recovery phase was not conducted during test 2. A total of 31.4 ML (8.3 MG) was injected over the five cycles at an average rate of 5 L/s. A total of 32.6 ML (8.6 MG) of water was recovered.

Water quality monitoring revealed no breakthrough of the reclaimed water beyond a 50-m radius of the ASR well over the five ASR cycles. Increases in the salinity of the injected reclaimed water during storage and recovery periods is primarily due to diffusive exchange with the brackish ambient groundwater held within less-permeable parts of the aquifer. The maximum proportion of injectant recovered in any cycle was 60%, with the remainder retained within the aquifer due to a combination of exchange and advective flow downgradient of the ASR well. It is expected that the recovery efficiency will be improved over time due to buffering caused by the residual injectant from previous injection cycles.

In situ pathogen survival studies suggest 1-log removal times of 5–35 days for the six organisms tested (poliovirus, coxsackievirus, adenovirus, *Salmonella enterica* serovar Typhimurium, *Aeromonas hydrophila*, *Escherichia coli*, and coliphage MS2). There is some evidence to suggest that indigenous groundwater microorganisms are, in part, responsible for the high rates of attenuation. The recovered water met all the requirements for unrestricted

irrigation, although small increases in arsenic concentrations were observed in the initial stages of pumping.

This trial demonstrated that reclaimed water, treated to Class A standards (turbidity of <2 NTU and chlorinated but without nutrient removal), can be viably injected into a limestone aquifer dominated by fissure flow to recover for irrigation purposes.

Planned Expansion

Modeling indicates the potential for 0.8 billion gal/year (3 gigaliters/year) to be stored and recovered. However, operation of ASR is on hold and awaiting further expansion of water demand and Environmental Protection Authority requirements to prove that after several decades of ASR operation there will be no discharge of nitrate-rich groundwater through an offshore reef, in a groundwater system that is poorly defined under the sea.

Acknowledgments

This project was funded by the South Australian Government through the Department of Administrative and Information Services and managed by Australian Groundwater Technologies. The research would not have been possible without support of the Bolivar Reclaimed Water ASR Research Project partners SA Water Corporation, SA Department for Water, Land and Biodiversity Conservation, CSIRO, and the Department of Administrative and Information Services. The WateReuse Foundation provided the support to enable this concise summary of the project to be documented.

RESULTS OF RESEARCH CONDUCTED BY CSIRO AT BOLIVAR, SA, AUSTRALIA

A research project at Bolivar, South Australia, has investigated the viability of ASR reclaimed water in a brackish aquifer for storage of water for irrigation of horticultural crops (Dillon et al., 1999; Martin et al., 2000). The field trial involved the injection via a single well of ~520,000 m³ of reclaimed water into a confined limestone aquifer over three ASR cycles and recovery of ~370,000 m³. The trial provides information necessary to design and operate a full-scale scheme on the NAP capable of expanding irrigation supplies by 9 M m³/year. The water is treated to a level that is suitable for unrestricted irrigation use, unlike other localities where treatment is to a much higher standard prior to ASR (e.g., Pyne, 1995).

Through intensive monitoring, an understanding of the movement, mixing, and water quality changes of injectant in the aquifer has been developed. The study demonstrated that the recovered water met the guidelines for unrestricted irrigation. The quality of the water improved during ASR, particularly with respect to pathogens, disinfection byproducts, suspended particles, organic carbon, and most metals. The anticipated clogging was found to be manageable using simple methods, and the cost of the operation was found to compare favorably with conventional alternatives. During the third cycle of injection, storage and recovery, additional samples were taken for analysis of trace organics, which is reported here.

METHODS

Site Location and Hydrogeology

The ASR site is located 25 km north of the centre of Adelaide in South Australia on farmland within the northern boundary of the Bolivar sewage treatment plant (Figures A1 and A2). The target aquifer is the lower of the two tertiary limestone aquifers known as the Port Willunga Formation. The brackish T2 aquifer is separated from the overlying fresh T1 aquifer by a 7.5-m-thick confining layer of Munno Para clay. The aquifer was moderately transmissive (180 m² day⁻¹), and the average porosity was 0.45. Locally, the groundwater in the T2 aquifer has a salinity of ~2100 mg of TDS L⁻¹. Mineralogical composition of the aquifer is dominated by calcite and quartz, and small quantities of ankerite, mica, and albite are also present.

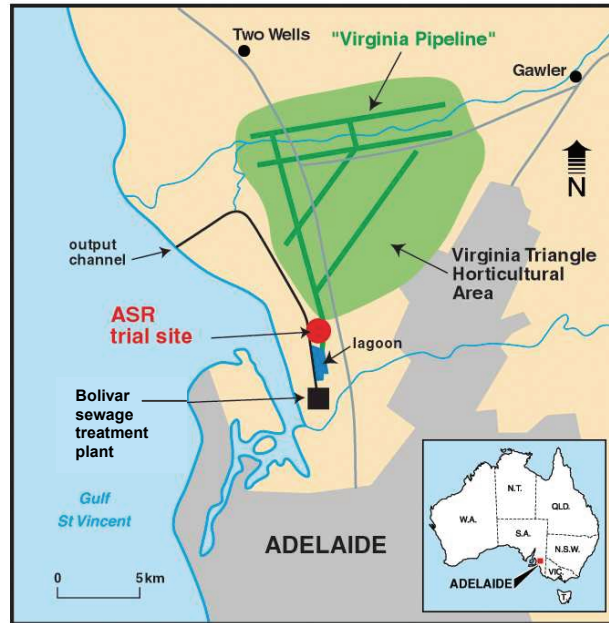


Figure A1. Location of Bolivar ASR trial site and Northern Adelaide Plains horticultural area.

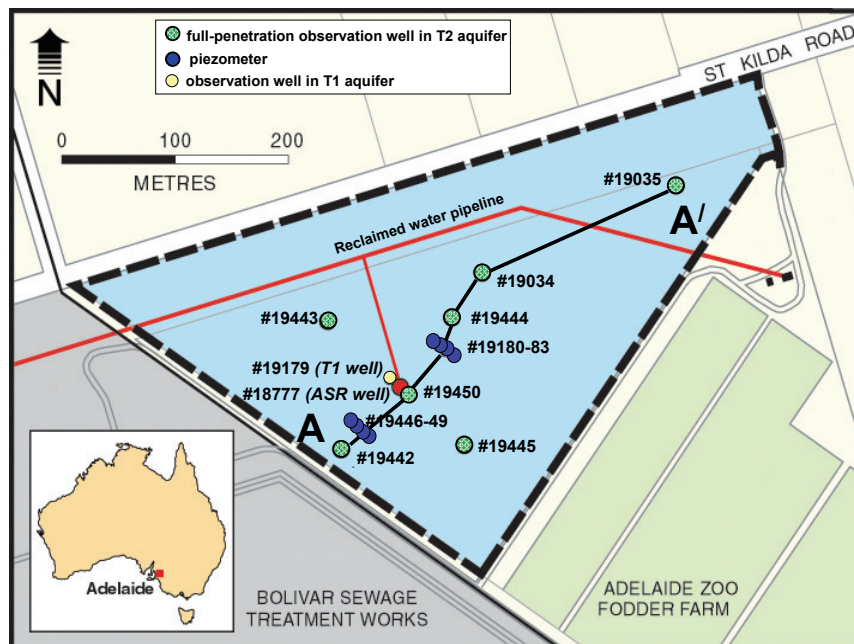


Figure A2. Location of wells and piezometers at the Bolivar site.

The ASR well was cased in 203-mm (ID) fiber-reinforced plastic to 103 m, and the remaining depth was completed as open hole to ~160 m. Wells at radial distances of 4, 75, 120, and 300 m fully penetrate the T2 (102–160 m), and the eight 50-m piezometers upgradient (northeast) and downgradient (southwest) of the ASR well are completed over four distinct intervals of the aquifer (Figure A3). The wells used in this study are the injection well (18777) and 4-m observation well (19450), both fully penetrating, and a piezometer 50 m north (19181), which was in a discrete layer of higher hydraulic conductivity within the aquifer (Pavelic et al., in press).

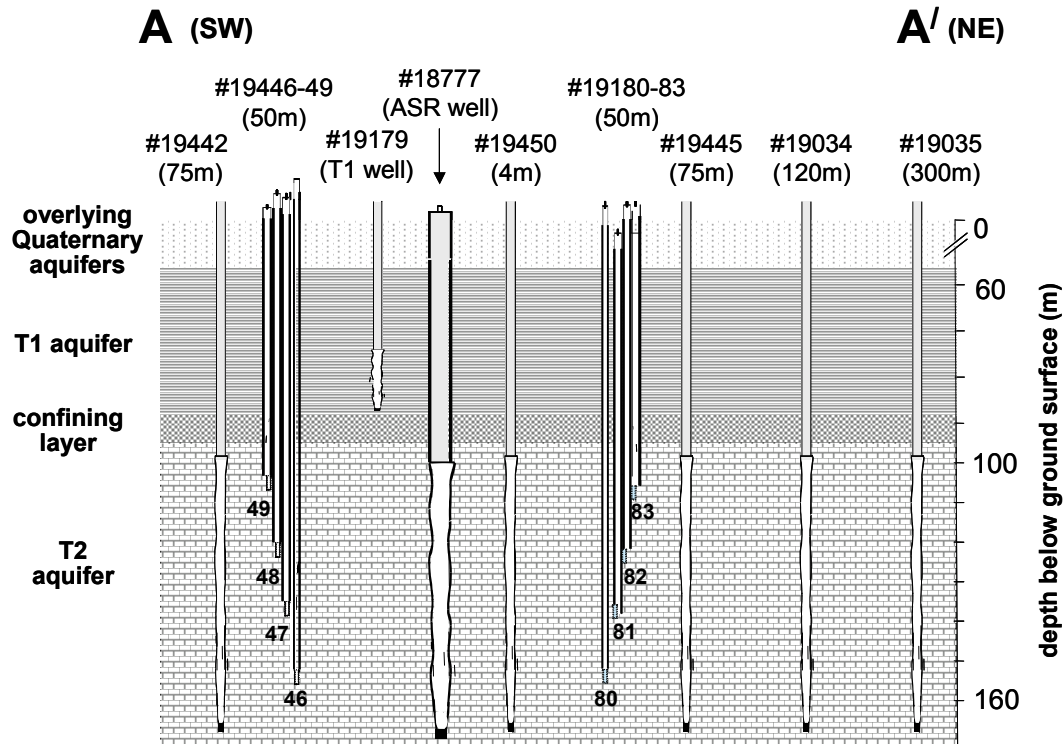


Figure A3. Simplified vertical section along transect A-A' showing location of the ASR well, observation wells, and piezometers.

Injection and Recovery Cycles

Between October 1999 and July 2005 there were three ASR cycles, with the first injection cycle divided into three separate tests (Table A1). Injection rates were controlled by the permeability of the aquifer, the degree of well clogging, and the line pressure at the wellhead.

The ASR trial used water from the nearby Bolivar sewage treatment plant. Secondary treatment by trickling filters was replaced in January 2001 by activated sludge reactors. The treated water was stored in stabilization ponds before treatment in a water reclamation plant that entailed coagulation and dissolved air flotation filtration followed by disinfection (chlorination). Water was then discharged to open balancing storage before being pumped to the ASR site via the Virginia Pipeline Scheme, which supplies reclaimed water for horticulture on the Northern Adelaide Plains (Kracman et al., 2000).

Studies at the Bolivar ASR site included hydraulic characterization of the aquifer, measuring and modeling piezometric head and conservative solute responses in the aquifer (Pavelic et al., in press), assessing physical and biological clogging (Rinck-Pfeiffer et al., 2002), exploring subsurface biogeochemical processes (Le Gal La Salle et al., 2005; Vanderzalm et al., 2006), quantifying pathogen survival rates including those within biofilms at the wellface (Toze and Hanna, 2002; Dillon and Toze, 2005), measuring the fate of trace organics, including disinfection byproducts (Pavelic et al., 2005, 2006) and selected endocrine disruptors (Ying et al., 2004), determining the cross-hole resistivity tomography, evaluating well maintenance procedures, and assessing the structural integrity of the overlying aquitard.

Table A1. Dates and volumes of injection and recovery events, October 1999–July 2005

Cycle No.	Test No.	Start	End	Duration, days	Net Vol, 10 ³ m ³	Cum. Net Vol, 10 ³ m ³	Avg. Flow Rate, L/s
1	I1	11 Oct 1999	23 Nov 1999	42	28.7	28.7	7.9
	S	23 Nov 1999	4 Apr 2000	132			
1	I2	4 Apr 2000	21 Apr 2000	8	6.6	35.3	9.5
	S	21 Apr 2000	4 Aug 2000	105			
1	I3	4 Aug 2000	29 Mar 2001	215	214.5	249.8	11.5
	S	29 Mar 2001	18 July 2001	111			
1	R	18 July 2001	28 Nov 2001	121	–152.0	97.8	15.0
	S	28 Nov 2001	5 Mar 2002	97			
2	I4	5 Mar 2002	27 Jun 2002	111	114.3	212.1	11.9
	S	27 Jun 2002	25 Jul 2002	28			
	R	25 July 2002	8 Oct 2002	70	–90.9	121.2	15.0
3	I5	11 Dec 2003	28 May 2004	169	154.5	275.7	11.2
	S	28 May 2004	13 May 2005	350			
	R	21 July 2005	13 May 2005	90	–123.4	152.3	15.9

Water Quality Sampling

A graphical water balance for the aquifer is shown in Figure A4, which also shows the timing of samples taken for this WaterReuse Foundation project.

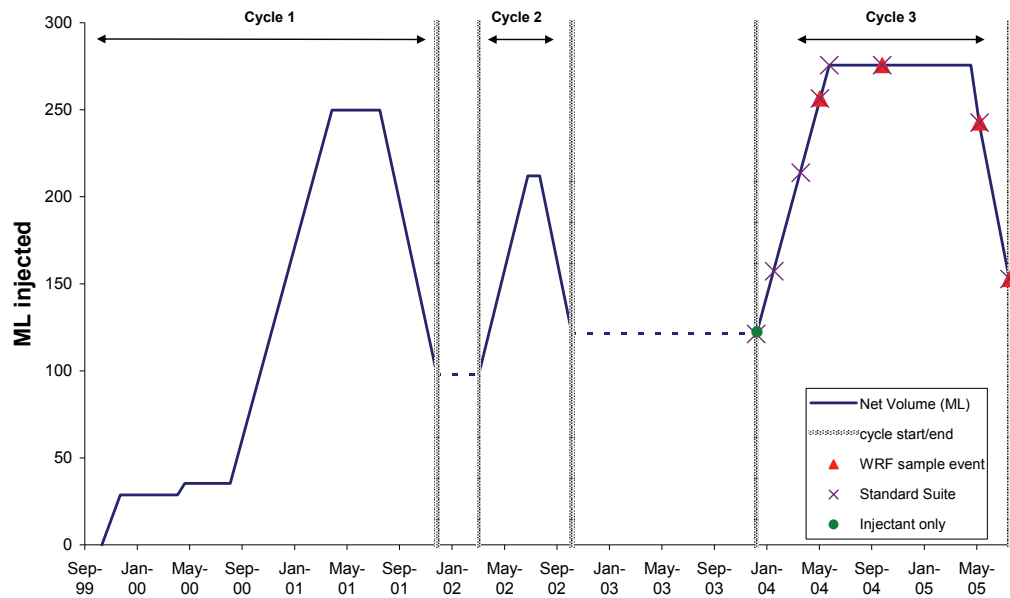


Figure A4. Net recharge at Bolivar during the first three ASR cycles, showing the sampling events in Cycle 3 (1 ML = 10^3 m^3).

Prior to the start of the third ASR cycle, groundwater samples were collected from wells along a transect ranging from 0–75-m radius from the injection well. The well in the overlying aquifer (T1) was also sampled to ensure there had been no breakthrough to this aquifer. Each of the observation wells (0, 4, and 75 m and T1) were pumped with a conventional monitoring pump until at least three times the volume of water in the well casing had been displaced prior to sample collection. Readings of water quality (EC, temperature, pH, DO, and Eh) were measured during the purging of the well through a flow cell using a TPS-90FL analyzer. These readings had stabilized before three casing volumes had been purged.

Pumping of the two 50-m well piezometers (100-mm ID) at the depths where breakthrough had been observed was done using an “air well” pump with a single inflatable packer, enabling the purging of only the open 5-m interval at the base of the piezometer. Once the piezometer had been purged, N_2 gas was used to activate the pump before sampling was begun, so as to minimize the entry of oxygen to the sample during collection. During the purging of the well, the TPS-90FL apparatus was also connected to monitor water quality. However, due to the stop and start nature of the air well pumping, attaining stable readings of DO and Eh in the sample was difficult.

