# Ambient Groundwater Quality of the Harquahala Basin A 2009-2014 Baseline Study By Douglas Towne

Arizona Dept. of Environmental Quality Water Quality Division Surface Water Section, Monitoring Unit 1110 West Washington Street Phoenix, AZ 85007-2935 **Publication Number: OFR-14-04** 



# Ambient Groundwater Quality of the Harquahala Basin: A 2009-2014 Baseline Study

By Douglas C. Towne

Arizona Department of Environmental Quality Open File Report 14-04

ADEQ Water Quality Division Surface Water Section Monitoring Unit 1110 West Washington St. Phoenix, Arizona 85007-2935

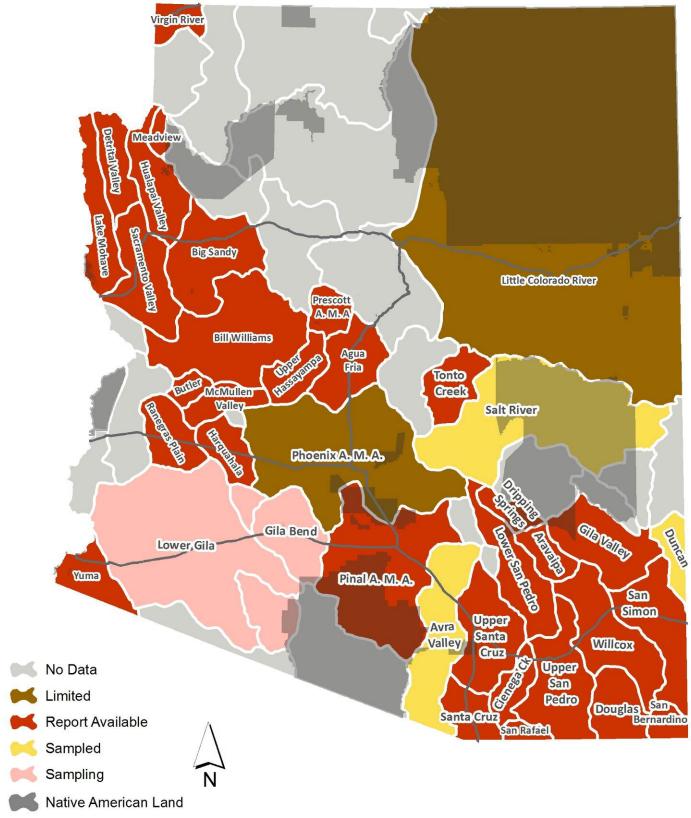
#### Thanks:

Field Assistance:	Elizabeth Boettcher, Susan Determann, Joanie Rhyner, and Dennis Turner. Special recognition is extended to the many well owners who were kind enough to give permission to collect groundwater data on their property.
Photo Credits:	Douglas Towne
Report Cover:	ADEQ's Elizabeth Boettcher collects a groundwater duplicate sample (HAR- 33/34) from Big Horn windmill on a blustery spring day. Located in the Big Horn Mountains, the well produces water that is piped to a former underground storage tank (UST) and subsequently distributed to troughs for use by livestock and wildlife. Overflowing water from the UST creates a micro-riparian habitat including a striking Palo Verde tree in blossom.

## ADEQ Ambient Groundwater Quality Open-File Reports (OFR) and Factsheets (FS):

Tonto Creek Basin	OFR 13-04, 50 p.	FS 13-18, 4 p.
Upper Hassayampa Basin	OFR 13-03, 52 p.	FS 13-11, 3 p.
Aravaipa Canyon Basin	OFR 13-01, 46 p.	FS 13-04, 4 p.
Butler Valley Basin	OFR 12-06, 44 p.	FS 12-10, 5.p.
Cienega Creek Basin	OFR 12-02, 46 p.	FS 12-05, 4.p.
Ranegras Plain Basin	OFR 11-07, 63 p.	FS 12-01, 4.p.
Groundwater Quality in Arizona	OFR 11-04, 26 p.	-
Bill Williams Basin	OFR 11-06, 77 p.	FS 12-01, 4.p.
San Bernardino Valley Basin	OFR 10-03, 43 p.	FS 10-31, 4 p.
Dripping Springs Wash Basin	OFR 10-02, 33 p.	FS 11-02, 4 p.
McMullen Valley Basin	OFR 11-02, 94 p.	FS 11-03, 6 p.
Gila Valley Sub-basin	OFR 09-12, 99 p.	FS 09-28, 8 p.
Agua Fria Basin	OFR 08-02, 60 p.	FS 08-15, 4 p.
Pinal Active Management Area	OFR 08-01, 97 p.	FS 07-27, 7 p.
Hualapai Valley Basin	OFR 07-05, 53 p.	FS 07-10, 4 p.
Big Sandy Basin	OFR 06-09, 66 p.	FS 06-24, 4 p.
Lake Mohave Basin	OFR 05-08, 66 p.	FS 05-21, 4 p.
Meadview Basin	OFR 05-01, 29 p.	FS 05-01, 4 p.
San Simon Sub-Basin	OFR 04-02, 78 p.	FS 04-06, 4 p.
Detrital Valley Basin	OFR 03-03, 65 p.	FS 03-07, 4 p.
San Rafael Basin	OFR 03-01, 42 p.	FS 03-03, 4 p.
Lower San Pedro Basin	OFR 02-01, 74 p.	FS 02-09, 4 p.
Willcox Basin	OFR 01-09, 55 p.	FS 01-13, 4 p.
Sacramento Valley Basin	OFR 01-04, 77 p.	FS 01-10, 4 p
Upper Santa Cruz Basin (w/ USGS)	OFR 00-06, 55 p.	-
Prescott Active Management Area	OFR 00-01, 77 p.	FS 00-13, 4 p.
Upper San Pedro Basin (w/ USGS)	OFR 99-12, 50 p.	FS 97-08, 2 p.
Douglas Basin	OFR 99-11, 155 p.	FS 00-08, 4 p.
Virgin River Basin	OFR 99-04, 98 p.	FS 01-02, 4 p.
Yuma Basin	OFR 98-07, 121 p.	FS 01-03, 4 p.

These publications are available at: <a href="http://www.azdeq.gov/environ/water/assessment/ambient.html">www.azdeq.gov/environ/water/assessment/ambient.html</a>



Map 1. ADEQ Ambient Groundwater Monitoring Program Studies

# **Table of Contents**

Abstract
Introduction
Purpose and Scope
Physical and Cultural Characteristics
Groundwater
Investigation Methods
Sample Collection
Laboratory Methods 11
Data Evaluation
Quality Assurance
Data Validation
Statistical Considerations
Groundwater Sampling Results
Water Quality Standards / Guidelines 19
Analytical Results
Groundwater Composition
General Summary
Constituent Co-Variation
Oxygen and Hydrogen, Isotopes
Nitrogen Isotopes
Groundwater Quality Variation
Discussion
References
Appendices
Appendix A – Data for Sample Sites, Harquahala Basin, 2009-2013
Appendix B – Groundwater Quality Data, Harquahala Basin, 2009-2013

# Maps

ADEQ A	mbient Monitoring Program Studies	. V
Map 1.	Harquahala Basin	3
Map 2.	Sample Sites	6
Map 3.	Water Quality Standards	. 20
Map 4.	Water Chemistry	. 26
Map 5.	Total Dissolved Solids	. 28
Map 6.	Hardness	. 29
Map 7.	Groundwater Age	. 34
Map 8.	Nitrate	. 39
Map 9.	Fluoride	. 41
Map 10.	Arsenic	. 45

# Tables

Table 1.	Laboratory water methods and minimum reporting levels used in the study	12
Table 2.	Summary results of duplicate samples from the Test America/Accutest laboratories	15
Table 3.	Summary results of split samples between the Test America/USGS laboratories	16
Table 4.	Summary results of split samples between the Accutest/Test America laboratories	17
Table 5.	Sampled sites exceeding health-based water quality guidelines or Primary MCLs	21
Table 6.	Sampled sites exceeding aesthetics-based water quality guidelines or Secondary MCLs	22
Table 7.	Summary statistics for groundwater quality data	23
Table 8.	Sodium and salinity hazards for sampled sites	27
Table 9.	Correlation among groundwater quality constituent concentrations	31
Table 10.	Variation in groundwater quality constituent concentrations among three land use groups	37
Table 11.	Summary statistics for three land use groups with significant constituent differences	38
Table 12.	Variation in groundwater quality constituent concentrations among three recharge groups	42
Table 13.	Summary statistics for three recharge groups with significant constituent differences	43

# Diagrams

Diagram 1.	Field pH – lab pH relationship	18
Diagram 2.	Water chemistry piper plot	25
Diagram 3.	Field pH – log arsenic relationship	31
Diagram 4.	Oxygen-18 – deuterium relationship	33
Diagram 5.	Nitrogen-15 – nitrate relationship	33
Diagram 6.	Temperature box plot using three land use groups	35
Diagram 7.	TDS box plot using three land use groups	35
Diagram 8.	Nitrate box plot using three land use groups	36
Diagram 9.	Oxygen-18 box plot using three land use groups	36
Diagram 10.	Sodium box plot using three recharge groups	40
Diagram 11.	Fluoride box plot using three recharge groups	40

# Figures

Figure 1.	CAP irrigation lateral	7
Figure 2.	U.S. Geological Survey NAWQA truck	7
Figure 3.	Irrigation Well #W12-1	8
Figure 4.	Basin view from Big Horn Mountains	8
Figure 5.	Windmill maintenance notes	8
Figure 6.	Alaska Mine windmill	8
Figure 7.	Burnt Mountain Rest Area well	9
Figure 8.	Irrigation Well #C9 5-1	9
Figure 9.	Harquahala Valley Irrigation District	9
Figure 10.	Rattlesnake well	9
Figure 11.	Rosemont Water Company well 1	0
Figure 12.	Abandoned irrigation well	0
Figure 13.	Shallow domestic well	0
Figure 14.	Harquahala Farm well	0

## Abbreviations

1	
amsl	above mean sea level
ac-ft	acre-feet
af/yr	acre-feet per year
ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
ADWR	Arizona Department of Water Resources
ARRA	Arizona Radiation Regulatory Agency
AZGS	Arizona Geological Survey
As	arsenic
bls	below land surface
BLM	U.S. Department of the Interior Bureau of Land Management
CAP	Central Arizona Project
°C	degrees Celsius
CI <sub>0.95</sub>	95 percent Confidence Interval
Cl	chloride
EPA	U.S. Environmental Protection Agency
F	fluoride
Fe	iron
gpm	gallons per minute
GWPL	Groundwater Protection List active ingredient
HAR	Harquahala Groundwater Basin
HC1	hydrochloric acid
LLD	Lower Limit of Detection
Mn	manganese
MCL	Maximum Contaminant Level
ml	milliliter
msl	mean sea level
ug/L	micrograms per liter
um	micron
μS/cm	microsiemens per centimeter at 25° Celsius
mg/L	milligrams per liter
MRL	Minimum Reporting Level
ns	not significant
ntu	nephelometric turbidity unit
pCi/L	picocuries per liter
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SAR	Sodium Adsorption Ratio
SDW	Safe Drinking Water
SC	Specific Conductivity
su	standard pH units
$SO_4$	sulfate
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound
WQARF	Water Quality Assurance Revolving Fund
*	significant at $p \le 0.05$ or 95% confidence level
**	significant at $p \le 0.01$ or 99% confidence level
***	for information only, statistical test for this constituent invalid because detections fewer than 50
	percent

х

#### Ambient Groundwater Quality of the Harquahala Basin: A 2009-2014 Baseline Study

**Abstract** - From 2009-2014, the Arizona Department of Environmental Quality (ADEQ) conducted a baseline groundwater quality study of the Harquahala basin in west-central Arizona located approximately 60 miles west of Phoenix. The basin comprises 766 square miles within La Paz and Maricopa counties and consists of a broad alluvial plain bordered by rugged mountain ranges.<sup>7</sup> Low-intensity livestock grazing is the predominant land use but there is irrigated acreage in the northwest and, especially, in the southeast portion within the Harquahala Valley Irrigation District (HVID). Land ownership consists of federal lands (62 percent) managed by the Bureau of Land Management (BLM), private land (25 percent), and State Trust lands (13 percent).<sup>7</sup> There are no incorporated communities within the basin, which had a population of approximately 600 people in 2000.<sup>7</sup>

The basin is drained by Centennial Wash, a tributary of the Gila River. Centennial Wash enters the basin from the northwest at the Harrisburg Valley "Narrows," and runs to the southeast until exiting at Mullins Cut. <sup>15</sup> All washes in the basin are ephemeral and flow only after heavy precipitation.<sup>15</sup> Groundwater is used for irrigation with minor amounts used for public water, domestic, industrial, and stock uses. Water from the Colorado River delivered via the Central Arizona Project (CAP) supplements irrigation and stock uses and is recharged at the Vidler Water facility.<sup>7</sup>

The main aquifer is the basin-fill alluvium composed of heterogeneous deposits of clay, silt, sand, and gravel that can yield up to 3,000 gallons per minute to wells.<sup>18</sup> In the HVID, irrigation pumping has created a large cone of depression. Overlying the coarse-grained deposits in the many areas are fine-grained beds composed mainly of clay, which can exceed 1,000 feet and create perched water zones.<sup>7</sup> In areas north of Interstate 10, the aquifer generally doesn't produce enough water for irrigation use. Fields in the northwest basin are irrigated with groundwater produced from wells located near the "Narrows" that predominantly capture underflow from the adjacent McMullen Valley basin.<sup>15</sup> Minor amounts of groundwater are found in mountain bedrock that surrounds the basin's alluvium.<sup>7</sup>