Through the course of the third cycle injection phase, five grab samples of injectant were collected directly from the delivery line adjacent to the ASR well along with groundwater samples at the 4-m and 50-m and, later, 75-m radii. At the end of injection, groundwater samples were also collected from the 120-m and 300-m and T1 wells. There was one sampling event during storage and two during recovery (at 3 weeks and at the end). Throughout the injection and recovery phases, a refrigerated ISCO autosampler was programmed to collect daily samples. These samples were periodically collected, and the EC

and turbidity of each was measured at the CSIRO laboratories. The samples were then mixed into weekly composite samples by sampling 200 mL from each daily sample. These weekly composite samples were then sent to the AWQC for the standard sampling suite (excluding algae in the case of injectant). Table A2 shows the locations and times at which samples were collected specifically for this WaterReuse Project and also the supporting samples that served other purposes. Analytical methods for samples analyzed at the Australian Water Quality Centre, a NATA-accredited laboratory, were based on the *Standard Methods for the Examination of Water and Wastewater* of Eaton et al. (1995). Samples for trace organics analyses were sent to the Las Vegas Valley Water District, as was done for other case study sites.

Table A2. Locations and times of sampling events of data used in this report.

	Injectant	Production Well (0m)	#19179 (T1)	#19450 (4m)	#19181 (50mN-L3)	#19449 (50mS-L1) ¹	#19445 (75mN)	#19034 (120mN)	#19035 (300mN)
10-Dec-03									
12-Dec-03									
21-Jan-04									
23-Mar-04									
6-May-04	WRF								
28-May-04									
28-Sep-04		WRF		WRF	WRF				
12-May-05		WRF		WRF	WRF				
21-Jul-05		WRF		WRF	WRF				

footnote

¹ sample collected from #19183 (50mN-L1) instead of #19449 (50mS-L1)

RESULTS

Fate of Injected Water

Complete breakthrough of injectant was observed at the observation well at the 4-m radius and at four of the eight 50-m piezometers (numbers 19447, 19449, 19181, and 19183) within two distinct high-permeability layers. Partial breakthrough occurred at the 75-m and 120-m wells, but not at the 300-m well. The travel time to 4 m was 1–2 days, and to 50 m it was 90–120 days. The total number of pore flushes was in excess of 300 for the nearest well and no more than 6 for the 50-m piezometers. Details of the hydraulic characterization can be found in a report of Pavelic et al. (in press), and those on recovery efficiency can be found in Pavelic et al. (2002).

Geochemical and Organic Matter Changes

The qualities of the injected and recovered waters were monitored to investigate the effects of redox processes and mineral dissolution and precipitation. Oxidation of organic matter was evident within 4 m of the ASR well during the injection phase and was responsible for removal of up to 4 mg of DOC/L, or 20% of that injected. In contrast, strongly reducing

conditions were evident around the ASR well during the storage phase. Sulfate reduction of up to 150 mg/L occurred. Calcite dissolution was evident during both the injection and storage periods (Vanderzalm et al., in press). Chloride and the stable isotopes of water were used as conservative tracers (Le Gal La Salle et al., 2005) and ^{13}C , ^{14}C , ^{34}S , and ^{15}N analyses verified reaction and exchange processes. These redox variations were larger than those observed by Herczeg et al. (2004) at an ASR site in the same aquifer when stormwater was injected. Redox state was found to be very important for attenuation of trihalomethanes and also had an influence on pathogen attenuation, both of which are summarized below. Figure A5 shows the spatial extent of redox zones at various times in the ASR cycle.

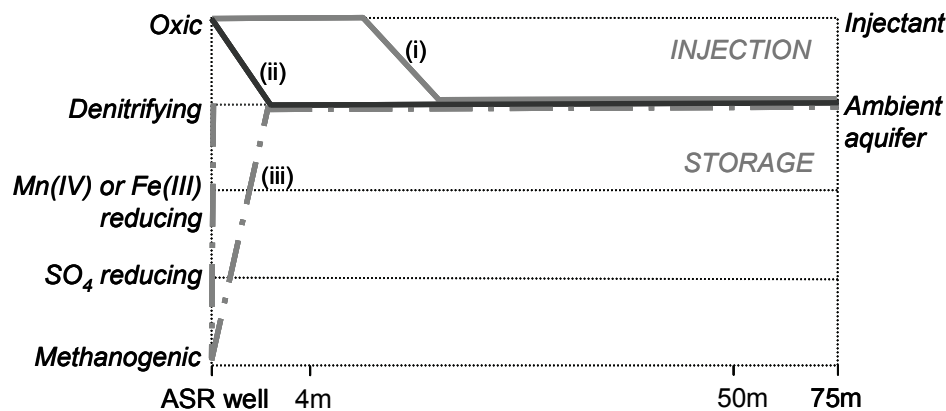


Figure A5. Schematic representation of redox zone development during an ASR cycle (i) oxic with the onset of injection, (ii) denitrifying for the greater part of the trial, or (iii) reducing at the ASR well during storage. During recovery, denitrifying conditions prevailed throughout. (Adapted from Vanderzalm et al., 2006).

Studies of the changes in dissolved organic matter showed that compounds with larger molecular weights and more reactive functional groups were absorbed or decomposed close to the ASR well. Recalcitrant organic matter that had the same characteristics as natural deep groundwaters was persistent in the aquifer (Skjemstad et al., 2002). Subsequently, carbon turnover has been modeled by Greskiowitz et al. (2005) at this site.

Fate of DBPs

Although the Bolivar site will not be used to provide potable water, this study has provided quantitative data on disinfection byproduct (DBP) fate in groundwater. The results identified that minimal adsorption of trihalomethanes (THMs) and haloacetic acids (HAAs) occurred due to the low organic content of the target aquifer. THM half-lives varied from <1 to 65 days, with persistence of chloroform being highest and bromoform lowest. HAA attenuation was rapid (Nicholson et al., 2002).

Differences in redox state between the ASR well and 4-m observation well had a substantial effect on rates of THM attenuation. At the ASR well, which became methanogenic during the

storage phase, chloroform degraded more than 5 times faster than at the well only 4 m away, which remained nitrate reducing (Pavelic et al., 2005). These trends were observed consistently at eight ASR sites in the United States and Australia (Pavelic et al., 2006), and at aerobic sites chloroform was found to be recalcitrant.

Pathogen Attenuation

The survival potential of microbial pathogens in groundwater and injected reclaimed water was assessed to determine the relative risk associated with ASR. The microbial pathogens tested were poliovirus, coxsackievirus, *Salmonella enterica* serovar Typhimurium, and the opportunistic pathogen *Aeromonas hydrophila*, as well as the indicator microorganisms *Escherichia coli* and the coliphage MS2.

The results obtained indicated that the bacteria had the fastest attenuation rates, followed by the coliphage MS2, with the enteric viruses being inactivating the slowest of all the organisms tested. In all cases the time for a 1-log removal was less than 1 mo. In laboratory studies, the attenuation rates of all of the tested microorganisms were highest when exposed to indigenous groundwater microorganisms. It can be inferred from these results that the risk of microbial pathogen presence in recovered water is low if the reclaimed water is stored in the aquifer for a sufficient time (Toze and Hanna, 2002). Related studies have developed methods to measure bacterial pathogen fate in microbial biofilms, which are found in ASR wells and to enumerate total and viable *Cryptosporidium* from in situ samplers. Attempts have also been made to account for biotic effects on pathogen attenuation (Gordon and Toze, 2003; Toze, 2004).

Biofilm growth were studied in laboratory columns using Bolivar reclaimed water and aquifer material to predict the possibility of bore-clogging issues at the ASR site before field trials proceeded (Rinck-Pfeiffer et al., 2000). The columns were used to investigate the combined effects of physical, biological, chemical, and mechanical factors on clogging and to quantify biogeochemical processes that would offset this on the perimeter of an injection well. This gave confidence that clogging could be managed and suggested management strategies that subsequently proved effective in maintaining injection rates.

Specifically, the experiments showed the depth of penetration of the zone of reduced permeability, the rate of decline in hydraulic conductivity with time under different conditions, the effect on clogging rates of waters of different quality and for different flow rates, and the effects of biomass and polysaccharide accumulation within the columns on hydraulic conductivity. Importantly, they also quantitatively defined the offsetting effect induced as a result of the establishment of preferential flow paths due to dissolution of the aquifer matrix. Further research is planned to evaluate bioaccumulation and biogeochemical reactions in the anoxic zone further from the well face, as well as to apply these techniques to other source waters and aquifer types.

Initial teething problems and infrequent redevelopment produced clogging at the beginning of the trial; however, periodic pumping of the ASR well was effective in restoring injection rates, which have been maintained over the 3-year duration of the trial. An association was found between rates of injection and the quality of the injectant, with higher-quality water leading to reduced clogging and higher injection rates. The minimum water quality criteria to maintain injection rates over the long term for this site have been tentatively identified.

Quality of Recovered Water

Following the recovery of the first 1000 m³ of water that was affected by enhanced microbial activity around the ASR well, the recovered water quality was found to satisfy the requirements for use as irrigation water according to ARMCANZ and ANZECC guidelines (National Water Quality Management Strategy) (Table A3). Subsurface storage reduced concentrations of suspended solids, organic carbon, and some metals, and *E. coli* was removed during aquifer storage, as predicted from the in situ and laboratory pathogen survival experiments by Toze and Hanna (2002).

The proportion of the injected volume that is recovered at a quality suitable for productive use is known as the recovery efficiency and may be constrained where the ambient groundwater is more saline than the injectant (Pavelic et al., 2002). Recovery efficiencies determined on the basis of the volumetric withdrawal until the salinity of the recovered water reached the maximum permissible level of 1500 mg of TDS/L (a requirement for the pipeline) were 66% in the first cycle and 80% in the second and third cycles. Improvements in further cycles are predicted, due to the development of a fresher buffer zone by injectant remaining in the aquifer.

Table A3. Quality of injected water, local ambient groundwater, and recovered water

Parameter (mg/L)	Irrigation Guidelines	Ambient Groundwater ^I (n=17)	cycle 1		cycle 2		cycle 3	
			Injectant (n=24)	Recovered Water ^{II} (final sample)	Injectant (n=14)	Recovered Water ^V (final sample)	Injectant (n=17)	Recovered Water ^{VI} (final sample)
Electrical Conductivity (uS/cm)		3592 ± 326	2265 ± 191	2470	1975 ± 92	2550	1975 ± 186	2460
Temperature (°C)		25.9 ± 1.0	20.4 ± 4.5	22.7	16.3 ± 3.6	21.1	18.5 ± 3.3	22.6
pH	4.5-9	7.3 ± 0.1	7.1 ± 0.4	7.06	6.9 ± 0.3	7.31	7.9 ± 0.5	7.36
Dissolved Oxygen	need to check field notes	0.77 ± 0.79	4.4 ± 3.4	0	6.0 ± 1.4	0	10.4 ± 2.1	0.002
Redox Potential (mV S.H.E)		29 ± 56	299 ± 258	52	853 ± 91	70	389 ± 32	-41
Turbidity (NTU)		13 ± 9	29 ± 50 ^{IV}	4.2	2.4 ± 2.1	5.8	1.7 ± 0.9	1.99
Total Dissolved Solids (bv EC)	1500	2023 ± 169	1026 ± 93	1490	1166 ± 66	1481	1093 ± 95	1515
Chloride		932 ± 92	429 ± 37	554	413 ± 36	575	421 ± 47	611
Bicarbonate		265 ± 19	282 ± 79	319	256 ± 17	308	162 ± 40	258
Sulphate		274 ± 39	208 ± 13	225	178 ± 10	220	189 ± 29	233
Calcium		155 ± 13	45.1 ± 7.5	77.4	47.6 ± 5.1	83.6	35.5 ± 3.5	85.7
Magnesium		81.4 ± 9	35.6 ± 3.5	47.7	38.4 ± 2.3	50.4	33.8 ± 3.2	50
Potassium		15.3 ± 4	48.8 ± 3.9	40.8	49.2 ± 2.4	40.2	39.5 ± 2.6	34.2
Sodium		493 ± 57	303 ± 25	357	306 ± 19	352	290 ± 36	370
Arsenic	0.1	0.006 ± 0.002	0.003	0.017	-	-	0.005 ± 0.006	0.011
Iron	1	1.0 ± 0.3	3.2 ± 5.5 ^{III}	0.586	0.08 ± 0.05	0.647	0.002 ± 0.008	0.039
Ammonia		0.067 ± 0.028	15.3 ± 11.5	13.5	2.1 ± 1.6	2.64	0.15 ± 0.1	<0.005
Total Kjeldahl Nitrogen		0.076 ± 0.04	18.5 ± 11.7	15.6	4.8 ± 1.6	4.12	1.5 ± 0.2	0.52
Nitrate + Nitrite Nitrogen		<0.005	1.9 ± 1.8	0.01	2.9 ± 1.5	<0.005	2.7 ± 3.5	<0.005
Total Phosphorus		0.02 ± 0.001	0.72 ± 0.65	0.24	2.3 ± 0.9	0.24	0.86 ± 0.9	0.49
Filterable Phosphorus		<0.005	0.37 ± 0.49	0.10	2.1 ± 0.8	0.79	1.3 ± 1.2 ^{VII}	0.34
Dissolved Organic Carbon		0.3	16.7 ± 2.1	10.5	19.5 ± 1.9	12	12.9 ± 1.1 ^{VII}	6.6
Total Organic Carbon		0.3	18.2 ± 2.3	10.6	20.1 ± 2.1	12.2	12.6 ± 0.8	6.8
Algae - total (cells/mL)		0	52000 ± 31900 ^{IV}	-	1726 ± 1427	-	13535 ± 27718	-

^I all wells and piezometers (pre-injection)

^{II} final sample from recovery cycle No.1 28.11.01

^{III} elevated due to sampling artefact during much of injection test 3 (refer to Vanderzalm *et al.*, 2001)

^{IV} based on 32 samples collected 29.06.00 to 11.08.00 at pumping station upstream of ASR site

^V final sample from recovery cycle No.2 8.10.02

^{VI} final sample from recovery cycle No.3 21.07.05

^{VII} only based on 5 sample events

Chloride was used to determine the proportion of injectant in any sample of groundwater, thus enabling a distinction between the effect of attenuation of any reactive species in the aquifer and mixing within native groundwater. Table A4 includes chloride and other data that may be useful in interpreting the results of trace organic analyses given in Tables A5 to A8 (blanks are reported in Table A9).

As shown in Table A5, although detection of DBPs occurred, injectant rates of attenuation were consistent with those previously calculated (Pavelic et al., 2005, 2006), and none was detected in recovered water. Pesticides were not detected in any sample at the detection levels available at AWQC. Tables A6 to A8 report raw concentrations and corrected concentrations to account for dilution where raw concentrations exceeded detection limits. Some considerable variations occurred for some species. Figure A6 shows that the chloride value was reduced during injection, giving a small but unknown bias to corrections. Total organic carbon varied between 12 and 16 mg/L, suggesting that input concentrations of trace organics may also be quite erratic and could explain some of the unexpected variations in species that were detected.

Table A4. Field data and AWQC data corresponding to samples sent to Las Vegas Valley Water for trace organic analysis