Fifty-one wells were sampled that were used for irrigation (32), domestic (8), stock (6), public supply (3), and monitoring (2) purposes. Inorganic constituents and isotopes (oxygen and deuterium) samples were collected at every well while nitrogen isotopes (34), radon (31) and radionuclide (10) samples were collected at selected sites. Based on sample results, groundwater in the basin is generally not suitable for drinking water uses without proper treatment. Of the 51 sites sampled, only two sites met all drinking water quality standards. Health-based, Primary Maximum Contaminant Levels (MCLs) were exceeded at 36 sites (71 percent). These enforceable standards define the maximum concentrations of constituents allowed in water supplied for drinking water purposes by a public water system and are based on a lifetime daily consumption of two liters.<sup>32</sup> Constituents exceeding these standards include nitrate (24 sites), arsenic (19 sites), fluoride (5 sites), and gross alpha and uranium (1 site each). Exceedances appear to be caused by natural sources, though nitrate may also be influenced by human activity. Isotope values suggest nitrate comes from natural soil organic matter, though elevated concentrations are usually near irrigated fields.<sup>26, 28</sup>

Aesthetics-based, Secondary MCLs were exceeded at 48 of the 51 sites (94 percent). These are unenforceable guidelines that define the maximum constituent concentration that can be present in drinking water without an unpleasant taste, color, or odor.<sup>32</sup> Constituents exceeding Secondary MCLs include Total Dissolved Solids (TDS) (48 sites), fluoride (38 sites), sulfate (19 sites), chloride (17 sites), pH-field (2 sites), and iron (1 site). Of the 31 sites sampled for radon, 25 sites (81 percent) exceeded the proposed 300 picocuries per liter standard.<sup>32</sup>

Groundwater is commonly a sodium-mixed chemistry, *slightly-alkaline*, *fresh* or *slightly-saline*, and has a varying hardness.<sup>12, 17</sup> Oxygen and deuterium isotope values of most samples are lighter and more depleted than would be expected from recharge occurring at elevations within the basin. This suggests that much of the groundwater was recharged long ago (8,000 to 12,000 years) during cooler climatic conditions<sup>14</sup> Isotope values did, however, have some variability that allowed them to be divided into three age groups for comparison purposes.

Groundwater constituent concentrations were influenced by land use and recharge age.<sup>14</sup> Constituents such as temperature, pH-field, pH-lab, Specific Conductivity (SC-field, SC-lab), TDS, sodium, bicarbonate, chloride, sulfate, nitrate, barium, chromium, strontium, oxygen, and deuterium had significantly different concentrations among sites located in the HVID, other irrigated lands, and lands with no irrigation. Constituents such as temperature, SC, TDS, sodium, and chloride had significantly higher constituent concentrations at sites with older, depleted samples than at sites with younger, enriched samples (Kruskal-Wallis and Tukey test,  $p \le 0.05$ ).

#### INTRODUCTION

#### **Purpose and Scope**

The Harquahala groundwater basin comprises approximately 766 square miles within Maricopa and La Paz counties in the west central portion of the state (Map 1).<sup>7</sup> The basin is located about 60 miles west of Phoenix and Interstate 10 passes east-west through its center. There are no incorporated towns in the rural basin, which had a population of approximately 600 people in 2000.<sup>7</sup>

The basin is characterized by the broad Harquahala alluvial plain that is bordered by rugged mountain ranges and drained by Centennial Wash, a tributary to the Gila River. All streams in the basin are ephemeral; washes and arroyos flow only after heavy precipitation.<sup>7</sup> Groundwater is used for irrigation with minor amounts used for public water, domestic, industrial, and stock uses. Colorado River water transported via the Central Arizona Project (CAP) is used for irrigation and stock uses and is recharged at the Vidler Water Company facility in the basin.<sup>7</sup>

Sampling by the Arizona Department of Environmental Quality (ADEQ) Ambient Groundwater Monitoring program is authorized by legislative mandate in the Arizona Revised Statutes §49-225, specifically: "...ongoing monitoring of waters of the state, including...aquifers to detect the presence of new and existing pollutants, determine compliance with applicable water quality standards, determine the effectiveness of best management practices, evaluate the effects of pollutants on public health or the environment, and determine water quality trends."<sup>4</sup>

**Benefits of ADEQ Study** – This study, which utilizes scientific sampling techniques and quantitative analyses, is designed to provide the following benefits:

- A characterization of regional groundwater quality conditions in the Harquahala basin by identifying water quality variations between groundwater impacted by land uses and of different ages.
- A process for evaluating potential groundwater quality impacts arising from mineralization, irrigation, livestock, septic tanks, and poor well construction.
- A guide for determining areas where further groundwater quality research is needed.

#### **Physical and Cultural Characteristics**

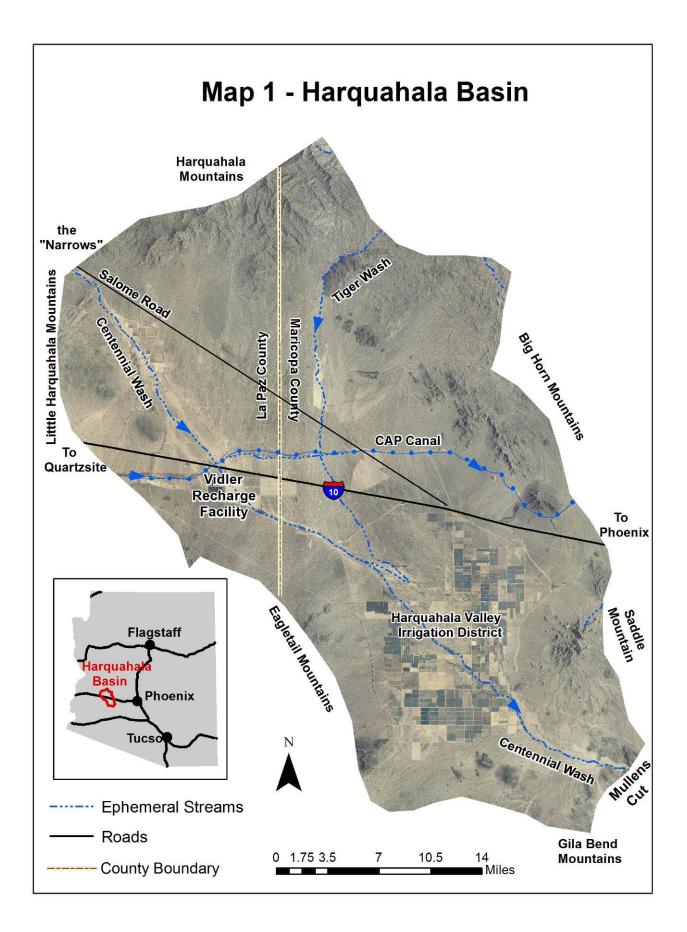
**Geography** – The Harquahala basin is located within the Basin and Range physiographic province of central Arizona. The basin is characterized by the Harquahala Plain drained by the Centennial Wash and bordered by rugged, low elevation mountains. The valley slopes to the southeast at 15 to 20 feet per mile.<sup>18</sup> Vegetation is composed of Arizona uplands Sonoran desert scrub with some interior chaparral on the northern boundary.<sup>7</sup>