WRF Sampling Event#	#1		#2			#3			#4		
	<u>3 weeks b4 end Inj</u>	<u>end of Inj</u>	<u>after 4 months of storage</u>			<u>20 days after start of recovery</u>			<u>Last day of recovery</u>		
Date	6/05/2004	28/05/2004	28/09/2004			12/05/2005			21/07/2005		
Well ID	Injectant	Injectant	18777	19450	19181	18777	19450	19181	18777	19450	19181
Well Location			0 m	4 m	50mN L3	0 m	4 m	50mN L3	0 m	4 m	50mN L3
Parameters (mg/L)											
EC-field (uS/cm)	1674	1660	1826	1668	2230	1971	2250	2330	2560	2210	2500
Temp-field (degrees C)	7.58	14.2	15.1	15.8	20.6	17.2	20.9	20.3	22.6	21.4	21.4
pH-field (-)	17.4	8.49	6.94	6.21	7.26	7.26	7.32	7.29	7.39	7.49	7.21
DO-field	11.88	12.63	2.68	0.43	0.08 ²	0.01	0.06	0.67	0.02	0.21 ³	0.11
Eh-field (mV SHE)		¹	¹	-32	-6 ²	9	-36	21	-41	-62 ³	9
CSIRO EC-Lab (uS/cm)	1769	1740	2060	1805	2290	1961	2270	na	2460	2320	2410
CSIRO Turbidity (NTU)	1.3	0.9	32.6	1.31	10.1	1.68	0.38	na	1.99	0.66	49.5
Ds Organic Carbon	12.4	12.4	23.8	9.1	9.7	7.4	6.8	7.8	6.6	5.3	8.5
Total Organic Carbon	13.7	12.3	31.8	9.9	9.8	7.9	7.4	8.6	6.8	5.3	8.9
TDS	900	919	1100	998	1270	1000	1200	1200	1510	1670	1330
Ca	37	38.9	78.4	55.5	68.3	59	67.8	68.2	85.7	105	70.3
Mg	32.4	31.9	47.1	34.9	37.1	34.2	39.0	36.6	50	57.8	37.9
K	35.9	35.7	32.9	36.7	35.1	41.2	38.3	33.5	34.2	31.8	31.2
Na	240	239	241	240	309	273	306	315	370	397	321
Cl	382	336	347	349	459	385	464	449	611	715	502
Cl dilution ratio (28/5/04)*			0.98	0.98	0.83	0.92	0.79	0.84	0.57	0.37	0.76
Cl dilution ratio (12/5/04)*			1.06	1.06	0.88	0.99	0.85	0.90	0.62	0.40	0.82
HCO ₃	166	169	391	242	278	235	249	292	258	264	322
SO ₄	154	145	148	162	219	187	214	201	233	237	209
Alkalinity as CaCO ₃	136		320	198	228	193	204	239	211	216	264
F	0.98		0.87	0.86	0.37	0.76	0.3	0.3	0.68	0.6	0.3
Br	<0.1	0.1	0.67	0.39	1.3	0.94	1.2	1.2	1.79	2.3	1.3
Ammonia as N	0.18	0.073	8.17	0.731	6.64	0.692	0.946	5.2	<0.005	<0.005	10.1
Fil. Reactive Phosphorus as P	1.91	2.86	0.984	0.829	0.02	0.406	0.300	0.020	0.342	0.20	0.037
Phosphorus - Total as P	1.58	3.11	2.64	0.85	0.04	0.641	0.338	0.033	0.494	0.43	0.074
TKN as nitrogen	1.42	1.89	9.41	1.24	7.16	1.05	1.120	5.930	0.52	0.46	11.3
Nitrate + Nitrite as N	6.78	8.39	<0.005	0.02	0.01	<0.005	0.005	<0.005	<0.005	1.43	0.026
Nitrite as N	-		<0.005	0.013	<0.005	-	-	-	-	-	-
Nitrate as N	-		<0.005	0.07	0.01	-	-	-	-	-	-
CN - Total	<0.05		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
As total	0.002	0.012	0.075	0.02	<0.002	0.02	0.007	0.001	0.011	0.007	<0.001
Fe total	<0.03	<0.03	6.91	0.044	0.248	0.542	0.481	0.26	0.389	0.358	0.354
Boron	0.286		0.473	0.297	0.389	0.304	0.307	0.332	0.306	0.302	0.318
Cd Total	<0.0005		<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu Total	0.009		0.006	0.002	<0.001	<0.001	0.002	0.002	<0.001	<0.001	<0.001
Pb Total	<0.0005		0.0008	<0.0005	<0.0005	<0.0005	0.0008	<0.0005	<0.0005	0.0006	<0.0005
Hg Total	<0.0005		<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0004	<0.0003
Se Total	<0.003		<0.001	0.001	<0.001	<0.003	<0.003	<0.003	0.007	0.007	0.005
Ba Total	0.0027		0.0041	0.0027	0.0329	0.0055	0.0114	0.0364	0.0136	0.0245	0.0341
U Total	-		<0.0005	0.0015	<0.0005	0.0009	0.0038	<0.0005	0.001	0.0027	<0.0005
E.coli (/100 mL)	6		0	0	0	0	0	0	0	0	0
Faecal Coliforms (/100 mL)	6		0	0	0	0	0	0	0	0	0
Coliforms (/100 mL)	110		68	15	7	0	1	0	0	1	1
Enterococci faecalis (/100 mL)	-		ND	ND	74	0	0	0	0	0	7.4
rRNA coliphage (/10 mL)	-		ND	ND	ND	ND	ND	ND	ND	ND	ND
Clostridium perfringens (/100 mL)	-		ND	ND	ND	ND	ND	ND	ND	ND	ND
Presumptive Giardia (/10 L)	-		<7	<7	<3	<3	<3	<3	<7	<2	<6
Presumptive Cryptosporidium (/10 L)	-		<6	<6	<5	<3	<5	<6	<7	<2	<5

* calculation of Cl dilution ratio based on the following values:

Ambient Cl measured in 1999 - #18777Cl 980 mg/L, #19450Cl 940 mg/L & #19181Cl 1040

footnotes:

¹ using Flinders Uni Meter - not calibrated

² unstable readings

³ readings measured in bucket rather than flow cell

Table A5. Disinfection byproduct and pesticide analyses from AWQC corresponding to samples sent to Las Vegas Valley Water for trace organic analysis

Date	3 weeks b4 end of injection	after 4 months of storage			20 days after start of recovery			Last day of recovery		
	6/05/2004	28/09/2004			12/05/2005			21/07/2005		
Well ID	Injectant	18777	19450	19181	18777	19450	19181	18777	19450	19181
Well Location		0 m	4 m	50mN L3	0 m	4 m	50mN L3	0 m	4 m	50mN L3
Parameters (ug/L)										
Total Trihalomethanes	234	18	80	<4	<4	<4	<4	<4	<4	<4
Chloroform	49	11	39	<1	<1	<1	<1	<1	<1	<1
Bromodichloromethane	86	5	30	<1	<1	<1	<1	<1	<1	<1
Dibromochloromethane	80	2	11	<1	<1	<1	<1	<1	<1	<1
Bromoform	19	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chloroacetic acid	5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Dichloroacetic Acid	23	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromochloroacetic acid	25	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dibromoacetic Acid	13	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromoacetic acid	5	<1	<1	<1	<1	<1	<1	<1	<1	<1
Trichloroacetic acid	26	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromodichloroacetic acid	39	<1	<1	<1	<1	<1	<1	<1	<2	<1
Aldrin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CHLORDANE-a	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Chlordane-g	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CHLOROTHALONIL	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
CHLORPYRIFOS	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
CHLORITHAL-DIMETHYL (DACTHAL)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
4,4-DDD (TDE)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
4,4-DDE	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
4,4-DDT	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
DIELDRIN	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
ENDOSULFAN	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Endosulfan 2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
ENDOSULFAN SULFATE	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
ENDRIN	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
HEPTACHLOR	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
HEPTACHLOR EPOXIDE	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
LINDANE	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
TRIFLURALIN	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
METHOXYCHLOR	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
VINCLOZOLIN	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
ATRAZINE	<0.05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
AZINPHOS-METHYL	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SIMAZINE	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
DIAZINON	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
FENITROTHION	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
HEXAZINONE	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MALATHION	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PARATHION	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PARATHION-METHYL	<0.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
PROMETRYNE	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Gross alpha particle activity (mBq/L)	-	59	28	58	42	35	23	110	66	101
Gross Beta particle activity (mBq/L)	-	121	<10	<10	<10	<10	<10	nr	nr	nr
Ion balance (%)	-	0.98	-0.49	-1.87	-	-	-	-1.92	-2.4	-5.4

Table A6. Trace organic analyses of injectant and ASR well samples during storage and recovery

WRF Sample Event#	#1	#2	Data adjusted for Injectant dilution factor		
SPE Batch ID	051005-6	120604-6	060105-1	080105-9	
Description	Injectant	Well #18777	Well #18777	Well #18777	Well #18777
		0 m	0 m	0 m	
Sample Date	6/05/2004	28/09/2004	12/05/2005	21/07/2005	
CI dilution ratio					
Analyte	ppt	ppt	ppt	ppt	
Hydrocodone	<1.0	<1.0	1.0	1.4	
Trimethoprim	<1.0	2.7	2.7	1.2	
Acetaminophen	<1.0	3.9	<1.0	2.4	
Caffeine	13	112	<10	17	
Erythromycin-H ₂ O	<1.0	484	14	26	
Sulfamethoxazole	<1.0	<1.0	<1.0	<1.0	
Fluoxetine	<1.0	1.6	<1.0	<1.0	
Pentoxifylline	<1.0	<1.0	<1.0	<1.0	
Meprobamate	<1.0	<1.0	<1.0	<1.0	
Dilantin	32	110	104	32	
TCEP	151	219	258	78	
Carbamazepine	125	319	388	173	
DEET	51	36	81	64	
Atrazine	9.2	1.8	5.0	2.2	
Diazepam	2.4	4.9	1.6	2.1	
Oxybenzone	<1.0	<1.0	<1.0	<1.0	
Progesterone - ESI	<1.0				
Estriol	177	<5.0	56	95	
Ethinylestradiol	27	7.0	25	23	
Estrone	32	26	<1.0	1.7	
Estradiol	<1.0	<1.0	<1.0	<1.0	
Testosterone	<1.0	<1.0	<1.0	<1.0	
Progesterone - APCI	<1.0	<1.0	<1.0	<1.0	
Androstenedione	7.9	1.2	1.5	3.5	
Iopromide	183	7.3	28	66	
Naproxen	<1.0	<1.0	<1.0	<1.0	
Ibuprofen	80	11	86	19	
Diclofenac	<1.0	<1.0	<1.0	<1.0	
Triclosan	<1.0	1.5	3.0	2.3	
Gemfibrozil	<1.0	3.9	95	44	
α-BHC	<5.0	14	<5.0	<5.0	
β-BHC	<5.0	<5.0	<5.0	<5.0	
γ-BHC	<5.0	<5.0	<5.0	<5.0	
Diazinon	<5.0	<5.0	<5.0	<5.0	
δ-BHC	<5.0	<5.0	<5.0	<5.0	
Aldrin	<5.0	<5.0	<5.0	<5.0	
Chlorpyrifos	<5.0	<5.0	<5.0	<5.0	
Fluoranthene	<5.0	5.3	<5.0	<5.0	
Dieldrin	<5.0	<5.0	<5.0	<5.0	
BDE #28	<10	<10	<10	<10	
BDE #47	<10	<10	<10	<10	
BDE #100	<10	<10	<10	<10	
BDE #99	<10	<10	<10	<10	
BDE #154	<10	<10	<10	<10	
BDE #153	<10	<10	<10	<10	
BHT	1756	2202	1632	2387	
Bisphenol A	<100	305	1324	<100	
Nonylphenol (sum)	269	259	1041	453	
NDMA	NA	<2.5	7.8	4.6	
Perchlorate	NA	<0.05	<0.05	<0.05	
Bromate	NA	<0.1	<0.1	<0.1	
Iodate	NA	<1.0	<1.0	<1.0	
Chlorate	NA	<0.1	0.12	<0.1	

* use CI dilution value of 1 rather than calculated 1.06 using injectant from 6/5/04

Table A7. Trace organic analyses of injectant and 4-m well samples during storage and recovery

[illegible]

* use CI dilution value of 1 rather than calculated 1.06 using injectant from 6/5/04

Table A8. Trace organic analyses of injectant and 50-m piezometer samples during storage and recovery

WRF Sample Event#	#1	#4		
SPE Batch ID	051005-6	120604-3	060305-1	080105-11
Description	Injectant	Well #19181	Well #19181	Well #19181
Sample Date	6/05/2004	28/09/2004	12/05/2005	21/07/2005
		50 mN-3	50 mN-3	50 mN-3
Analyte	ppt	ppt	ppt	ppt
Hydrocodone	<1.0	<1.0	<1.0	<1.0
Trimethoprim	<1.0	<1.0	<1.0	<1.0
Acetaminophen	<1.0	<1.0	<1.0	<1.0
Caffeine	13	<10	<10	17
Erythromycin-H ₂ O	<1.0	<1.0	1.6	<1.0
Sulfamethoxazole	<1.0	<1.0	<1.0	<1.0
Fluoxetine	<1.0	<1.0	<1.0	<1.0
Pentoxifylline	<1.0	<1.0	<1.0	<1.0
Meprobamate	<1.0	<1.0	<1.0	<1.0
Dilantin	32	82	85	18
TCEP	151	184	166	46
Carbamazepine	125	284	356	164
DEET	51	209	151	160
Atrazine	9.2	3.4	1.7	2.0
Diazepam	2.4	1.4	1.4	1.6
Oxybenzone	<1.0	<1.0	<1.0	<1.0
Progesterone - ESI	<1.0			
Estriol	177	98	96	81
Ethinylestradiol	27	14	23	21
Estrone	32	45	37	5.6
Estradiol	<1.0	<1.0	<1.0	<1.0
Testosterone	<1.0	<1.0	<1.0	<1.0
Progesterone - APCI	<1.0	<1.0	<1.0	<1.0
Androstenedione	7.9	20	18	14
Iopromide	183	224	174	171
Naproxen	<1.0	<1.0	<1.0	<1.0
Ibuprofen	80	32	182	23
Diclofenac	<1.0	1.1	1.2	<1.0
Triclosan	<1.0	<1.0	<1.0	<1.0
Gemfibrozil	<1.0	756	836	151
α-BHC	<5.0	12	<5.0	<5.0
β-BHC	<5.0	<5.0	<5.0	<5.0
γ-BHC	<5.0	<5.0	<5.0	<5.0
Diazinon	<5.0	<5.0	<5.0	<5.0
δ-BHC	<5.0	5.8	<5.0	<5.0
Aldrin	<5.0	<5.0	<5.0	<5.0
Chlorpyrifos	<5.0	<5.0	<5.0	<5.0
Fluoranthene	<5.0	5.0	<5.0	<5.0
Dieldrin	<5.0	<5.0	<5.0	<5.0
BDE #28	<10	<10	<10	<10
BDE #47	<10	<10	<10	<10
BDE # 100	<10	<10	<10	<10
BDE #99	<10	<10	<10	<10
BDE #154	<10	<10	<10	<10
BDE #153	<10	<10	<10	<10
BHT	1756	2415	2604	2757
Bisphenol A	<100.0	6555	2665	1971
Nonylphenol (sum)	269	759	1395	1196
NDMA	NA	2.5		3.6
Perchlorate	NA	<0.05	<0.05	<0.05
Bromate	NA	<0.1	<0.1	<0.1
Iodate	NA	<1.0	<1.0	<1.0
Chlorate	NA	<0.1	0.12	<0.1

Data adjusted for Injectant dilution factor		
Well #19181	Well #19181	Well #19181
28/09/2004	12/05/2005	21/07/2005
0.88	0.90	0.82
ppt	ppt	ppt
		20.7
	1.8	
93.2	94.4	22.0
209	184	56.1
323	396	200
238	168	195
3.9	1.9	2.4
1.6	1.6	2.0
0.0	0.0	0.0
111	107	98.8
15.9	25.6	25.6
51.1	41.1	6.8
22.7	20.0	17.1
255	193	209
36.4	202	28.0
1.3	1.3	
859	929	184
13.6		
6.6		
5.7		
2744	2893	3362
7449	2961	2404
863	1550	1459
2.8	5.4	4.4
	0.1	

Table A9. Trace organic analyses of blanks used as controls

SPE Batch ID	120604-5	060305-3	080105-12	Key
Description	Travel Blank	Travel Blank	Travel Blank	LC/MS ESI - Positive
Sample Date	28/09/2004	12/05/2005	21/07/2005	LC/MS APCI - Positive
Analyte	ppt	ppt	ppt	LC/MS ESI - Negative
Hydrocodone	<1.0	<1.0	<1.0	GC/MS #1
Trimethoprim	<1.0	<1.0	<1.0	GC/MS #2
Acetaminophen	<1.0	<1.0	<1.0	GC/MS #3 - NDMA
Caffeine	<10	<10	<10	LC/MS - Oxyhalides
Erythromycin-H ₂ O	<1.0	<1.0	<1.0	Bold - Off calibration curve
Sulfamethoxazole	<1.0	<1.0	<1.0	NS - Not in spike mix
Fluoxetine	<1.0	<1.0	<1.0	NA - Not applicable
Pentoxifylline	<1.0	<1.0	<1.0	
Meprobamate	<1.0	<1.0	<1.0	
Dilantin	<1.0	<1.0	<1.0	
TCEP	<10	<10	<10	
Carbamazepine	<1.0	<1.0	<1.0	
DEET	<1.0	1.2	1.1	
Atrazine	<1.0	<1.0	<1.0	
Diazepam	<1.0	<1.0	<1.0	
Oxybenzone	<1.0	<1.0	<1.0	
Progesterone - ESI				
Estrilol	<5.0	<5.0	<5.0	
Ethynylestradiol	<1.0	<1.0	<1.0	
Estrone	<1.0	<1.0	<1.0	
Estradiol	<1.0	<1.0	<1.0	
Testosterone	<1.0	<1.0	<1.0	
Progesterone - APCI	<1.0	<1.0	<1.0	
Androstenedione	<1.0	<1.0	<1.0	
Iopromide	<1.0	<1.0	<1.0	
Naproxen	<1.0	<1.0	<1.0	
Ibuprofen	<1.0	<1.0	<1.0	
Diclofenac	<1.0	<1.0	<1.0	
Triclosan	<1.0	<1.0	<1.0	
Gemfibrozil	<1.0	<1.0	<1.0	
α -BHC	<5.0	<5.0	<5.0	
β -BHC	<5.0	<5.0	<5.0	
γ -BHC	<5.0	<5.0	<5.0	
Diazinon	<5.0	<5.0	<5.0	
δ -BHC	<5.0	<5.0	<5.0	
Aldrin	<5.0	<5.0	<5.0	
Chlorpyrifos	<5.0	<5.0	<5.0	
Fluoranthene	<5.0	<5.0	<5.0	
Dieldrin	<5.0	<5.0	<5.0	
BDE #28	<10	<10	<10	
BDE #47	<10	<10	<10	
BDE # 100	<10	<10	<10	
BDE #99	<10	<10	<10	
BDE #154	<10	<10	<10	
BDE #153	<10	<10	<10	
BHT	3337	1955	2969	
Bisphenol A	163	<100.0	<100.0	
Nonylphenol (sum)	194	22000	10380	
NDMA	<2.5	27	<2.5	
Perchlorate	<0.05	<0.05	<0.05	
Bromate	<0.1	<0.1	<0.1	
Iodate	<1.0	<1.0	<1.0	
Chlorate	<0.1	<0.1	<0.1	

1:100 dilution data

1:10 dilution

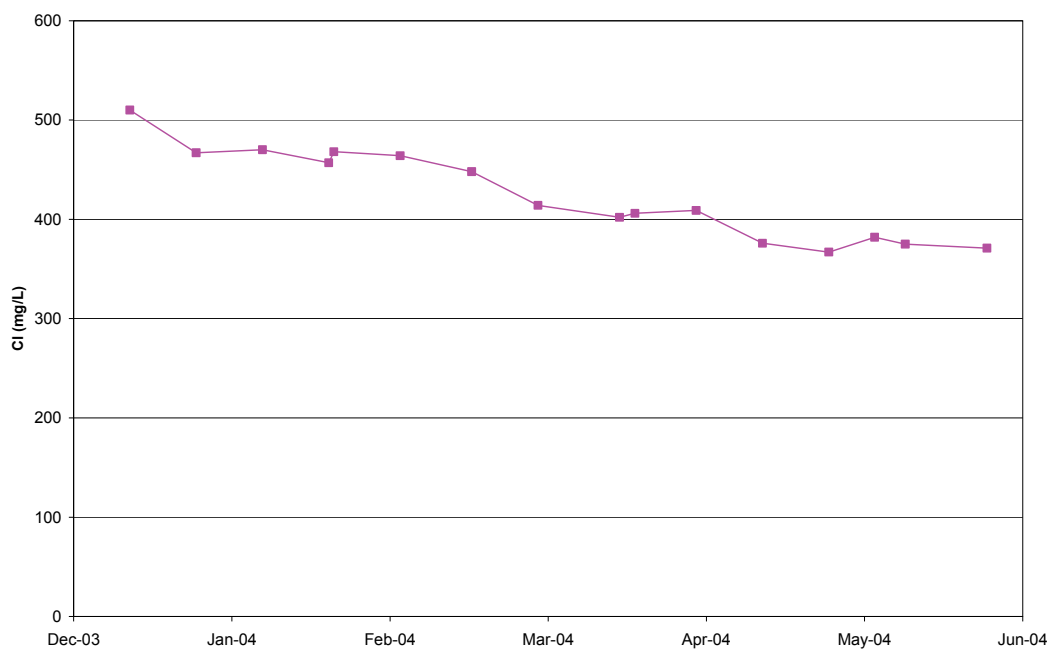


Figure A6. Chloride concentration of injectant from composite samples from autosampler.