The basin is bounded on the north by the Harquahala Mountains, on the west by the Little Harquahala Mountains, on the southwest by the Eagletail Mountains, and on the east by the Big Horn Mountains and Saddle Mountain, and on the south by the Gila Bend Mountains. Elevations range from a high of approximately 5,681 feet above mean sea level (amsl) atop Harquahala Mountain to a low of approximately 1,000 feet amsl at Mullens Cut where Centennial Wash exits into the Hassayampa sub-basin of the Phoenix Active Management Area (AMA).

Centennial Wash enters the basin at the Harrisburg Valley "Narrows," and runs 42 miles, northwest to southeast, exiting the basin through a similar bedrock constriction at Mullens Cut.<sup>15</sup> There are no perennial or intermittent streams or springs in the basin.<sup>7</sup> Flow occurs approximately five percent of the time in Centennial Wash based on a U.S. Geological Survey (USGS) stream gauge at Arlington, located 12 miles east of the Harquahala basin.

Land Ownership - The Harquahala basin consists of federal land (62 percent) managed by the U.S. Bureau of Land Management (BLM). The BLM's holdings include 52,800 acres of wilderness including portions of the Eagletail Mountains, Big Horn Mountains, and Harquahala Mountains wilderness areas.<sup>7</sup> The remainder of the basin is composed of private lands (25 percent), State Trust lands (13 percent) and U.S. Bureau of Reclamation lands (0.1 percent).<sup>5</sup> Private and State lands are generally located in the Harquahala Plain that follows the Centennial Wash in a northwest-southeast path through the basin.

**Climate** – The Harquahala basin is in a semiarid climate characterized by hot, dry summers and mild winters. There is wide variation in precipitation amounts which range annually from 18 inches atop the Harquahala Mountains to 4 inches in the lower portions of the basin. Precipitation occurs predominantly as rain in either late summer, localized thunderstorms or, less often, as widespread, low intensity winter rain that occasionally includes snow at higher elevations.<sup>7</sup>



**Agriculture** - The vast majority of water use in the basin is used for irrigation. There are three main areas of the basin where farming has occurred:

- A small tract just south of the "Narrows" irrigated with groundwater supplied by wells producing water predominantly from underflow from the adjacent McMullen Valley basin.<sup>15</sup>
- A much larger expanse of farmland is in the Harquahala Valley Irrigation District (HVID) which is supplied by a combination of groundwater and surface water from the Colorado River supplied via the Central Arizona Project (CAP).<sup>6</sup>
- A small, formerly-farmed, area along Interstate 10 that is now the location of the Vidler Recharge Project using Colorado River water transported by the CAP.<sup>36</sup>

Farming began in the Harquahala basin when the first irrigation well was drilled in 1951. Irrigated acreage in the basin increased until peaking in the mid-1960s.<sup>7</sup> The HVID was organized in 1964 to permit unified action in applying for CAP water and for flood control.<sup>6</sup> Declining groundwater levels, increasing power costs, and variable commodity prices resulted in fewer acres being irrigated until the mid-1980s.

Groundwater was supplemented by Colorado River water deliveries via the CAP in 1985. CAP supplies soon replaced groundwater as the major source for irrigation. CAP water use peaked at approximately 116,000 acre-feet in 1997 and was used to irrigate the HVID for the majority of the year with individually owned wells only used to help meet peak summertime demands with a low of 2,000 af pumped in 1991.<sup>6</sup> The recent drought in the Colorado River watershed, however, has limited CAP supplies to the basin. In 2012, irrigation in the basin consisted of 68,000 af of groundwater and 51,000 af of surface water from the CAP.<sup>33</sup>

The Harquahala basin is within an Irrigation Non-Expansion Area (INA) which does not allow any new agricultural lands to be irrigated with groundwater. The Harquahala INA was established in 1981 and is administered by the Arizona Department of Water Resources (ADWR).<sup>7</sup>

#### Groundwater

**Aquifers** - The main aquifer in the Harquahala basin is the basin-fill alluvium composed of heterogeneous deposits of clay, silt, sand, and gravel. The basin-fill begins at the mountain fronts and increases in thickness up to an estimated 5,000 feet. Coarse deposits of sand and gravel characterize the alluvium in the southeastern part of the basin. North of Baseline Road that runs through the southern part of the HVID, fine-grained beds composed mainly of clay overlies the coarse-grained deposits. The fine-grained bed increases in thickness, exceeding 1,000 feet thick near the northwest part of the HVID. Although included with the main water-bearing unit, the fine-grained beds likely contribute little water to wells.<sup>15</sup>

The aquifer is generally unconfined but the localized clay layers create some semi-confined to confined conditions within central portions of the HVID. These areas of perched groundwater atop the fine-grained deposits occur from the downward percolation of excess irrigation water. The perched groundwater can move to the lower, basin-fill aquifer via cascading wells perforated in both aquifers.<sup>18</sup>

In the former agricultural area that is now part of the Vidler Recharge Project, wells produce water through alternating fine and coarse layers until conglomerate is encountered about 900 feet below land surface (bls).<sup>15</sup> In the northwest part of the Harquahala Plain are alternating layers of moderately coarse to coarse materials underlain by conglomerate.<sup>18</sup> The aquifer in this area only produces enough water for limited irrigation use.

Minor amounts of groundwater suitable for domestic or stock use also occur in the alluvium deposited along mountain washes. Limited groundwater is also found in fractured and faulted areas of the surrounding mountain ranges that are composed of Precambrian granitic and metamorphic rocks, Tertiary volcanic rocks, and Quaternary volcanic rocks.<sup>7</sup>

**Groundwater Development** - Groundwater development has mainly occurred in the southern portion of the basin for irrigation use within the HVID. North of Interstate 10, few wells have been constructed and these are typically for domestic or stock purposes and yield limited groundwater.

Groundwater yields from irrigation wells within the HVID vary from 350 gpm to 3,000 gpm with the highest yields occurring from the alternating sequence of fine-grained and coarse-grained deposits in the west central part of the district. In the eastern part of the HVID, wells generally penetrate fine-grained layers to draw water from the underlying coarse-grained bed. In the southeastern part of the HVID, most wells draw water from the coarse-grained, sand and gravel layer.<sup>7</sup>

After the first irrigation wells were drilled in 1951, groundwater use increased from 33,000 acre-feet (af) in

1954 to a peak of approximately 200,000 af in 1966.<sup>7</sup> Irrigation withdrawals declined into the 1980s, and dropped precipitously with the first delivery of CAP water in 1985. By 1987, 85,000 af of CAP water and 10,000 af of pumped groundwater were used to irrigate 18,000 acres. By 2005, irrigation use averaged 69,600 af of CAP water and 36,500 af of groundwater.<sup>7</sup>

**Groundwater Characteristics** - There is an estimated 15.5 million af of groundwater stored in the basin above a depth of 1,200 feet bls. Natural recharge is estimated to average 1,000 af annually, occurring largely through infiltration of ephemeral flow in Centennial Wash.<sup>7</sup> Additional recharge has occurred since the late 1980s via the CAP canal, which runs west to east across the southern part of the basin. Recharge to the basin from the CAP is estimated at almost 6,000 acre-feet per year.<sup>7</sup>

Before irrigation development began in the early 1950s, groundwater movement was from the northwest to the southeast paralleling Centennial Wash, discharging from the basin at Mullens Cut. Irrigation withdrawals had halted groundwater outflow from the basin by 1957.<sup>7</sup> By 1963, groundwater overdraft had created three cones of depression in the central portion of the HVID that coalesced into one large cone of depression by 1966. Groundwater movement continues to be from the basin edges to the large cone of depression in the center of the HVID.<sup>18</sup>

The irrigation pumping associated with the groundwater cone of depression had caused water level declines in wells as much as 27 feet per year and 325 feet over a 30-year period (1950-1980). Starting in the early 1970s, water level declines slowed as less groundwater was pumped for irrigation. The introduction of CAP water in 1985 resulted in water level increases of up to 70 feet in some wells. The basin is still in hydrologic overdraft however, because of limited recharge and the recent increase in groundwater pumping due to reduced applications of CAP water because of the drought in the Colorado River watershed.

#### **INVESTIGATION METHODS**

ADEQ collected samples from 51 wells to characterize regional groundwater quality in the Harquahala basin (Map 2). The following types of samples were collected:

- inorganic suites at 51 sites
- oxygen and deuterium isotopes at 51 sites
- nitrogen isotopes at 34 sites
- radon at 31 sites
- radionuclides at 10 sites

No bacteria sampling was conducted because microbiological contamination problems in groundwater are often transient and subject to a variety of changing environmental conditions including soil moisture content and temperature.<sup>16</sup>

Fifty-one wells were sampled for the study. The wells were predominantly used for irrigation (32), domestic (8), stock (6), public supply (3), and monitoring (2) purposes were sampled for the study, provided each well met ADEQ requirements. A well was considered suitable for sampling when the following conditions were met: the owner has given permission to sample, a sampling point existed near the wellhead, and the well casing and surface seal appeared to be intact and undamaged.<sup>2, 8</sup>

Additional information on groundwater sample sites is compiled from the Arizona Department of Water Resources (ADWR) well registry in Appendix A.<sup>7</sup>

#### Sample Collection

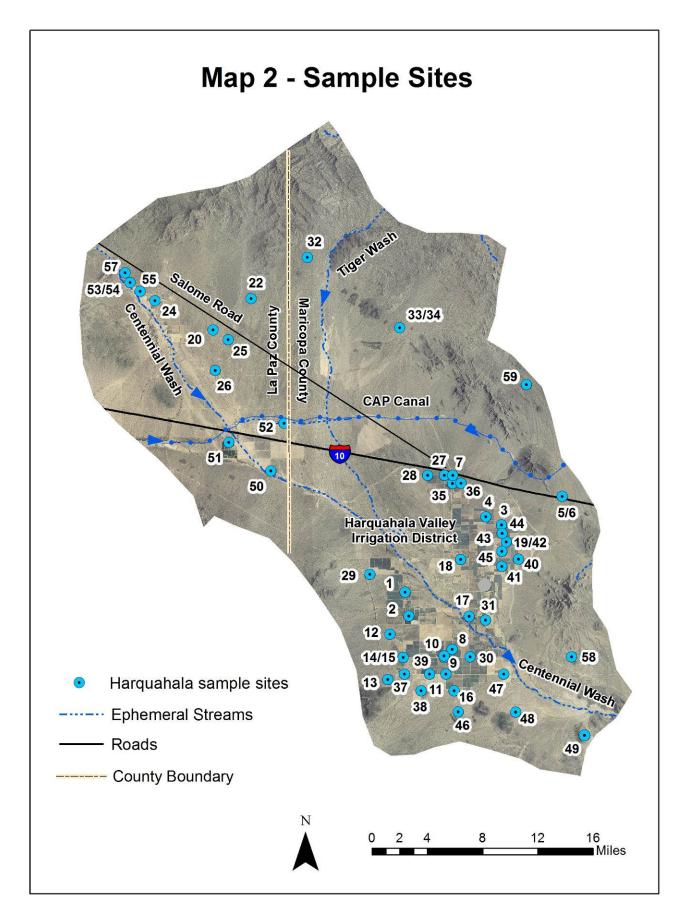
The sample collection methods for this study conformed to the *Quality Assurance Project Plan* (QAPP)<sup>2</sup> and the *Field Manual for Water Quality Sampling*.<sup>8</sup> While these sources should be consulted as references to specific sampling questions, a brief synopsis of the procedures involved in collecting a groundwater sample is provided.

After obtaining permission from the well owner, the volume of water needed to purge the well three borehole volumes was calculated from well log and on-site information. Physical parameters—temperature, pH, and Specific conductivity (SC)—were monitored every five minutes using a YSI multi-parameter instrument.

To assure obtaining fresh water from the aquifer, after three bore volumes had been pumped and physical parameter measurements had stabilized within 10 percent, a sample representative of the aquifer was collected from a point as close to the wellhead as possible.

In certain instances, it was not possible to purge three bore volumes. In these cases, at least one bore volume was evacuated and the physical parameters had stabilized within 10 percent. Sample bottles were labeled with a Harquahala prefix (HAR) and filled in the following order:

- 1. Radon
- 2. Inorganics
- 3. Radionuclide
- 4. Isotopes





**Figure 1** – Agriculture is the largest water use in the basin, with most farmland located in the Harquahala Valley Irrigation District (HVID). Irrigation needs are met by a combination of groundwater and surface water from the Colorado River provided by the Central Arizona Project (CAP) lateral canal shown here by the Eagletail Mountains. The basin received the first ever delivery of CAP water in 1985.