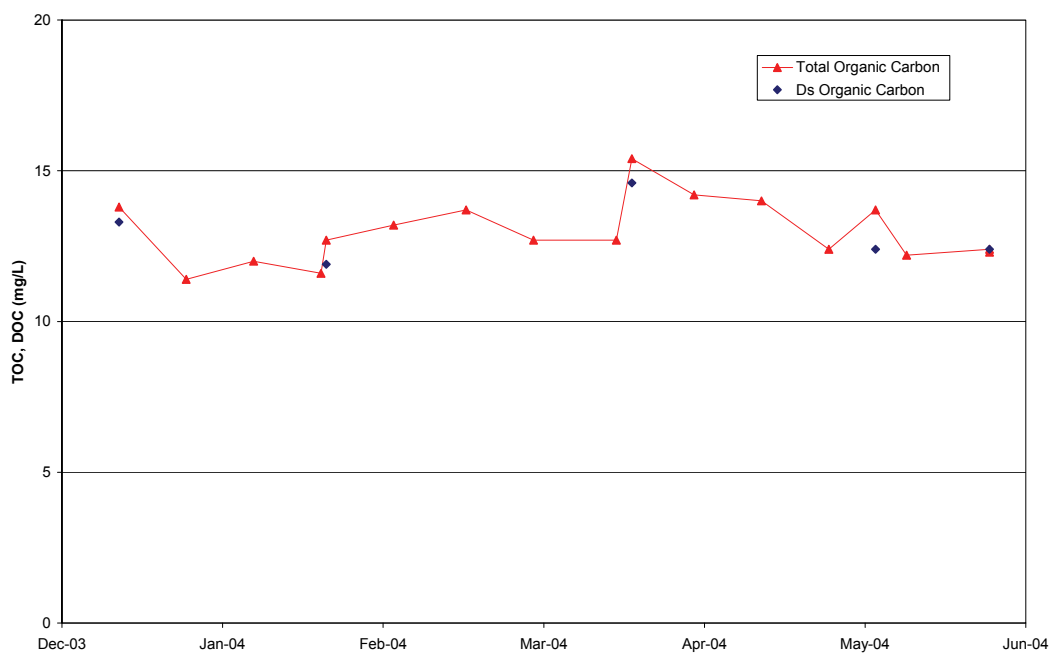


Figure A7. Total organic carbon concentration of injectant from composite samples from the autosampler.

CONCLUSIONS

The Bolivar Reclaimed Water ASR research project has been the first reclaimed water ASR project in Australia and is the first known successful trial with nutrient-rich irrigation water. The distribution of injectant in the aquifer was identified by collecting water quality data at eight fully penetrating observation wells and eight short-interval piezometers. Continuous pressure and water quality monitoring of the injectant and at selected piezometers enabled mass balances to be determined. The contrasting quality of injectant and groundwater enabled studies of geochemical reactions, fate of natural organic matter, attenuation of disinfection byproducts, endocrine disruptors, pathogens, nutrients, metals, and suspended solids. Changes in hydraulic conductivity near the injection well and deeper within the aquifer have been determined, and methods to maintain injection rates have been demonstrated. Recovery efficiency has been found to be high and is not an impediment to economic operation. It has also been demonstrated that no drinking water wells beyond the trial site or in the overlying aquifer would be adversely affected by ASR.

In addition to establishing the viability of ASR with reclaimed water in this limestone aquifer containing brackish groundwater, the research undertaken at this site has provided valuable new information about water treatment processes in aquifers. These suggest conditions under which ASR with reclaimed water is likely to be viable.

Success at Bolivar suggests that further applications, such as sustainable recovery of potable water from nonpotable sources, may be robust low-cost solutions to water supply problems in arid developing countries. Further research is proposed to explore and validate these opportunities.

The trial is continuing and will assess the long-term operational feasibility of reclaimed water ASR. This is intended to offer confidence in applying reclaimed water ASR and allow research to facilitate application elsewhere.

ACKNOWLEDGMENTS

The work reported was undertaken within the Bolivar Reclaimed Water ASR Research Project. The project partners are CSIRO, SA Department of Water Land and Biodiversity Conservation, United Water International Pty. Ltd., SA Water Corporation, and SA Department of Administrative and Information Services. The American Water Works Association Research Foundation also contributed through research project no. 2618, "Water Quality Improvements During ASR." The WateReuse Foundation provided support for additional trace organic measurements and for documentation of the methods and results.

Analytes, methods, and detection limits for samples analyzed in the field at Australian Water Quality Centre or by Las Vegas Valley Water

Analyte	AWQC Bolivar SA	CSIRO Land and Water	Southern Nevada Water Authority	Detection Method	Detection Limit
Metals					
Arsenic - total		X		USEPA 200.8	0.001 mg/L
Barium - total	X			USEPA 200.8	0.0005 mg/L
Cadmium - total	X			USEPA 200.8	0.0005 mg/L
Copper - total	X			USEPA 200.8	0.001 mg/L
Iron - total		X		USEPA 200.8	0.03 mg/l
Lead - total	X			USEPA 200.8	0.0005 mg/L
Mercury - total	X			USEPA 200.8	0.0005 mg/L
Uranium - total	X			USEPA 200.8	0.0005 mg/L
Field Parameters					
Electical Conductivity		X			
Temperature		X			
Redox potential		X		Redox Electrode with mV meter	
DO		X		Apha 4500-O-C	0.1 mg/L
Turbidity		X			
General Minerals					
pH		X		APHA 4500-H-B	0.1 pH units
EC		X		APHA 2520 B	1 mg/L
TDS	X			(Derived EC)	
Calcium				APHA 3120 B	0.1 mg/L
Magnesium				APHA 3120 B	0.3 mg/L
Sodium				APHA 3120 B	0.5 mg/L
Chloride				APHA 4500-Cl-E	4.0 mg/L
Bicarbonate				APHA 2320 B	1 mg/L
Fluoride	X			APHA 4500-F-C	0.1 mg/L
Boron	X			APHA 3120 B	0.04 mg/L
Alkalinity	X			(Derived HCO ₃)	
Gross Organics					
TOC	X			OI analytical TOC Anal	0.3 mg/L
Pathogen Indicators					
E. coli	X			APHA 9225	/100ml
Total coliform	X			APHA 9225	/100ml
Fecal coliform	X			APHA 9225	/100ml
Enterococci bacteria		X			
Coliphage		X			
Cryptosporidium	X			USEPA 1623	1/10L
Giardia	X			USEPA 1623	1/10L
Pesticides					
Lindane	X			OC Scan	0.05 ug/L
Aldrin	X			OC Scan	0.1 ug/L
Dieldrin	X			OC Scan	0.01 ug/L
Atrazine	X			OP scan	0.5 ug/L
Chlorpyrifos	X			OP scan	0.05 ug/L
Diazinon	X			OP scan	0.5 ug/L
Disinfection Byproducts					
NDMA			X	???	20 ng/L
Cyanide	X			APHA 4500-CN	50 ug/L
TTHMs	X			HEADSPACE GC-ECD	5 ug/L
HAA ₅	X			USEPA 552	5 ug/L
Radioactivity					
gross alpha particle activity	X			(outsourced)	10 mBq/L
EDC/PPCP					
17α-Ethinyl Estradiol			X	LC/MS/MS	1 ng/L
17β-Estradiol			X	LC/MS/MS	1 ng/L
Estrone			X	LC/MS/MS	1 ng/L
Fluoranthene			X	GC/MS/MS	10 ng/L
Acetaminophen			X	LC/MS/MS	1 ng/L
Hydrocone			X	LC/MS/MS	1 ng/L
Ibuprofen			X	LC/MS/MS	1 ng/L
Erythromycin			X	LC/MS/MS	1 ng/L
sulfamethoxazole			X	LC/MS/MS	1 ng/L
4-Nonylphenol			X	LC/MS/MS	100 ng/L
Bisphenol A			X	LC/MS/MS	50 ng/L
Triclosan			X	LC/MS/MS	1 ng/L
Iopromide			X	LC/MS/MS	1 ng/L
Carbamazepine			X	LC/MS/MS	1 ng/L
Meprobamate			X	LC/MS/MS	1 ng/L
Butylated hydroxy toluene			X	GC/MS/MS	20 ng/L
EDTA			X	unsure	?
Caffeine			X	LC/MS/MS	1 ng/L
Perchlorate			X	LC/MS/MS	50 ng/L
chlorate			X	LC/MS/MS	
Organics					
Polybrominated Diphenyl Ethers			X	GC/MS/MS	20 - 50 ng/L

Analytes not included in draft list

RESULTS OF RESEARCH CONDUCTED BY CSIRO AT WILLUNGA, AUSTRALIA

ASR projects that store and recover reclaimed water have typically been conducted with waters that have undergone advanced tertiary treatment to produce water that is at or near potable standards (Pyne, 1995; Pavelic and Dillon, 1997). The Bolivar ASR site described in section 4.2.4 of this report was the first site to successfully demonstrate the use of nutrient-rich reclaimed water for ASR (Dillon et al., 1999; Dillon et al., 2003).

Drawing upon the success of the Bolivar project, an ASR trial was conducted at Willunga in a similar limestone aquifer that is also within the Adelaide region to establish the feasibility of storing excess reclaimed water to meet peak demand for irrigation. The trial was intended to provide information necessary to design and operate a full-scale scheme in the McLaren Vale area.

This report provides a summary of the main findings from a series of studies from the Willunga ASR trial on the movement and mixing of injected water, recovery efficiencies, geochemical processes, and pathogen survival. Further details have been reported by Sibenaler et al. (2002), Buisine and Oemcke (2002), and Dillon et al. (2001). Studies were also carried out on physical and biological clogging at lab and field scales, groundwater modeling, and algal management, but they are not discussed in this report.

METHODS

Site Location and Hydrogeology

The ASR trial site was located immediately east of the Aldinga airport near the township of Willunga, approximately 50 km south of the center of Adelaide in South Australia (Figure A8). The location of the site was chosen based upon (1) favorable aquifer thickness and transmissivity, as evidenced by lower local groundwater potentiometric surface gradients, (2) absence of domestic groundwater users within a 2-km radius of the site, (3) access to reclaimed water from the distribution pipeline, (4) proximity to power and site security, (5) relatively low ambient groundwater salinity, and (6) infrastructure for the disposal of recovered water (Sibenaler et al., 2002).

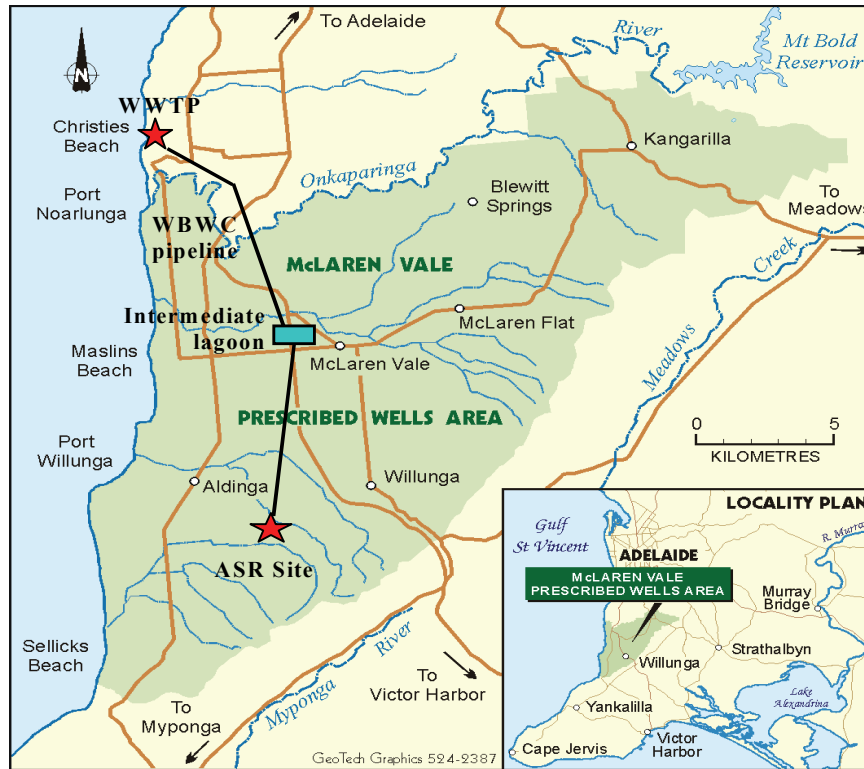


Figure A8. McLaren Vale region, indicating the location of the Willunga ASR trial site (from Buisine and Oemcke, 2002).

The target aquifer is known as the Port Willunga Formation and consists of 30 to 60 m of limestone and calcareous sands with varying shell and fossil content. Within a 50-m radius of the ASR well, the aquifer has dual porosity, with the hydraulic characteristic of the aquifer dominated by fissure flow. Downhole EM flow meter data revealed a 2–4-m-thick layer of high permeability that has the potential to transmit most of the injected water. Further to the west, at radial distances of greater than 200 m from the ASR well, the behavior is more typical of a porous flow system, with pump test-derived transmissivities of 70–80 m²/day.

The ASR well (no. 6627-10489) was completed as an open hole (i.e., without a screen) between the depths of 56–73 m below ground surface. Observation wells (nos. 6627-10490 and 6627-10491) were drilled 8 m and 55 m to the west and north of the ASR well, respectively, and a third observation well (Tinlin's production well 6627-7392) is located 26 m northwest of the ASR well. During the initial cycle testing, the rate of movement of injected water appeared to be much greater than originally anticipated, and two observation wells (nos. 6527-1369 and 6527-1368) were subsequently drilled 200 m and 500 m northwest and west of the ASR well, respectively.

Source Water Quality

The injectant is secondary treated sewage effluent from the Christies Beach Waste Water Treatment Plant that enters the Willunga Basin Water Company pipeline, which provides reclaimed water to vineyards in the McLaren Vale region. A pilot treatment plant was established at the ASR site, and this reclaimed water was filtered with a continuous backwashing sand filter and rechlorinated to meet the South Australian Reclaimed Water Guidelines for Class A water. The choice of this treatment was based on a previous study that compared the technical and economic performance of three different pretreatment technologies (Buisine and Oemcke, 2002).

Injection and Recovery Cycles

Five cycles of ASR were conducted between 31 July 2001 and 26 February 2002. For precautionary purposes, a staged program of ASR cycling was carried out. The time scale was progressively increased in each successive cycle from a 2-h injection, 2.8-h storage, and 1.3-h recovery in the first cycle through to a 56-day injection, 13-day storage, and 58-day recovery in the last cycle. A recovery phase was not conducted during test 2. A total of 31,400 m³ was injected over the five cycles at an average rate of 5 L/s. A total of 32,600 m³ of water was recovered.