**Figure 2** –ADEQ had an opportunity to collect a groundwater split with the U.S. Geological Survey (USGS), which was conducting research on public supply wells in the Southwest. The USGS's Henry Sanger and Kimberly Beisner along with ADEQ's Elizabeth Boettcher fill sample bottles in the National Water-Quality Assessment Program (NAWQA) truck parked at the Eagletail Water Company public supply well (HAR-37).



**Figure 3** –Former ADEQ employee Susan Determann collects a duplicate sample (HAR-14/15) from the 1,200 foot-deep irrigation well (#W12-1) in the HVID.



**Figure 4** – The basin's remoteness is reflected in this image oriented towards the west showing the Alaska Mine windmill (HAR-32/33) in the distance along with the Little Harquahala Mountains.



**Figure 5** – The "graffiti" on the stanchion of the Carmelita windmill (HAR-22) is valuable hydrologic notes left by Balow Pump when the company serviced the well in February, 2007.



**Figure 6** – ADEQ employee Joanie Rhyner collects a sample from the Alaska Mine windmill located north of Interstate 10 in the Big Horn Mountains.



**Figure 7** – ADEQ's Elizabeth Boettcher collects a radionuclide sample from the Burnt Mountain Rest Area well located along Interstate 10. A duplicate sample (HAR-5/6) was collected at the site. Laboratory analysis revealed the sample from the 770-foot deep well was soft water with a high pH level (8.89 su) and elevated arsenic concentrations (0.0395 mg/L).



**Figure 8** – Former ADEQ employee Susan Determann poses by a hearse incongruously parked next to an irrigation well (HAR-17). There was no apparent reason for the vehicle as the sample from the well (#C9 5-1) met all health-based water quality standards.



**Figure 9** – The Harquahala Valley Irrigation District was formed in 1964 to permit a unified application for Central Arizona Project (CAP) water as well as to mitigate flood hazards.<sup>6</sup> Recent limits on the availability of CAP water have necessitated additional groundwater pumping in the district.



Figure 10 – Rattlesnake well, which is used for stock watering, is located in a remote area on the south slope of Saddle Mountain. The sample collected from this well was one of two sites in the Harquahala basin which did not exceed any health or aesthetics-based water quality standards.



**Figure 11** – ADEQ's Elizabeth Boettcher displays a sample (HAR-40) collected from the Rosemont Water Company well which exceeded water quality standards for arsenic. The public water system was approved by the Maricopa County Environmental Services Department for point of use arsenic treatment in 2008.<sup>3</sup>



**Figure 12** – An irrigation well once powered by a diesel pump sits abandoned in the southeast portion of the basin. The groundwater cone of depression that developed within the HVID severely reduced the amount of water available for agriculture in this area near Mullens Cut. <sup>15</sup>



**Figure 13** – ADEQ sampled a private domestic well located in the southwest part of the HVID. Lab analysis revealed the sample exceeded water quality standards for TDS, chloride, sulfate, nitrate, and fluoride.



**Figure 14** – ADEQ employee Dennis Turner collects a duplicate sample (HAR-53/54) from an irrigation well located at Harquahala Farms south of the Harrisburg Valley "Narrows." The samples had one of the lowest TDS concentrations (672 mg/L) in the basin. Most of the water produced by wells in this area originates from underflow from the adjacent McMullen Valley basin.

Radon, a naturally occurring, intermediate breakdown from the radioactive decay of uranium-238 to lead-206, was collected in two unpreserved, 40 milliliter (ml) clear glass vials. Radon samples were filled to minimize volatilization and sealed so that no headspace remained.<sup>1, 27</sup>

The inorganic constituents were collected in three, one-liter polyethylene bottles. Samples to be analyzed for dissolved metals were filtered into bottles using a positive pressure filtering apparatus with a 0.45 micron ( $\mu$ m) pore size groundwater capsule filter and preserved with 5 ml nitric acid (70 percent). Samples to be analyzed for nutrients were preserved with 2 ml sulfuric acid (95.5 percent). Samples to be analyzed for other inorganic parameters were unpreserved.<sup>1, 24, 27</sup>

Radiochemistry samples were collected in two collapsible four-liter plastic containers and preserved with 5 ml nitric acid to reduce the pH below 2.5 su.<sup>1, 24, 27</sup> Oxygen and hydrogen isotope samples were collected in a 250 ml polyethylene bottle with no preservative.<sup>31</sup> Nitrogen isotope samples were collected in a 500 ml polyethylene bottle and filled <sup>34</sup> full to allow room for expansion when frozen.<sup>31</sup>

All samples were kept at 4°C with ice in an insulated cooler, with the exception of the oxygen and hydrogen isotope samples.<sup>31</sup> Nitrogen samples were frozen upon returning from the field and shipped in dry ice to the laboratory.<sup>31</sup> Chain of custody procedures were followed in sample handling. Samples for this study were collected during 14 field trips conducted between 2009 and 2014.

#### Laboratory Methods

Inorganic analyses for the study were analyzed by three laboratories. The first four inorganic samples (HAR-1 to HAR-4) were conducted by the Arizona Department of Health Services (ADHS) Laboratory in Phoenix, Arizona. Inorganic analyses for the subsequent 39 samples (HAR-5 to HAR-49) were conducted by Test America Laboratory of Phoenix, Arizona. Inorganic analyses for the last eight samples (HAR-50 to HAR-59) were conducted by Accutest Northern California Laboratory in San Jose, California. A complete listing of inorganic parameters, including laboratory method and Minimum Reporting Level (MRL) for each laboratory is provided in Table 1.

Radionuclide analyses were conducted by Radiation Safety Engineering, Inc. Laboratory in Chandler, Arizona. The following EPA Safe Drinking Water (SDW) protocols were used: gross alpha was analyzed, and if levels exceeded 5 picocuries per liter (pCi/L), then radium-226 was measured. If radium-226 exceeded 3 pCi/L, radium-228 was measured. If gross alpha levels exceeded 15 pCi/L initially, then radium-226/228 and total uranium were measured.<sup>2</sup>

Radon samples were also analyzed by Radiation Safety Engineering, Inc. Laboratory in Chandler, Arizona. Isotope samples were analyzed by the Laboratory of Isotope Geochemistry at the University of Arizona in Tucson, Arizona.

#### DATA EVALUATION

#### **Quality Assurance**

Quality-assurance (QA) procedures were followed and quality-control (QC) samples were collected to quantify data bias and variability for the Harquahala basin study. The design of the QA/QC plan was based on recommendations included in the *Quality Assurance Project Plan (QAPP)* and *the Field Manual For Water Quality Sampling*.<sup>2, 8</sup> Types and numbers of QC inorganic samples collected for this study include two blanks, four duplicates, three splits, and one well was sampled twice for time trend data.