Table A10. ASR test program and water balance, July 2001 to February 2002

ASR Test no	Activity	Period	Duration	Vol, 10 ³ m ³	Flow rate, L/s
0	Injection	31 July 2001	2 h	0.0366	5.1
	Storage		2 h 50 min		
	Recovery		1 h 20 min	0.0265	5.5
1	Injection	2 Aug–5 Aug 2001	25 h	0.447	5.0
	Storage		25 h 30 min		
	Recovery		22 h	0.427	5.4
2	Injection	6 Aug–9 Aug 2001	2 d 21 h	1.37	5.5
3	Injection	24 Aug–17 Sept 2001	7 d 1 h 30 min	3.34	5.5
	Storage		7 d		
	Recovery		2 d 10 h	1.15	5.5
4	Injection	29 Sept 2001–26 Feb 2002	56 d	26.2	5.4
	Storage		13 d		
	Recovery		58 d	31.0	6.2

RESULTS

Movement and Mixing of Injected Water

The patterns of EC in groundwater at the ASR well and five observation wells over the trial period is shown in Figure A9. In the near-well zone, which is characterized by a higher degree of aquifer heterogeneity and salinity and includes the 8-, 26-, and 50-m observation wells, rapid and complete breakthrough of injectant occurred in all three observation wells within hours of the commencement of each injection cycle. The three solute breakthrough curves were virtually identical due to the direct hydraulic connection with the ASR well. Only during the periods of storage and recovery did the behavior of the 50-m well deviate noticeably from that of the 8-m and 26-m wells. The variability in groundwater EC is due to source water quality variations and not mixing. Mixing between the injectant and ambient groundwater occurred during intervening periods of storage and recovery. After the earliest injection tests, ECs tended to increase most rapidly with time, since the contrast between the EC of the injectant and the receiving groundwater was greatest, but with subsequent test cycles the effects appeared to be less significant. Thus, there appears to be localized mixing between the high-permeability (fissured) zones, which contain the fresher injected water, and the less-permeable (matrix) zones, which contain the brackish native groundwater. Similar solute responses during early cycles of ASR are typical of aquifers with dual porosity characteristics (Pavelic et al., 2000). Other mechanisms, such as regional drift, were initially considered but were discounted. In the far-well zone, which includes the 200-m and 500-m observation wells, there was no significant variation in EC, which can be attributed to the breakthrough of injected water. This was supported by an evaluation of a broader suite of water quality parameters.

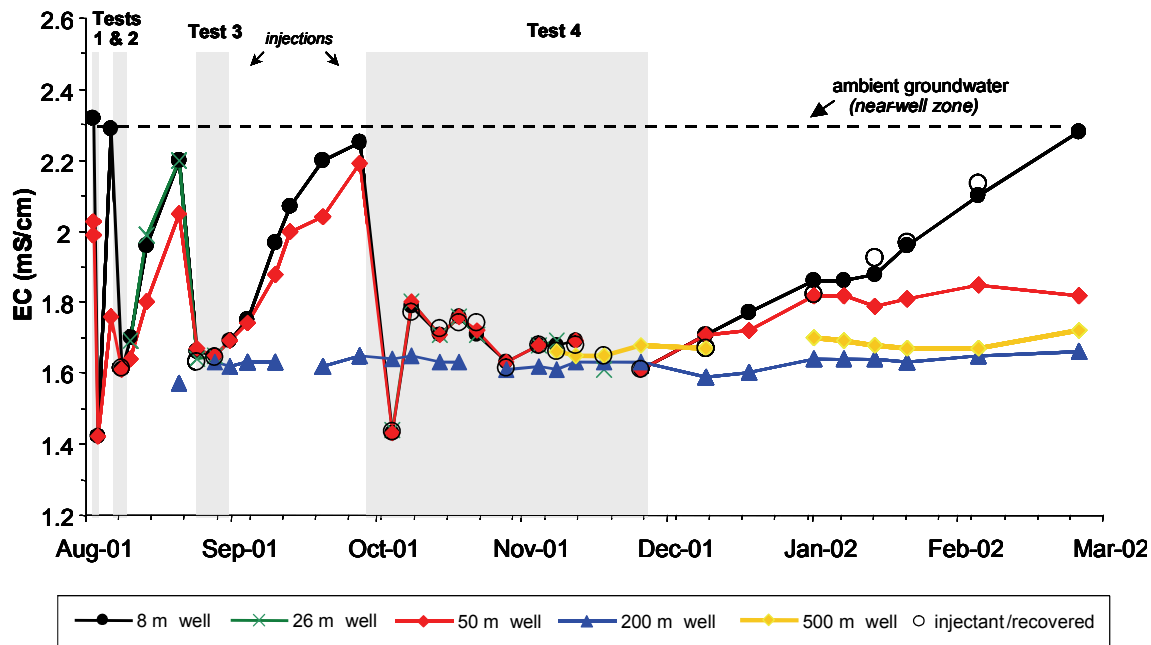


Figure A9. EC responses at all observation wells and in injected and recovered water. (The groundwater EC data represent the average value over the entire depth of the well as determined from downhole at approximately 1-m intervals.)

Recovery Efficiency

Table A11 presents a summary of the recovery efficiency data for tests 3 and 4 (note that water quality data for tests 0 and 1 were unsuitable for analysis and that data from tests 2 and 3 have been combined). Only 24% of the volume injected was recovered during the smaller-scale test 3, while the corresponding value for test 4 was 118%. It is estimated that only 11% of the injectant was recovered during test 3, while the corresponding figure in test 4 was ~60% (using equation 3 of Pavelic et al., 2002). Since the ambient groundwater quality was reached in the latter stages of the test 4 recovery, it is probable that further pumping would not have yielded significant additional contribution from injectant. In the case of test 3, the percent injectant appears low since the total volume recovered was also low. Although the average composition of injectant in the recovered water was similar for both tests, plots of the EC data expressed as a function of the cumulative volume of water recovered indicate temporal responses that are quite different, with much greater changes occurring in test 4 than in test 3 (Figure A10).

The proportion of recovered water of good quality water (defined for demonstration purposes as an EC < 2000 $\mu\text{S}/\text{cm}$) improves substantially in the latter test. RE significantly increases from 6% in test 3 to 60% in test 4. The unrecovered fraction remained in the aquifer due to a combination of exchange and advective flow downgradient of the ASR well, as previously noted. Clearly, this residual from the previous cycles and the increasing scale of the latter test have beneficial effects on recovery efficiency.

Table A11. Summary of recovery efficiencies during test cycles 3 and 4

Test Cycle No.	Vol Injected, ML	Vol Recovered, ML	% Water Recovered	% Injectant Recovered	% Injectant <2000 $\mu\text{S}/\text{cm}$
3	4.47 ^a	1.15	24	11	6
4	26.2	31.0	118	60	~60

^aIncludes the volume injected during test 2.

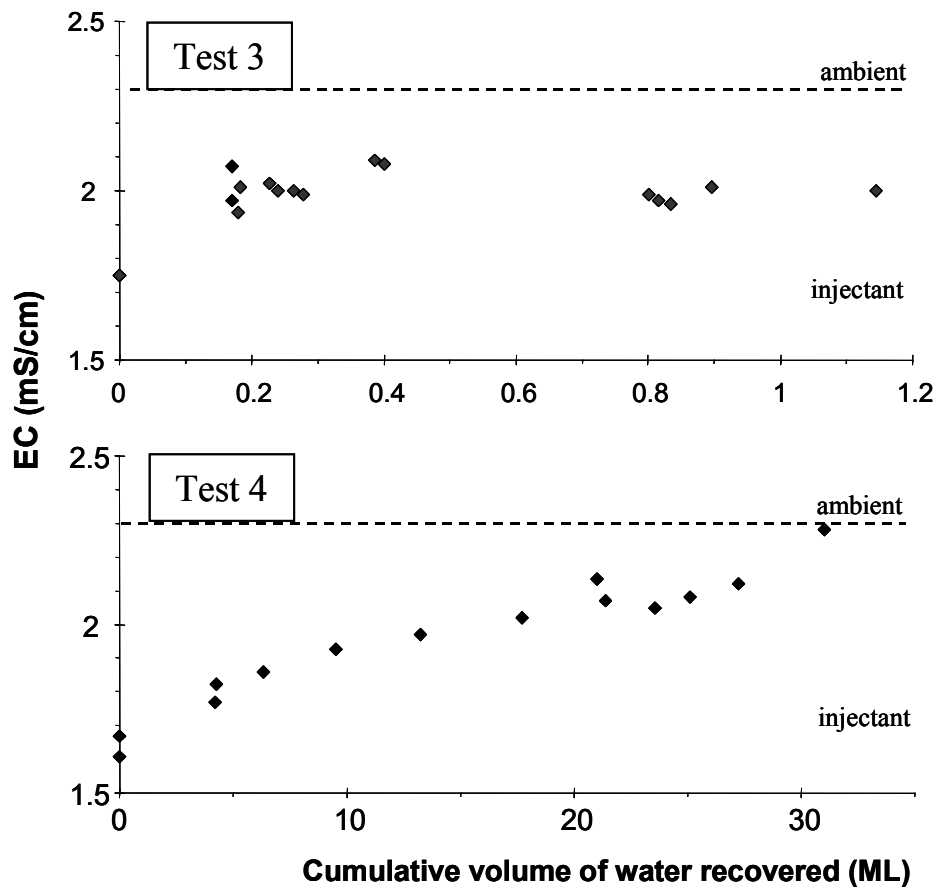


Figure A10. EC changes during the recovery phases of tests 3 and 4.

Pathogen Attenuation

The survival potential of microbial pathogens and indicator organisms in groundwater was assessed by conducting an in situ field experiment to determine the relative risk associated with ASR. Due to the level of pretreatment given to the injectant and the beneficial use of the recovered water, the experiment was conducted mainly for research purposes but also to address “what if” scenarios, such as failure at the treatment plant. The microbial pathogens tested were poliovirus, coxsackievirus, adenovirus, *Salmonella enterica* serovar Typhimurium, and the opportunistic pathogen *Aeromonas hydrophila*, as well as the indicator microorganisms *Escherichia coli* and the coliphage MS2.

Microbes were introduced in the contained environment of diffusion chambers and placed down the 200-m observation well, and a subset of chambers was periodically retrieved over a 5-week study period. At the 200-m well, there was no evidence of injectant breakthrough and was, therefore, entirely reflective of the native groundwater in the aquifer. Similar investigations at the Bolivar site indicated that the rate of microbial attenuation is slower in ambient groundwater than in the injected reclaimed water, and these results are therefore considered to be conservative estimates of survival rates in reclaimed water.

All pathogens and indicator organisms for which measurements were made were shown to attenuate significantly in Willunga groundwater (Table A12). One-log₁₀ removal (T90) times of all species ranged from 3 to 35 days. There was evidence that indigenous groundwater microorganisms are responsible for the high attenuation rates observed, as indicated by the lower T90 times for chambers suspended in ‘non-sterile’ groundwater (i.e., where indigenous microorganisms were present).

These results are supportive of the data from the Bolivar ASR site that suggest that the risk of microbial pathogen presence in recovered water is low if the reclaimed water is stored in the aquifer for a sufficient period of time (Toze and Hanna, 2002).

Table A12. Summary of attenuation rates for the tested microorganisms

Microorganism	Sterile		Nonsterile	
	Log/day	T ₉₀	Log/day	T ₉₀
Coxsackievirus	0.029	34.8	0.107	9.3
Poliovirus	–0.009	NA	0.227	4.4
Adenovirus	NR	NR	0.322	3.1
MS2	0.041	24.2	0.083	12.1
<i>E. coli</i>	NR	NR	NR	NR
<i>S. typhimurium</i>	0.066	15.2	0.078	12.8
<i>A. hydrophila</i>	0.340	5.3	0.233	17.6

Notes: NA, not applicable; NR, not recorded.

Geochemical Changes and Quality of Recovered Water

A snapshot summary of ambient groundwater quality in the ASR well (25 June 2001), injectant quality (5 August 2001, test 1), and an example of the quality of water recovered from the ASR well (29 January 2002, test 4) is shown in Table A13. The following discussion draws upon a more detailed data set presented by Sibenaler et al. (2002).

The inorganic data, with the exception of sulfate, indicate that the recovered water on that date had resembled a mixture of primarily injectant with a small amount of ambient groundwater. The sulfate increase could be due to either sulfide oxidation in the aquifer or to a variation in the sulfate concentration in the injectant. In either case, the increase is inconsequential with respect to beneficial uses of the water. The elevated nutrient concentrations in recovered water are almost certainly due to variations in nutrient concentrations in injectant over the injection periods, for which data are unavailable.

The weight of evidence suggests that all nitrogen values were unchanged with the exception of TKN at the 500-m well, indicating the possibility of a local source of contamination or cross-well sampling contamination. The latter is supported by a single concurrent spike of *E.coli* and total coliforms above background in October 2001. During the recovery phase, *E. coli* was not detected in the recovered water.

It was noted that arsenic concentrations increased slightly in the recovered water, possibly derived from oxidation of arsenopyrites (which would also increase sulfate). However, the peak concentrations observed were less than 10 µg/L and declined to below 5 µg/L within 1 mo. This suggests that the oxidation occurred only in close proximity to the ASR well and would have ceased once the injectant became anaerobic.

The recovered water quality data confirm that the recovered water meets its intended beneficial uses for irrigation. Along with ambient groundwater the recovered water fails to meet drinking water quality criteria, but it does satisfy essential requirements for irrigation water and, in the case of injectant, restrictions apply concerning the pathogen status (Sibenaler et al., 2002).

Table A13. Composition of typical injected water from test 1, ambient groundwater for ASR well (pretest cycles), and recovered water during test 4

Parameter	Ambient Groundwater ^a	Source Water ^b	Recovered Groundwater ^c
pH	7.4	7.8	7.3
EC (µS/cm)	2060	1810	1870
Turbidity (NTU)	3	1.7	0.70
Total Dissolved Solids (mg/L)	1210	1070	1080
Suspended Solids (mg/L)	14	<1	<1.0
Alkalinity (mg/L)	379	315	294
Calcium (mg/L)	92.8	76.5	78.1
Magnesium (mg/L)	64.3	47.5	47.5
Potassium (mg/L)	6.8	13.4	13.4
Sodium (mg/L)	289	246	251
Bicarbonate (mg/L)	463	384	359
Chloride (mg/L)	482	398	410
Fluoride (mg/L)	0.7	0.9	0.85
Sulfate (mg/L)	52	68.3	79.4
Ammonium N (mg/L)	0.007	0.915	0.452
Nitrate N (mg/L)	0.46 ^d	2.98	7.62
Nitrite N (mg/L)	NA	0.016	0.206
TKN N (mg/L)	0.09	1.2	0.89
Phosphorus (mg/L)	0.009	1.65	1.38
Silica (mg/L)	NA	21	23.0
Aluminium (mg/L)	NA	0.059	0.057
Arsenic (mg/L)	<0.001	0.003	<0.001
Boron (mg/L)	0.26	0.241	0.293
Cadmium (mg/L)	<0.0005	<0.0005	<0.0005
Chromium (mg/L)	<0.003	<0.003	<0.003
Copper (mg/L)	<0.001	0.012	0.001
Iron (mg/L)	<0.03	0.042	<0.030
Lead (mg/L)	<0.0005	<0.0005	0.0009
Manganese (mg/L)	0.002	0.0234	0.0023
Mercury (mg/L)	<0.0005	<0.0005	<0.0005
Nickel (mg/L)	0.0006	0.0018	0.0006
Zinc (mg/L)	<0.003	0.004	0.007
Bromide (mg/L)	NA	1.15	1.24
Total Organic Carbon (mg/L)	0.4	3.5	3.8
<i>E. coli</i> (/100 mL)	NA	0	0
Total Coliforms (/100 mL)	250	NA	4.0
Heterotrophic Iron Bacteria (/mL)	900	NA	NA
Total Algae (/mL)	NA	4	NA
Methoxychlor (µg/L)	<0.05	NA	0.09

^aASR well (PN 55318) on 25 June 2001.

^bSampled on 5 Aug 2001 (test 1).

^cSampled on 29 Jan 2002 (test 4).

^dAs NO_x.

Notes: NA, not analyzed.

CONCLUSIONS

This trial demonstrated that reclaimed water, treated to Class A standards (turbidity < 2 NTU and chlorinated but without nutrient removal), can be viably injected into a limestone aquifer dominated by fissure flow to recover for irrigation purposes.

Based on downhole flow metering and water quality changes within the aquifer, the 31 ML of reclaimed water injectant over five ASR cycles remained within the near-well zone, and no breakthrough was observed beyond the 50-m radius of the ASR well. Increases in the salinity of the injected reclaimed water during storage and recovery periods are primarily due to diffusive exchange with the brackish ambient groundwater held within less-permeable parts of the aquifer. The maximum proportion of injectant recovered in any cycle was 60%, with the remainder retained within the aquifer due to a combination of exchange and advective flow downgradient of the ASR well. It is expected that the recovery efficiency will be improved over time due to buffering caused by the residual injectant from previous injection cycles.

In situ pathogen survival studies suggest 1-log removal times of 5–35 days for the six organisms tested. There is some evidence to suggest that indigenous groundwater microorganisms are, in part, responsible for the high rates of attenuation. The recovered water met all the requirements for unrestricted irrigation, although small increases in arsenic concentrations were observed in the initial stages of pumping.

ACKNOWLEDGMENTS

This project was funded by the South Australian Government through the Department of Administrative and Information Services and managed by Australian Groundwater Technologies (AGT). The research would not have been possible without support of the Bolivar Reclaimed Water ASR Research Project partners: SA Water Corporation, SA Department for Water, Land and Biodiversity Conservation, CSIRO, and Department of Administrative and Information Services. The WateReuse Foundation provided the support to enable this concise summary of the project to be documented.

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APPENDIX B

ANALYTICAL METHODS

BACKGROUND

In order to evaluate trace levels (nanograms per liter) of target compounds in aquifer storage recovery (ASR) samples, sensitive and robust analytical methods using equipment available to the project team were employed. The team has extensive experience in the analyses of trace contaminants using a variety of analytical and bioanalytical tools (Snyder et al., 1999, 2000, 2001a, 2001b, 2001c, 2003). Since the target compounds selected encompass a wide range of chemical structures and properties, the analytical methods employed required a great deal of flexibility. We determined that a single solid-phase extraction (SPE) followed by gas chromatography with tandem mass spectrometry (GC-MS/MS) and liquid chromatography with tandem mass spectrometry (LC-MS/MS) were suitable for the microcontaminants selected for this project. Additionally, we desired to use sample volumes no greater than 1 L in order to minimize the shipment of handling of large volumes of water. By coupling automated SPE with highly sensitive and selective MS/MS instruments, robust analytical methods were developed.

SAMPLE COLLECTION AND PRESERVATION

Precleaned and presilanized 1-L amber glass sample bottles were provided to utilities for sample collection. Each sample bottle contained 1 g of sodium azide (0.1%) for sample preservation, as it has been shown previously that some compounds can undergo microbial degradation during sample storage (Vanderford et al., 2003). In addition, samples for *N*-nitrosodimethylamine (NDMA) analyses contained 80 mg of sodium thiosulfate as a quenching agent. Samples were shipped cold by packaging custom-made coolers with ice packs for transport to the laboratory. Once received, samples were stored at 4 °C until SPE could be performed.

Samples for oxyhalide analysis were collected in 125-mL plastic bottles and stored at 4 °C until analysis.

EXTRACTION AND CONCENTRATION

All compounds were extracted using SPE except NDMA and polybrominated biphenyl ethers (PBDEs), which were extracted using continuous liquid–liquid extraction (LLE), and oxyhalides, which were analyzed directly without extraction.

Complete SPE and LC-MS/MS and GC-MS/MS analysis details have been published previously (Vanderford et al., 2003; Trenholm et al., 2006). A flow chart of the extraction and analysis procedures is provided in Figure B1. In brief, 1-L samples were extracted in batches of six using hydrophilic-lipophilic balance cartridges from Waters Corporation. All extractions were performed using a Zymark Autotrace automated SPE system. Prior to extraction, the samples were spiked with GC-MS/MS and LC-MS/MS ¹³C- and deuterium-labeled surrogate standards (Table B2). The hydrophilic-lipophilic balance cartridges were sequentially preconditioned with dichloromethane (DCM), methyl *tert*-butyl ether, methanol, and reagent water. The samples were then loaded onto the SPE cartridges at 15 mL/min.

After sample loading, the SPE cartridges were rinsed with reagent water and dried with a stream of nitrogen. The SPE cartridges were eluted in two separate fractions. The first fraction (F1) was eluted with a combination of methanol and a solution of 10% methanol–90% methyl *tert*-butyl ether. The second fraction (F2) was eluted using DCM. F1 was concentrated with a gentle stream of nitrogen to a final volume of 1 mL of methanol. Five hundred microliters was removed from F1 and placed into an autosampler vial for LC-MS/MS analysis. The remaining 500 μ L was retained for a LLE cleanup and solvent exchange. F2 was concentrated to 3 mL of DCM with a gentle stream of nitrogen.

Prior to GC-MS/MS analysis, an LLE was performed on the 500- μ L aliquot from F1 to remove polar interferences and, subsequently, to combine the resulting extract with F2. Sodium chloride (2.5 mL of a 25% w/v solution) was added to F1 in order to increase the ionic strength of the solution. A solution of 10% DCM in hexane (3.5 mL) was added, and the mixture was shaken vigorously and allowed to settle. The top layer (organic) was removed and combined with F2. This procedure was performed on F1 two more times, and the resulting extracts were each combined with F2. The final combined organic extract was then concentrated with a gentle stream of nitrogen to 1 mL. Two milliliters of iso-octane was added, and the extract was concentrated to \sim 450 μ L. A solution of ^{13}C - and deuterium-labeled internal standards was then added. The extract was adjusted to a final volume of 500 μ L using iso-octane and transferred to an autosampler vial for GC-MS/MS analysis.

Since SPE recovery of PBDEs was quite poor (14–47%) (Table B3) due to the extreme hydrophobicity of these compounds, we also investigated a continuous LLE (CLLE) with DCM. The CCLE method is more applicable for nonpolar compounds, such as PBDEs, which become strongly bound to SPE resins and are difficult to elute. This CCLE method was developed during the course of the project and resulted in higher compound recoveries than the previous SPE technique. Duplicate samples were extracted using both the CCLE and the SPE methods in order to make direct method comparisons. The CCLE method began with the addition of labeled surrogate standards to a 1-L water sample. The sample was then extracted by CCLE with DCM for 18–24 hours. The DCM extract was then removed and concentrated to 1 mL. Two milliliters of iso-octane was added, and the extract was concentrated to \sim 450 μ L using nitrogen evaporation. Stable isotope-labeled internal standards were added, and the extract was adjusted to a final volume of 500 μ L. Both extractions yielded the same results of nondetect for all of the PBDE congeners. This was expected, since PBDEs are extremely hydrophobic and are not expected to occur dissolved in water at the method reporting limits for this study (10 ng/L). One study investigating PBDEs did detect PBDEs dissolved in a wastewater treatment plant effluent from northern California; however, the concentrations detected were less than our analytical method reporting limits.

NDMA was also extracted using CLLE with DCM. An isotopically labeled NDMA surrogate was added to a 1-L water sample. The sample was adjusted to pH 11 with sodium hydroxide, and 100 grams of sodium chloride was added. The sample was extracted for 18–24 hours, at which time the DCM was removed and concentrated to \sim 450 μ L. A labeled internal standard was then added, and the final extract was adjusted to 500 μ L with DCM.

Oxyhalides were not extracted or concentrated; however, each sample was eluted through one 1-cm³ Dionex OnGuard II Ba and one 1-cm³ Dionex H cartridge in series to remove sulfate and carbonate interferences. Samples were eluted at a flow rate of 2.0 mL/min, and the first 6 mL was discarded. Two milliliters of sample was then collected in a 2-mL autosampler vial. Next, 980 μ L of sample was combined with 20 μ L of a 50-ng/L $^{18}\text{O}_4$ -perchlorate solution that was used as an internal standard.

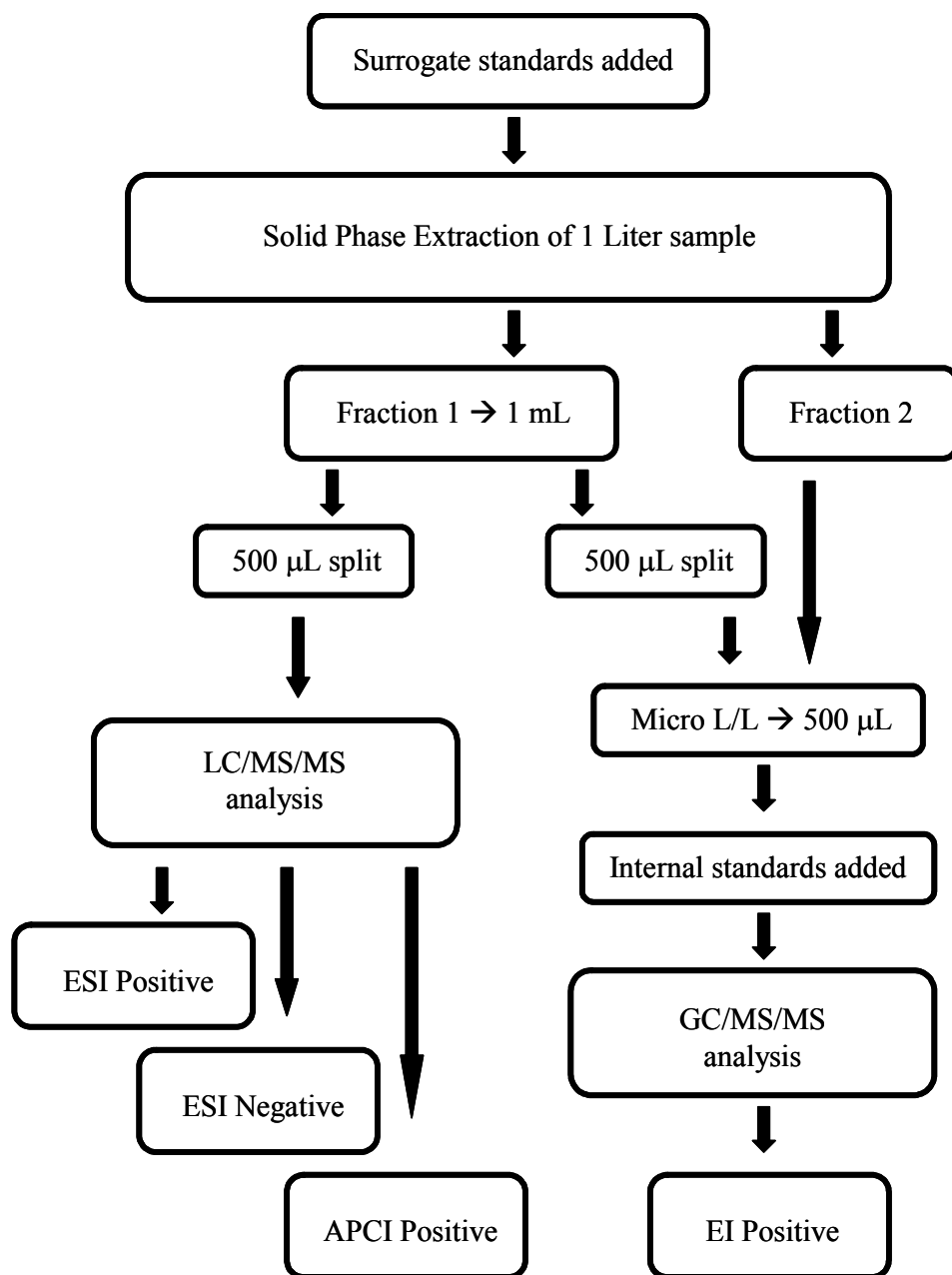


Figure B1. Analytical Method for Target EDCs and Pharmaceuticals

LIQUID CHROMATOGRAPHY WITH TANDEM MASS SPECTROMETRY

The complete LC-MS/MS method for endocrine-disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) has been published previously (Vanderford et al., 2003). Briefly, an Agilent binary pump and a CTC autosampler were used for all analyses. Analytes were separated using a Phenomenex 250- by 4.6-mm Synergi Max-RP C₁₂ column. A binary gradient consisting of 0.1% (v/v) formic acid in water (A) and 100% methanol (B) at a flow rate of 700 µL/min was used throughout. A 9-min equilibration step at 5% B was also used at the beginning of each run. An injection volume of 10 µL was used for all analyses.

The complete LC-MS/MS method for oxyhalides has also been published previously (Snyder et al., 2005). In brief, analytes were separated using a 250- by 4.6-mm Synergi Max-RP C₁₂ column with a 4-µm pore size (Phenomenex, Torrance, CA). A binary gradient consisting of 0.1% (v/v) formic acid in water (A) and 100% methanol (B) at a flow rate of 700 µL/min was used. The gradient was as follows: 5% B held for 3.5 min, increased linearly to 80% by 10 min, held for 3 min. A 9-min equilibration step at 5% B was used at the beginning of each run to bring the total run time per sample to 22 min. An injection volume of 20 µL was used for all samples.

Mass spectrometry was performed using an Applied Biosystems API 4000 triple-quadrupole mass spectrometer. All analyses were performed using multiple reaction monitoring with electrospray ionization (ESI) in both positive and negative modes and atmospheric pressure chemical ionization (APCI) in positive mode. Full LC-MS/MS method parameters have been previously published (Vanderford et al., 2003; Snyder et al., 2005).

GAS CHROMATOGRAPHY WITH TANDEM MASS SPECTROMETRY

A detailed description of the GC-MS/MS methodology used has been described by Trenholm et al. (2006). Briefly, a Varian CP-3800 gas chromatograph and autosampler were used for all analyses. Analytes were separated using an Agilent 30-m by 0.25-mm (inner diameter) by 0.25-m DB5-MS column with a 1.0-mL/min helium flow rate and an initial pressure pulse of 45 psi for 0.85 min. The temperature program was as follows: 90 °C, hold for 2.0 min; 90–150 °C at 20 °C/min; 150–280 °C at 3 °C/min, hold for 5.0 min; 280–315 °C at 30 °C/min, hold for 2.5 min. An injection volume of 2 µL was used for all analyses.

NDMA was analyzed using a 30-m by 0.25-mm (inner diameter) by 1.4-µm DB-624 MS column with a 1.0-mL/min helium flow rate and initial pressure pulse of 35 psi for 0.85 min. The temperature program was as follows: 30 °C, hold for 5.0 min; 30–80 °C at 7 °C/min, hold for 5 min; 80–280 °C at 50 °C/min, hold for 3.86 min. An injection volume of 2 µL was used for all analyses.

Mass spectrometry was performed using a Varian 2200 or a Varian 4000 ion trap mass spectrometer. All analyses were performed using multiple reaction monitoring in positive electron impact (EI) mode (Table B1), except for NDMA, which was analyzed in positive chemical ionization (CI) mode. Helium was used for the collision gas, and methanol was used for the CI gas.

Table B1. Analytical Methods for Target Compounds, Surrogates, and Internal Standards

<i>LC/MS/MS</i>		
ESI Positive	ESI Negative	APCI Positive
Acetaminophen	Diclofenac	Androstenedione
Atrazine	Gemfibrozil	Estradiol
Caffeine	Ibuprofen	Estriol
Carbamazepine	Iopromide	Estrone
DEET	Naproxen	Ethinylestradiol
Diazepam	Triclosan	Progesterone
Dilantin		Testosterone
Erythromycin-H ₂ O		
Fluoxetine	¹³ C ₃ -Ibuprofen (SU)	¹³ C ₂ -Estradiol (SU)
Hydrocodone	¹³ C ₁₂ -Triclosan (SU)	Testosterone- <i>d</i> ₃ (SU)
Meprobamate		
Oxybenzone	Perchlorate*	
Pentoxifylline	Chlorate	
Sulfamethoxazole	Bromate	
TCEP	Iodate	
Trimethoprim		
¹³ C ₃ -Caffeine (SU) ^a	* ¹⁸ O ₄ -Perchlorate (IS)	
¹³ C ₃ -Atrazine (SU)		
Diazepam- <i>d</i> ₅ (SU)		
<i>GC/MS/MS</i>		
EI Positive	CI Positive	
α-BHC	NDMA	
β-BHC	<i>N</i> -Nitrosodipropylamine- <i>d</i> ₁₄ (SU)	
γ-BHC	<i>N</i> -Nitrosodimethylamine- <i>d</i> ₆ (IU)	
δ-BHC		
Diazinon		
Aldrin		
Chlorpyrifos		
Fluoranthene		
Dieldrin		
BDE #28		
BDE #47		
BDE #99		
BDE #100		
BDE #153		
BDE #154		
Bisphenol A		
BHT		
Nonylphenol		
Fluorene- <i>d</i> ₁₀ (SU)		
¹³ C ₁₂ -Methoxychlor (SU)		
¹³ C ₁₀ -BDE #28 (SU)		
¹³ C ₁₀ -BDE #100 (SU)		
¹³ C ₆ -Nonylphenol (SU)		
¹³ C ₆ -α-BHC (IS)		
DDD- <i>d</i> ₈ (IS)		

Notes: SU, surrogate; IS, internal standard.

QUALITY ASSURANCE AND QUALITY CONTROL

Method reporting limits were chosen at the lowest calibration point in which the analyte peak had a signal-to-noise ratio greater than 10 (Table B2). Reporting limits of EDCs and PPCPs ranged from 1.0 ng/L to 100 ng/L for LC-MS/MS and GC-MS/MS compounds, while reporting limits for the oxyhalides ranged from 0.05 µg/L to 1.0 µg/L. During the project, a study of deionized water blanks was performed using the entire method in order to determine if any of the target compounds were introduced during the analytical procedure as contaminants. It was determined that high levels of butylated hydroxytoluene (BHT) originated from the SPE cartridges, causing observed spiked recoveries to exceed 100%. For nonylphenol there was also a small amount of contamination linked to the SPE cartridges.

During instrumental analysis, calibration was performed using a minimum of five calibration points, with resulting regression coefficients in excess of 0.990. LC-MS/MS for EDC and PPCP analyses used external calibration, and GC-MS/MS analyses used internal calibration with the internal standards shown in Table B2. For oxyhalides, perchlorate was internally calibrated, and chlorate, bromate, and iodate were used for external calibration. Continuing calibration verifications were analyzed at regular intervals to ensure the performance of the instruments.

Analyte recoveries were determined by adding an appropriate amount of a stock solution of the target compounds to 1 L of deionized water, which was subsequently extracted by the procedure described previously. Table B3 shows the mean recovery and percent relative standard deviation (% RSD) for both LC-MS/MS and GC-MS/MS compounds. Within each batch of six extracted samples, a deionized water blank and spike were added to monitor the reliability of the extraction process. As discussed above, surrogate standards were added to each sample to monitor the sample extraction and determine possible matrix effects.