Blanks - Two equipment blanks for inorganic analysis was collected and delivered to the Test America (HAR-21) and Accutest (HAR-56) laboratories to ensure adequate decontamination of sampling equipment, and that the filter apparatus and/or de-ionized water were not impacting the groundwater quality sampling.<sup>8</sup> The equipment blank sample for major ion and nutrient analyses were collected by filling unpreserved bottles with deionized water. The nutrient bottle was subsequently preserved with sulfuric acid. The equipment blank sample for dissolved metal analysis was collected with de-ionized water that had been filtered into bottles and preserved with nitric acid.

Ammonia was detected in the Test America equipment blank while SC and TKN were detected in the Accutest equipment blank. For SC, the equipment blank had a value of 3.0 micro-siemens per cm (uS/cm) which was less than 1 percent of the SC mean concentration for the study. This was not considered to significantly affect the sample results. The SC detections may have occurred when water passing through a de-ionizing exchange unit normally has an SC value of at least 1 uS/cm. Carbon dioxide from the air can also dissolve in de-ionized water with the resulting bicarbonate and hydrogen ions imparting the observed conductivity.<sup>24</sup>

Constituent	Instrumentation ADHS / Test America / Accutest Water Method		ADHS / Test America/ Accutest Minimum Reporting Level		
Physical Parameters and General Mineral Characteristics					
Alkalinity	Electrometric Titration	SM18 2320B	2/6/5		
SC (µS/cm)	Electrometric	EPA 120.1/ SM 2510 B / EPA 120.1	/2/1		
Hardness	Titrimetric, EDTA	SM 2340 C	10 / - / -		
Hardness	Calculation	SM 2340 B			
pH (su)	Electrometric	SM 4500 H-B	0.1		
TDS	Gravimetric	SM 2540C	10		
Turbidity (NTU)	Nephelometric	EPA 180.1/ EPA 180.1 / SM 2130B	0.01 / 0.2 / 0.5		
		Major Ions			
Calcium	ICP-AES	EPA 200.7	1/2/5		
Magnesium	ICP-AES	EPA 200.7	1 / 0.25 / 5		
Sodium	ICP-AES	EPA 200.8	1 / 2 / 0.50		
Potassium	Flame AA	EPA 200.8	0.5 / 2 / 0.5		
Bicarbonate	Calculation	Calculation / SM 2320 B	2/2/5		
Carbonate	Calculation	Calculation / SM 2320 B	2/2/5		
Chloride	Potentiometric Titration	SM 4500 CL D / EPA 300 / EPA 300	5 / 2 / 0.5		
Sulfate	Colorimetric	EPA 375.4 / EPA 300 / EPA 300	1/2/0.5		
		Nutrients			
Nitrate as N	Colorimetric	EPA 353.2 / EPA 353.2 / EPA 300	0.02 / 0.1 / 0.25		
Nitrite as N	Colorimetric	EPA 353.2 / EPA 353.2 / EPA 300	0.02/0.1/0.25		
Ammonia	Colorimetric	EPA 350.1/ EPA 350.3 / SM 4500	0.02/0.5/1.0		
TKN	Colorimetric	EPA 351.2 / SM 4500 / SM 4500	0.05 / 1.3 / 0.2		
Total Phosphorus	Colorimetric	EPA 365.4 / SM 4500 / SM 4500	0.02 / 0.1 / 0.02		

Table 1. Laboratory Water Methods and Minimum Reporting Levels Used in the Study

All units are mg/L except as noted Source  $^{1, 24, 27}$ 

Constituent	Instrumentation ADHS / Test America / Accutest Water Method		ADHS / Test America/ Accutest Minimum Reporting Level
		<b>Trace Elements</b>	
Aluminum	ICP-AES	EPA 200.7	0.5 / 0.2 / 0.2
Antimony	Graphite Furnace AA	EPA 200.8	0.005 / 0.003 / 0.004
Arsenic	Graphite Furnace AA	EPA 200.9 / EPA 200.8 / EPA 200.8	0.005 / 0.001 / 0.004
Barium	ICP-AES	EPA 200.8 / EPA 200.7 / EPA 200.8	0.1 / 0.01 / 0.002
Beryllium	Graphite Furnace AA	EPA 200.9 / EPA 200.8 / EPA 200.7	0.0005 / 0.001 / 0.005
Boron	ICP-AES	EPA 200.7	0.1 / 0.2 / 0.10
Cadmium	Graphite Furnace AA	EPA 200.8	0.0005 / 0.001 / 0.002
Chromium	Graphite Furnace AA	EPA 200.8 / EPA 200.7 / EPA 200.8	0.01 / 0.01 / 0.002
Copper	Graphite Furnace AA	EPA 200.8 / EPA 200.7 / EPA 200.8	0.01 / 0.01 / 0.004
Fluoride	Ion Selective Electrode	SM 4500 F-C / SM 4500 F-C / EPA 300	0.2 / 0.4 / 0.10
Iron	ICP-AES	EPA 200.7	0.1 / 0.05 / 0.20
Lead	Graphite Furnace AA	EPA 200.8	0.005 / 0.001 / 0.002
Manganese	ICP-AES	EPA 200.7	0.05 / 0.01 / 0.15
Mercury	Cold Vapor AA	SM 3112 B / EPA 245.1/ EPA 245.1	0.0002
Nickel	ICP-AES	EPA 200.7	0.1 / 0.01 / 0.005
Selenium	Graphite Furnace AA	EPA 200.9 / EPA 200.8 / EPA 200.8	0.005 / 0.002 / 0.004
Silver	Graphite Furnace AA	EPA 200.9 / EPA 200.7 / EPA 200.8	0.001 / 0.01 / 0.002
Strontium	ICP-AES	EPA 200.7	0.1 / 0.1 / 0.01
Thallium	Graphite Furnace AA	EPA 200.9 / EPA 200.8 / EPA 200.8	0.002 / 0.001 / 0.002
Zinc	ICP-AES	EPA 200.7	0.05 / 0.05 / 0.02
		Radionuclides	
Gross alpha	Gas flow counter	EPA 900.0	varies
Radium 226	Gas flow counter	EPA 903.0	varies
Radium 228	Gas flow counter	EPA 904.0	varies
Radon	Liquid scantill. counter	EPA 913.1	varies
Uranium	Kinetic phosphorimeter	EPA Laser Phosphorimetry	varies

Table 1. Laboratory Water Methods and Minimum Reporting Levels Used in the Study-Continued

All units are mg/L Source <sup>1, 24, 27</sup>

**Duplicate Samples –** Duplicate samples are identical sets of samples collected from the same source at the same time and submitted to the same laboratory. Data from duplicate samples provide a measure of variability from the combined effects of field and laboratory procedures.<sup>8</sup> Duplicate samples were collected from sampling sites that were believed to have elevated or unique constituent concentrations as judged by SC and pH field values.