Table B2. Method Reporting Limits

LC-MS/MS		GC-MS/MS	
Compound	Method Reporting Limit, ng/L	Compound	Method Reporting Limit, ng/L
Hydrocodone	1.0	α -BHC	5.0
Trimethoprim	1.0	β -BHC	5.0
Acetaminophen	1.0	γ -BHC	5.0
Caffeine	1.0	δ -BHC	5.0
Erythromycin-H ₂ O	1.0	Diazinon	5.0
Sulfamethoxazole	1.0	Aldrin	5.0
Fluoxetine	1.0	Chlorpyrifos	5.0
Pentoxifylline	1.0	Fluoranthene	5.0
Meprobamate	1.0	Dieldrin	5.0
Dilantin	1.0	BDE #28	10
TCEP	1.0	BDE #47	10
Carbamazepine	1.0	BDE # 100	10
DEET	1.0	BDE #99	10
Atrazine	1.0	BDE #154	10
Diazepam	1.0	BDE #153	10
Oxybenzone	1.0	BHT	100
Iopromide	1.0	Bisphenol A	100
Naproxen	1.0	Nonylphenol	100
Ibuprofen	1.0	NDMA	2.5
Diclofenac	1.0		
Triclosan	1.0		
Gemfibrozil	1.0		
Estriol	5.0		
Ethinylestradiol	1.0		
Estrone	1.0		
Estradiol	1.0		
Testosterone	1.0		
Progesterone	1.0		
Androstenedione	1.0		
Perchlorate	50		
Chlorate	100		
Bromate	100		
Iodate	1000		

Table B3. Recovery and RSD for Target Analytes

<i>LC-MS/MS</i>			<i>GC-MS/MS</i>		
Compound	% Recovery	% RSD	Compound	% Recovery	% RSD
Acetaminophen	41	14	Aldrin	48	13
Androstenedione	96	12	α -BHC	59	19
Atrazine	89	8	β -BHC	81	11
Caffeine	93	10	γ -BHC	65	17
Carbamazepine	91	12	δ -BHC	74	12
DEET	81	19	Fluoranthene	91	8
Diazepam	80	19	Diazinon	77	19
Diclofenac	83	11	Chlorpyrifos	50	32
Dilantin	86	11	BDE #28	47	18
Erythromycin	71	10	BDE #47	26	29
Estradiol	92	14	BDE # 100	20	31
Estriol	101	9	BDE #99	20	40
Estrone	90	7	BDE #154	19	31
Ethinylestradiol	92	11	BDE #153	14	51
Fluoxetine	80	7	BHT	433	20
Gemfibrozil	94	10	Bisphenol A	59	18
Hydrocodone	112	7	Nonylphenol	115	26
Ibuprofen	96	15	NDMA	34	36
Meprobamate	96	11			
Naproxen	91	9			
Oxybenzone	68	19			
Pentoxifylline	84	15			
Progesterone	90	12			
Sulfamethoxazole	72	16			
TCEP	75	18			
Testosterone	83	9			
Triclosan	79	17			
Trimethoprim	91	9			

Methods

		Units	Englewood, FL	Manatee, FL	Chandler, AZ	Bolivar, Australia
General Parameters						
Alkalinity	mg/L	SM 2320B	SM 2320B	SM 2320B	SM2320 B	Potentiometric titration to endpoint pH 4.5
Bicarbonate	mg/L	SM 2320B	SM 2320B	SM 2320B	SM2320 B	Potentiometric titration from pH 8.3 to endpoint pH 4.5
Boron	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	200.7	515-01
Calcium	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	200.7	0.45-um filtration, acidification to 1% HNO ₃ , ICP-ES
Chloride	mg/L	EPA 300.0	EPA 300.0	EPA 300.0	300	Automated ferricyanide colorimetric method
DO	mg/L	Field	EPA 360.1	EPA 360.1	DO probe	Field
Fluoride	mg/L	EPA 300.0	EPA 300.0	EPA 300.0	300	Specific ion electrode
Magnesium	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	200.7	Acid digestion, acidification to 1% HNO ₃ , ICP-ES
pH		EPA 150.1	EPA 150.1	EPA 150.1	SM 4500H B	Field
Redox Potential	mV	ASTM D1498			SM 2580	Field
Sodium	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	273.1	0.45-um filtration, acidification to 1% HNO ₃ , ICP-ES
Specific Conductance	uS/cm	SM 2510B		NA	SM 2510 B	Field
Conductivity	umhos/cm	NA	EPA 120.1	EPA 120.1		16-01
TDS	mg/L	EPA 160.1	SM 2540	SM 2540	TDS probe	15-01
Temperature	°C	Field	Field	Field	SM 2550 B	Field
TOC	mg/L	SM3510.B	EPA 415.1	EPA 415.1	SM 5310 C	Persulfate oxidation - SKALAR total organic
Turbidity	NTU	EPA 180.1	EPA 180.0	EPA 180.0	SM 2130 B	Hach 2100P turbidimeter
Nutrients						
Total Kjeldahl Nitrogen	mg/L	EPA 351.2	EPA 351.2	EPA 351.2	SM4500-NORG,C	Kjeldahl digestion followed by automated colorimetric
Total Nitrogen	mg/L	EPA 353, 351	TKN + NH3-N	TKN + NH3-N	Calculation	Derived from total of 112-01 and 161-01
Ammonia	mg/L	EPA 350.2	EPA 350.1	EPA 350.1	350.3	Automated colorimetric
Nitrate-N as N	mg/L	EPA 353.2	EPA 300.0	EPA 300.0	300	Automated colorimetric cadmium reduction (for nitrate and nitrite)
Nitrite-N as N	mg/L	EPA 353.2	EPA 300.0	EPA 300.0	300	
Total Phosphorous	mg/L	EPA 365.3	EPA 365.1	EPA 365.1	365.3	H ₂ SO ₄ /K ₂ SO ₄ /HgO digestion, automated colorimetric
Orthophosphate	mg/L	EPA 365.3	EPA 300.0	EPA 300.0	300	Filtered, 0.45 um; automated colorimetric
Metals						
Arsenic - total	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	200.7/200.9	512-21
Barium - total	mg/L	EPA 200.7	EPA 200.7	EPA 200.7	200.7	615-61

Methods

	Units	Englewood, FL	Manatee, FL	Chandler, AZ	Bolivar, Australia
Cadmium - total	mg/L	EPA 200.7	EPA 200.7	200.7/200.9	525-61
Copper - total	mg/L	EPA 200.7	EPA 200.7	200.7	540-61
Iron - total	mg/L	EPA 200.7	EPA 200.7	200.7	545-01
Lead - total	mg/L	EPA 200.7	EPA 200.7	200.7/200.9	550-61
Mercury - total	mg/L	EPA 245.1	EPA 245.1	245.1	565-01
Selenium - total	mg/L	EPA 200.7	EPA 200.7	200.7/200.9	585-22
Disinfection Byproducts					
Cyanide	mg/L	EPA 335.2	SM 4500CN-E	SM 4500-CN-C,E	167-03
TTHMs	ug/L	EPA 524.2	EPA 601	524.2	50-03
HAA5	ug/L	EPA 552.1	SM 6215B	552.2	MS7
Radioactive Parameters					
Gross Alpha Particle Activity	mBq/L	EPA 900.0	EPA 00-02	600/00-02	230-01
Total Uranium	mg/L	EPA 908.0	EPA 908.0	00-07	680-61
Microbiological Parameters					
Total Coliform	/100 mL	SM 9222B	SM 9222B	SM 9221 B, E	80-07
Fecal Coliform	/100 mL	SM 9222D	WM 9222D	SM 9221 B, E	76-01
<i>E. coli</i>	/100 mL	SM 9222B		SM 9221 F	81-01
Enterococci Bacteria	/100 mL	SM 18 9230C		SM 9230 B	Toze et al. (2000) ^a
Coliphage	PFU/100 mL	EPA 1602	EPA 1601, 1602	SM 9211 D	Souter et al. (2000) ^b
<i>Cryptosporidium</i>	oocysts/L	EPA 1623	EPA 1623	1623	2247-11
<i>Giardia</i>	cysts/L	EPA 1623	EPA 1623	1623	2248-11
Heterotrophic Plate Count	/mL	SM 9215B		SIMPLATE	Not measured

^aDirect enumeration using dual layer method; enrichment involves an overnight enrichment of phage in the presence of active *E. coli* host cells followed by detection of phage by dual layer method.

^bConcentration of water sample using hollow fibre tangential flow filtration, followed by detection of viruses using PCR/RT-PCR.

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APPENDIX C

RAW DATA

Microcontaminant Laboratory Blanks

Compound	No. Positive	Avg Conc'n, ng/L	% RSD
Androstenedione	0	<1	0
BDE #28	0	<10	0
Bisphenol A	0	<100	0
Caffeine	0	<10	0
Carbamazepine	0	<1	0
Chlorate	0	<100	0
Chlorpyrifos	0	<5	0
DEET	1	2.4	0
Dilantin	0	<1	0
Erythromycin-H2O	0	<1	0
Estradiol	0	<1	0
Estrone	0	<1	0
Fluoranthene	1	5.1	0
Gemfibrozil	0	<1	0
Hydrocodone	0	<1	0
Ibuprofen	0	<1	0
Iopromide	0	<1	0
Meprobamate	0	<1	0
Naproxen	0	<1	0
NDMA	0	<2.5	0
Nonylphenol	7	174	31
Pentoxifylline	0	<1	0
Perchlorate	0	<50	0
Sulfamethoxazole	0	<1	0
TCEP	0	<10	0
Triclosan	0	<1	0
Trimethoprim	0	<1	0

Bolivar, Australia							
		Injectant	Well 18777	Well 19450	Well 19181	Travel Blank	Well 18777
			AWQC ID 11008	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008
			ASR	4-m MW	50-m Piez.		ASR
	Units	5/6/2004	9/28/2004	9/28/2004	9/28/04	9/28/2004	5/12/2005
		3 wks prior to end of recharge	4 mo storage	4 mo storage	4 mo storage	4 mo storage	3 wks into recovery
		0.256 mgd	0 mgd	0 mgd	0 mgd	0 mgd	0.454 mgd
		35.7 MG	40.8 MG	40.8 MG	40.8 MG	40.8 MG	32.1 MG
General Parameters							
Alkalinity	mg/L	136	320	198	228	NA	193
Bicarbonate	mg/L	166	391	242	278	NA	235
Boron	mg/L	0.286	0.473	0.297	0.389	NA	0.304
Calcium	mg/L	37	78.4	55.5	68.3	NA	59
Chloride	mg/L	382	347	349	459	NA	385
DO	mg/L	11.88	2.68	0.43	0.08	NA	0.01
Fluoride	mg/L	0.98	0.87	0.86	0.37	NA	0.76
Magnesium	mg/L	32.4	47.1	34.9	37.1	NA	34.2
pH		7.4	6.94	6.21	7.26	NA	7.26
Redox potential	mV	NA	112	-32	-6	NA	9
Sodium	mg/L	240	241	240	309	NA	273
Specific Conductance	uS/cm	1652	1826	1668	223	NA	1971
Conductivity	umhos/cm					NA	
TDS	mg/L	900	1100	998	1270	NA	1000
Temperature	°C	7.58	15.1	15.8	20.6	NA	17.2
TOC	mg/L	13.7	31.8	9.9	9.8	NA	7.9
Turbidity	NTU	1.3	32.6	1.31	10.1	NA	1.68
Nutrients							
Total Kjeldahl Nitrogen	mg/L	1.42 as N	9.41	1.24	7.16	NA	1.05
Total Nitrogen	mg/L	8.2	9.41	1.26	7.17	NA	0.692
Ammonia	mg/L					NA	0.692
Nitrate-N as N	mg/L	sum = 6.78	<0.005	0.07	0.01	NA	<0.005
Nitrite-N as N	mg/L		<0.005	0.013	<0.005	NA	
Total Phosphorous	mg/L	1.58 as P	2.64	0.85	0.04	NA	0.641
Ortho-phosphate	mg/L	1.91 as P	0.984	0.829	0.02	NA	0.406
Metals							
Arsenic - total	mg/L	0.002	0.075	0.02	<0.002	NA	0.02
Barium - total	mg/L	0.0027	0.0041	0.0027	0.0329	NA	0.0055
Cadmium - total	mg/L	<0.0005	<0.0005	<0.0005	<0.0005	NA	<0.0005
Copper - total	mg/L	0.009	0.006	0.002	<0.001	NA	<0.001
Iron - total	mg/L	<0.03	6.91	0.044	0.248	NA	0.542
Lead - total	mg/L	<0.0005	0.0008	<0.0005	<0.0005	NA	<0.0005
Mercury - total	mg/L	<0.0005	<0.0003	<0.0003	<0.0003	NA	<0.0003
Selenium - total	mg/L	<0.003	<0.001	<0.001	<0.001	NA	<0.003

Bolivar, Australia							
	Well 19450	Well 19181	Travel Blank	Well 18777	Well 19450	Well 19181	Travel Blank
	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008	AWQC ID 11073	AWQC ID 11013	
	4-m MW	50-m Piez.		ASR	4-m MW	50-m Piez.	
	5/12/2005	5/12/2005	5/12/2005	7/21/05	7/21/2005	7/21/2005	7/21/2005
Status	3 wks into recovery	3 wks into recovery	3 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery
Flow	0.454 mgd	0.454 mgd	0.454 mgd	0.342 mgd	0.342 mgd	0.342 mgd	0.342 mgd
Volume	32.1 MG	32.1 MG	32.1 MG	8.35 MG	8.35 MG	8.35 MG	8.35 MG
General Parameters							
Alkalinity	204	239	NA	211	216	264	NA
Bicarbonate	249	292	NA	258	264	322	NA
Boron	0.307	0.332	NA	0.306	0.302	0.318	NA
Calcium	67.8	68.2	NA	85.7	105	70.3	NA
Chloride	464	449	NA	611	715	502	NA
DO	0.06	0.67	NA	0.02	0.21	0.11	NA
Fluoride	0.3	0.3	NA	0.68	0.6	0.3	NA
Magnesium	39	36.6	NA	50	57.8	37.9	NA
pH	7.32	7.29	NA	7.39	7.49	7.21	NA
Redox potential	-36	21	NA	-41	-62	9	NA
Sodium	306	315	NA	370	397	321	NA
Specific Conductance	2250	2330	NA	2560	2210	2500	NA
Conductivity			NA				NA
TDS	1200	1200	NA	1510	1670	1330	NA
Temperature	20.9	20.3	NA	22.6	21.4	21.4	NA
TOC	7.4	8.6	NA	6.8	5.3	8.9	NA
Turbidity	0.38	na	NA	1.99	0.66	49.5	NA
Nutrients							
Total Kjeldahl Nitrogen	1.12	5.93	NA	0.52	0.46	11.3	NA
Total Nitrogen	0.951	5.2	NA	<0.005	1.43	10.126	NA
Ammonia	0.946	5.2	NA	<0.005	<0.005	10.1	NA
Nitrate-N as N			NA				NA
Nitrite-N as N	0.005	<0.005	NA	<0.005	1.43	0.026	NA
Total Phosphorous	0.338	0.033	NA	0.494	0.43	0.074	NA
Ortho-phosphate	0.3	0.02	NA	0.342	0.2	0.037	NA
Metals							
Arsenic - total	0.007	0.001	NA	0.011	0.007	<0.001	NA
Barium - total	0.0114	0.0364	NA	0.0136	0.0245	0.0341	NA
Cadmium - total	<0.0005	<0.0005	NA	<0.0005	<0.0005	<0.0005	NA
Copper - total	0.002	0.002	NA	<0.001	<0.001	<0.001	NA
Iron - total	0.481	0.26	NA	0.389	0.358	0.354	NA
Lead - total	0.0008	<0.0005	NA	<0.0005	0.0006	<0.0005	NA
Mercury - total	<0.0003	<0.0003	NA	<0.0003	<0.0004	<0.0003	NA
Selenium - total	<0.003	<0.003	NA	0.007	0.007	0.005	NA

Bolivar, Australia							
		Injectant	Well 18777	Well 19450	Well 19181	Travel Blank	Well 18777
			AWQC ID 11008	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008
			ASR	4-m MW	50-m Piez.		ASR
	Units	5/6/2004	9/28/2004	9/28/2004	9/28/04	9/28/2004	5/12/2005
Status		3 wks prior to end of recharge	4 mo storage	4 mo storage	4 mo storage	4 mo storage	3 wks into recovery
Flow		0.256 mgd	0 mgd	0 mgd	0 mgd	0 mgd	0.454 mgd
Volume		35.7 MG	40.8 MG	40.8 MG	40.8 MG	40.8 MG	32.1 MG
Disinfection Byproducts							
Cyanide	mg/L	<0.05	<0.05	<0.05	<0.05	NA	<0.05
TTHMs	ug/L	234	18	80	<4	NA	<4
HAA5	ug/L	72	<9	<9	<9	NA	<9
Radioactive Parameters							
gross alpha particle activity	mBq/L		59	28	58	NA	42
Total uranium	mg/L		<0.0005	0.0015	<0.0005	NA	0.0009
Microbiological Parameters							
Total coliform	/100 mL	110	68	15	7	NA	0
Fecal coliform	/100 mL	6	0	0	0	NA	0
<i>E. coli</i>	/100 mL	6	0	0	0	NA	0
Enterococci bacteria	/100 mL		ND	ND	74	NA	0
Coliphage	PFU/100 mL		ND	ND	ND	NA	ND
<i>Cryptosporidium</i>	oocysts/L		<0.6	<0.6	<0.5	NA	<0.3
<i>Giardia</i>	cysts/L		<0.7	<0.7	<0.3	NA	<0.3
Heterotrophic Plate Count	/mL	NA	NA	NA	NA	NA	NA
Microcontaminants							
Hydrocodone	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	1.0
Trimethoprim	ng/L	<1.0	2.7	<1.0	<1.0	<1.0	2.7
Acetaminophen	ng/L	<1.0	3.9	<1.0	<1.0	<1.0	<1.0
Caffeine	ng/L	13	112	13	<10	<10	<10
Erythromycin-H2O	ng/L	<1.0	484	8.6	<1.0	<1.0	14
Sulfamethoxazole	ng/L	<1.0	<1.0	3.4	<1.0	<1.0	<1.0
Fluoxetine	ng/L	<1.0	1.6	<1.0	<1.0	<1.0	<1.0
Pentoxifylline	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Meprobamate	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Dilantin	ng/L	32	110	126	82	<1.0	104
TCEP	ng/L	151	219	293	184	<10	258
Carbamazepine	ng/L	125	319	373	284	<1.0	388
DEET	ng/L	51	36	47	209	<1.0	81
Atrazine	ng/L	9.2	1.8	8.2	3.4	<1.0	5.0
Diazepam	ng/L	2.4	4.9	2.5	1.4	<1.0	1.6
Oxybenzone	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Estriol	ng/L	177	<5.0	73	98	<5.0	56
Ethinylestradiol	ng/L	27	7.0	10	14	<1.0	25

Bolivar, Australia							
	Well 19450	Well 19181	Travel Blank	Well 18777	Well 19450	Well 19181	Travel Blank
	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008	AWQC ID 11073	AWQC ID 11013	
	4-m MW	50-m Piez.		ASR	4-m MW	50-m Piez.	
	5/12/2005	5/12/2005	5/12/2005	7/21/05	7/21/2005	7/21/2005	7/21/2005
Status	3 wks into recovery	3 wks into recovery	3 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery
Flow	0.454 mgd	0.454 mgd	0.454 mgd	0.342 mgd	0.342 mgd	0.342 mgd	0.342 mgd
Volume	32.1 MG	32.1 MG	32.1 MG	8.35 MG	8.35 MG	8.35 MG	8.35 MG
Disinfection Byproducts							
Cyanide	<0.05	<0.05	NA	<0.05	<0.05	<0.05	NA
TTHMs	<4	<4	NA	<4	<4	<4	NA
HAA5	<9	<9	NA	<9	<9	<9	NA
Radioactive Parameters							NA
gross alpha particle activity	35	23	NA	110	66	101	NA
Total uranium	0.0038	<0.0005	NA	0.001	0.0027	<0.0005	NA
Microbiological Parameters							
Total coliform	1	0	NA	0	1	1	NA
Fecal coliform	0	0	NA	0	0	0	NA
<i>E. coli</i>	0	0	NA	0	0	0	NA
Enterococci bacteria	0	0	NA	0	0	7.4	NA
Coliphage	ND	ND	NA	ND	ND	ND	NA
<i>Cryptosporidium</i>	<0.5	<0.6	NA	<0.7	<0.2	<0.5	NA
<i>Giardia</i>	<0.3	<0.3	NA	<0.7	<0.2	<0.6	NA
Heterotrophic Plate Count	NA	NA	NA	NA	NA	NA	NA
Microcontaminants							
Hydrocodone	1.1	<1.0	<1.0	1.4	1.4	<1.0	<1.0
Trimethoprim	2.6	<1.0	<1.0	1.2	<1.0	<1.0	<1.0
Acetaminophen	<1.0	<1.0	<1.0	2.4	179	<1.0	<1.0
Caffeine	<10	<10	<10	17	141	17	<10
Erythromycin-H2O	14	1.6	<1.0	26	29	<1.0	<1.0
Sulfamethoxazole	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fluoxetine	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pentoxifylline	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Meprobamate	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Dilantin	91	85	<1.0	32	26	18	<1.0
TCEP	222	166	<10	78	74	46	<10
Carbamazepine	438	356	<1.0	173	131	164	<1.0
DEET	87	151	1.2	64	55	160	1.1
Atrazine	3.8	1.7	<1.0	2.2	1.9	2.0	<1.0
Diazepam	1.4	1.4	<1.0	2.1	1.8	1.6	<1.0
Oxybenzone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Estriol	49	96	<5.0	95	96	81	<5.0
Ethinylestradiol	22	23	<1.0	23	17	21	<1.0

Bolivar, Australia							
		Injectant	Well 18777	Well 19450	Well 19181	Travel Blank	Well 18777
			AWQC ID 11008	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008
			ASR	4-m MW	50-m Piez.		ASR
	Units	5/6/2004	9/28/2004	9/28/2004	9/28/04	9/28/2004	5/12/2005
Status		3 wks prior to end of recharge	4 mo storage	4 mo storage	4 mo storage	4 mo storage	3 wks into recovery
Flow		0.256 mgd	0 mgd	0 mgd	0 mgd	0 mgd	0.454 mgd
Volume		35.7 MG	40.8 MG	40.8 MG	40.8 MG	40.8 MG	32.1 MG
Microcontaminants (cont.)							
Estrone	ng/L	32	26	<1.0	45	<1.0	<1.0
Estradiol	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Testosterone	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Progesterone	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Androstenedione	ng/L	7.9	1.2	1.0	20	<1.0	1.5
Iopromide	ng/L	183	7.3	<1.0	224	<1.0	28
Naproxen	ng/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ibuprofen	ng/L	80	11	<1.0	32	<1.0	86
Diclofenac	ng/L	<1.0	<1.0	<1.0	1.1	<1.0	<1.0
Triclosan	ng/L	<1.0	1.5	<1.0	<1.0	<1.0	3.0
Gemfibrozil	ng/L	<1.0	3.9	<1.0	756	<1.0	95
α -BHC	ng/L	<5.0	14	<5.0	12	<5.0	<5.0
β -BHC	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
γ -BHC	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diazinon	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
δ -BHC	ng/L	<5.0	<5.0	<5.0	5.8	<5.0	<5.0
Aldrin	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Chlorpyrifos	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fluoranthene	ng/L	<5.0	5.3	<5.0	5.0	<5.0	<5.0
Dieldrin	ng/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
BDE #28	ng/L	<10	<10	<10	<10	<10	<10
BDE #47	ng/L	<10	<10	<10	<10	<10	<10
BDE # 100	ng/L	<10	<10	<10	<10	<10	<10
BDE #99	ng/L	<10	<10	<10	<10	<10	<10
BDE #154	ng/L	<10	<10	<10	<10	<10	<10
BDE #153	ng/L	<10	<10	<10	<10	<10	<10
BHT	ng/L	1756	2202	2892	2415	3337	1632
Bisphenol A	ng/L	<100.0	305	478	6555	163	1324
Nonylphenol (sum)	ng/L	269	259	450	759	194	1041
NDMA	ng/L	na	<2.5	<2.5	2.5	<2.5	7.8
Perchlorate	ng/L	na	<50	240	<50	<50	<50
Bromate	ng/L	na	<100	<100	<100	<100	<100
Iodate	ng/L	na	<1000	<1000	<1000	<1000	<1000
Chlorate	ng/L	na	<100	760	<100	<100	120

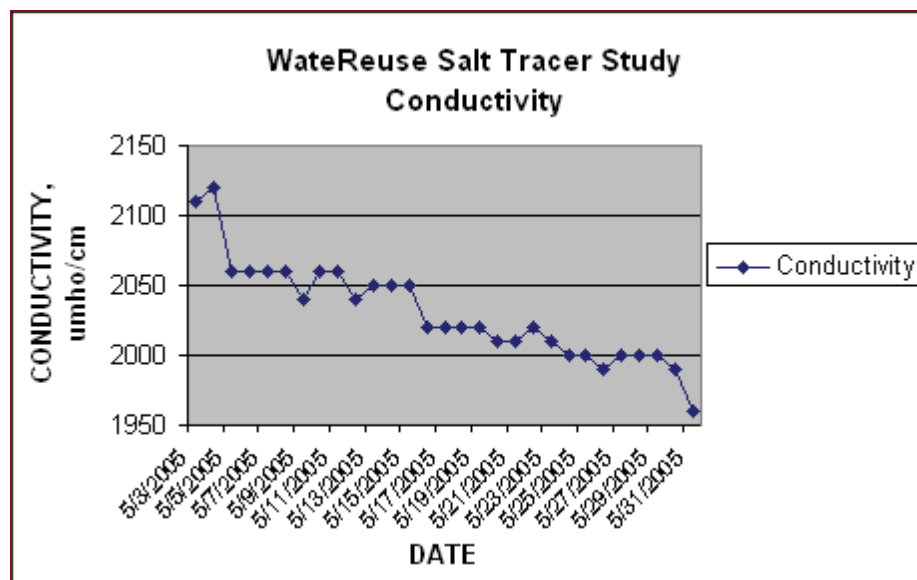
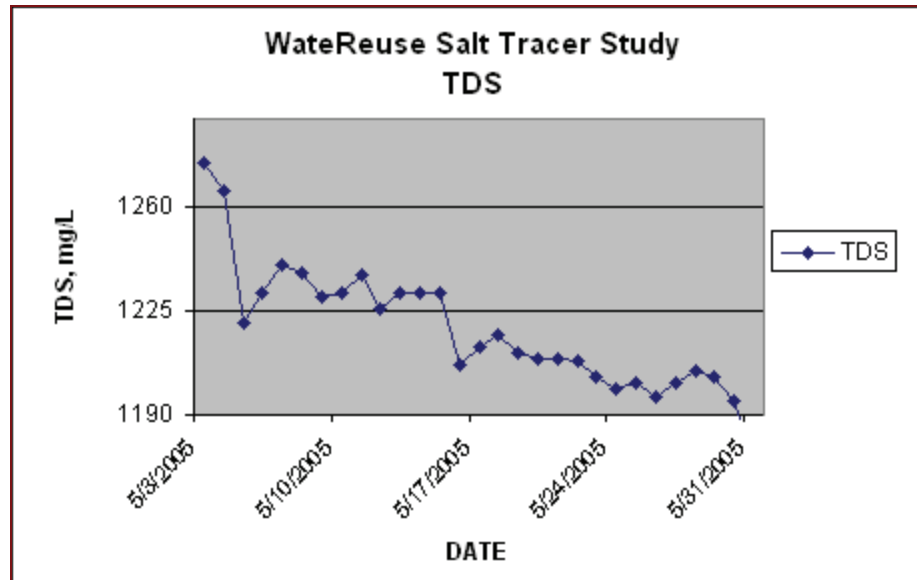
NA= not available, ND = not detected, bold = off calibration curve

Bolivar, Australia							
	Well 19450	Well 19181	Travel Blank	Well 18777	Well 19450	Well 19181	Travel Blank
	AWQC ID 11073	AWQC ID 11013		AWQC ID 11008	AWQC ID 11073	AWQC ID 11013	
	4-m MW	50-m Piez.		ASR	4-m MW	50-m Piez.	
	5/12/2005	5/12/2005	5/12/2005	7/21/05	7/21/2005	7/21/2005	7/21/2005
Status	3 wks into recovery	3 wks into recovery	3 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery	13 wks into recovery
Flow	0.454 mgd	0.454 mgd	0.454 mgd	0.342 mgd	0.342 mgd	0.342 mgd	0.342 mgd
Volume	32.1 MG	32.1 MG	32.1 MG	8.35 MG	8.35 MG	8.35 MG	8.35 MG
Microcontaminants (cont.)							
Estrone	7.8	37	<1.0	1.7	6.2	5.6	<1.0
Estradiol	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Testosterone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Progesterone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Androstenedione	1.5	18	<1.0	3.5	2.3	14	<1.0
Iopromide	47	174	<1.0	66	120	171	<1.0
Naproxen	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ibuprofen	87	182	<1.0	19	18	23	<1.0
Diclofenac	<1.0	1.2	<1.0	<1.0	<1.0	<1.0	<1.0
Triclosan	1.7	<1.0	<1.0	2.3	2.6	<1.0	<1.0
Gemfibrozil	109	836	<1.0	44	44	151	<1.0
α -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
β -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
γ -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diazinon	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
δ -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Aldrin	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Chlorpyrifos	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fluoranthene	5.1	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Dieldrin	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
BDE #28	<10	<10	<10	<10	<10	<10	<10
BDE #47	<10	<10	<10	<10	<10	<10	<10
BDE # 100	<10	<10	<10	<10	<10	<10	<10
BDE #99	<10	<10	<10	<10	<10	<10	<10
BDE #154	<10	<10	<10	<10	<10	<10	<10
BDE #153	<10	<10	<10	<10	<10	<10	<10
BHT	2507	2604	1955	2387	2622	2757	2969
Bisphenol A	1009	2665	<100.0	<100.0	129	1971	<100.0
Nonylphenol (sum)	1912	1395	22,000	453	759	1196	10380
NDMA	8.4	4.9	27	4.6	2.5	3.6	<2.5
Perchlorate	<50	<50	<50	<50	<50	<50	<50
Bromate	<100	<100	<100	<100	<100	<100	<100
Iodate	<1000	<1000	<1000	<1000	<1000	<1000	<1000
Chlorate	550	120	<100	<100	480	<100	<100
		1:100 dilution data					1:10 dilution

Salt Tracer Data from Chander, AZ, Site

**Total Dissolved Solids and Conductivity Measured at Obs.
Well 2A following Salt Slug Injection to ASR Well 5**

Date	TDS	Conductivity
5/3/2005	1275	2110
5/4/2005	1266	2120
5/5/2005	1221	2060
5/6/2005	1231	2060
5/7/2005	1241	2060
5/8/2005	1238	2060
5/9/2005	1230	2040
5/10/2005	1231	2060
5/11/2005	1237	2060
5/12/2005	1226	2040
5/13/2005	1231	2050
5/14/2005	1231	2050
5/15/2005	1231	2050
5/16/2005	1207	2020
5/17/2005	1213	2020
5/18/2005	1217	2020
5/19/2005	1211	2020
5/20/2005	1209	2010
5/21/2005	1209	2010
5/22/2005	1208	2020
5/23/2005	1203	2010
5/24/2005	1199	2000
5/25/2005	1201	2000
5/26/2005	1196	1990
5/27/2005	1201	2000
5/28/2005	1205	2000
5/29/2005	1203	2000
5/30/2005	1195	1990
5/31/2005	1176	1960



Microcontaminant Travel Blanks for All Sites

Compound	Concn, ng/L					
	Englewood 5/18/05	Manatee 12/1/04	Chandler 5/3/05	Bolivar		
				9/28/04	5/12/05	7/21/05
Acetaminophen	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Aldrin	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Androstenedione	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Atrazine	<1.0	<1.0	9.6	<1.0	<1.0	<1.0
BDE # 100	<10	<10	<10	<10	<10	<10
BDE #153	<10	<10	<10	<10	<10	<10
BDE #154	<10	<10	<10	<10	<10	<10
BDE #28	<10	<10	<10	<10	<10	<10
BDE #47	<10	<10	<10	<10	<10	<10
BDE #99	<10	<10	<10	<10	<10	<10
α -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
β -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
δ -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
δ -BHC	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
BHT	2368	2688	1574	3337	1955	2969
Bisphenol A	<100.0	<100	<100.0	163	<100.0	<100.0
Bromate	<100	<100	<100	<100	<100	<100
Caffeine	<10	<10	<10	<10	<10	<10
Carbamazepine	<1.0	<1.0	2.3	<1.0	<1.0	<1.0
Chlorate	<100	<100	<100	<100	<100	<100
Chlorpyrifos	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
DEET	7.3	<1.0	1.4	<1.0	1.2	1.1
Diazepam	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Diazinon	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Diclofenac	<1.0	8	<1.0	<1.0	<1.0	<1.0
Dieldrin	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Dilantin	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Erythromycin-H2O	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Estradiol	<1.0	11	11	<1.0	<1.0	<1.0
Estriol	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Estrone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ethinylestradiol	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fluoranthene	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fluoxetine	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Gemfibrozil	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Hydrocodone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ibuprofen	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Iodate	<1000	<1000	<1000	<1000	<1000	<1000
Iopromide	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Meprobamate	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Naproxen	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
NDMA	<2.5	2.5	24	<2.5	27	<2.5
Nonylphenol (sum)	593	139	132	194	22,000	10,380
Oxybenzone	3	<1.0	2.5	<1.0	<1.0	<1.0
Pentoxifylline	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Perchlorate	<50	<50	<50	<50	<50	<50
Progesterone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sulfamethoxazole	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
TCEP	<10	<10	<10	<10	<10	<10
Testosterone	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Triclosan	3.4	<1.0	264	<1.0	<1.0	<1.0
Trimethoprim	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

Advancing the Science of Water Reuse and Desalination



1199 North Fairfax Street, Suite 410

Alexandria, VA 22314 USA

(703) 548-0880

Fax (703) 548-5085

E-mail: Foundation@WaterReuse.org

www.WaterReuse.org/Foundation