Four duplicate samples were collected for this study and submitted to Test America laboratory (three duplicate samples) and Accutest laboratory (one duplicate sample). Analytical results indicate that of the 40 constituents examined, 24 had concentrations above the MRL. The duplicate samples had a maximum variation between constituents less than 10 percent except for turbidity (14 percent), selenium (14 percent), iron (17 percent), copper (25 percent), and barium (79 percent) (Table 2). Two constituents were detected in only one of the duplicate samples. Total phosphorus was detected in sample (HAR-53) at a concentration of 0.021 mg/L and not detected in the duplicate (HAR-54). TKN was detected in sample (HAR-54) at a concentration of 3.3 mg/L and not detected in the duplicate (HAR-53). Test America could not explain this large TKN difference.<sup>2</sup>

A well that provides water for irrigation was sampled on two separate occasions (October 2011 and August 2013) to examine the influence of time on constituent concentrations. All constituents detected in the original sample (HAR-19) were detected in subsequent sample (HAR-42). Constituent concentration variation was below 12 percent with the exception of copper that was 36 percent. In addition, total phosphorus was detected just over the 0.010 MRL in the second sample and was undetected in the original sample.

**Split Samples –** Split samples are identical sets of samples collected from the same source at the same time that are submitted to two different laboratories to check for laboratory differences.<sup>8</sup> Three inorganic split samples were collected. One inorganic split sample was distributed between the Test America and the U.S. Geological Survey labs and two inorganic split samples were collected and distributed between the Accutest and Test America labs, the latter submitted by the Vidler Water Company.<sup>34, 36</sup> The analytical results were evaluated by examining the variability in constituent concentrations in terms of absolute levels and as the percent difference.

Analytical results indicate that of the 41 constituents examined, 23 had concentrations above MRLs for both the Test America and U.S. Geological Survey laboratories. The maximum variation between constituents was below 12 percent (Table 3). Analytical results indicate that of the 29 constituents examined, 17 had concentrations above MRLs for both the Accutest and Test America labs. The maximum variation between constituents was 16 percent (Table 4).

Based on the results of blank, duplicate, split, timetrend samples collected for this study, no significant QA/QC problems were apparent with the study.

#### **Data Validation**

The analytical work for this study was subjected to four QA/QC correlations and considered valid based on the following results.<sup>20</sup>

**Cation/Anion Balances** – In theory, water samples exhibit electrical neutrality. Therefore, the sum of milliequivalents per liter (meq/L) of cations should equal the sum of meq/L of anions. However, this neutrality rarely occurs due to unavoidable variation inherent in all water quality analyses. Still, if the cation/anion balance is found to be within acceptable limits, it can be assumed there are no gross errors in concentrations reported for major ions.<sup>20</sup>

Overall, cation/anion meq/L balances of Harquahala basin samples were significantly correlated (regression analysis,  $p \le 0.01$ ). Of the 51 samples, all were within +/-10 percent and 38 samples were within +/- 5 percent. Forty-four samples had low cation/high anion sums; seven samples had high cation/low anion sums.

**SC/TDS** – The SC-lab and Total Dissolved Solids (TDS) concentrations measured by contract laboratories were significantly correlated as were SC-field and TDS concentrations (regression analysis, r = 0.97,  $p \le 0.01$ ). The TDS concentration in mg/L should be from 0.55 to 0.75 times the SC in  $\mu$ S/cm for groundwater up to several thousand TDS mg/L.<sup>20</sup>

Groundwater high in bicarbonate and chloride will have a multiplication factor near the lower end of this range; groundwater high in sulfate may reach or even exceed the higher factor. The relationship of TDS to SC becomes undefined with very high or low concentrations of dissolved solids.<sup>20</sup>

<b>D</b>	Number	Diff	Difference in Percent		Differe	Difference in Concentrations		
Parameter	of Dup. Samples	Minimum	Maximum	Median	Minimum	Maximum	Median	
		Physical Para	meters and Gen	eral Mineral	Characteristics			
Alk., Total	4	0 %	4 %	0 %	0	7	0	
SC (µS/cm)	4	0 %	1 %	0 %	0	10	0	
Hardness	4	0 %	4 %	0 %	0	10	0	
pH (su)	4	0 %	0 %	0 %	0	0.07	0	
TDS	4	0 %	9 %	0 %	0	40	0	
Turbidity (ntu)	2	0 %	14 %	-	0	0.9	-	
			Major	· Ions				
Calcium	4	0 %	5 %	2 %	0	3.1	0.1	
Magnesium	2	0 %	3 %	-	0	1	-	
Sodium	4	0 %	5 %	2 %	0	20	5	
Potassium	4	0 %	2 %	-	0	0.12	-	
Chloride	4	0 %	1 %	0 %	0	2.3	0	
Sulfate	4	0 %	1 %	0 %	0	1	0	
			Nutri	ients				
Nitrate (as N)	4	0 %	10 %	1 %	0	2.1	0.1	
			Trace E	lements				
Arsenic	4	1 %	2 %	1 %	0.0003	0.001	0.0004	
Barium	3	0 %	79 %	0 %	0	0.0433	0.0031	
Boron	4	1 %	2 %	1 %	0.010	0.02	0.011	
Copper	2	7 %	25 %	-	0.0003	0.0012	-	
Chromium	4	0 %	7 %	5 %	0.00096	0.004	0.001	
Fluoride	4	0 %	6%	0%	0	0.3	0	
Iron	1	-	-	17 %	-	-	0.27	
Lead	1	-	-	4 %	-	-	0.0001	
Nickel	1	-	-	5 %	-	-	0.001	
Selenium	2	2 %	14 %	-	0.0001	.0014	-	
Strontium	2	2 %	2 %	-	0.04	0.04	-	

### Table 2. Summary Results of Duplicate Samples from Test America/Accutest Laboratories

All concentration units are mg/L except as noted with certain physical parameters.

Constituents	Number of Split Sites	Difference in Percent	Difference in Concentration
	Physical P	arameters and General Mineral	Characteristics
Alkalinity, total	1	1 %	2
SC (µS/cm)	1	3 %	55
Hardness	1	1 %	1
pH (su)	1	1 %	0.15
TDS	1	7 %	79
		Major Ions	
Calcium	1	0 %	0.1
Magnesium	1	3 %	0.41
Sodium	1	2 %	6
Potassium	1	1 %	0.11
Chloride	1	2 %	4
Sulfate	1	1 %	2
		Nutrients	
Nitrate as N	1	2 %	0.14
		Trace Elements	
Arsenic	1	0 %	0
Barium	1	0 %	0.00004
Beryllium	1	11 %	0.00006
Boron	1	8 %	0.078
Chromium	1	3 %	0.006
Fluoride	1	2 %	0.12
Selenium	1	2 %	0.0004
Strontium	1	1 %	0.006
		Other	
Radon 222 (pCi/L)	1	4 %	72
Deuterium (0/00)	1	0 %	0.4
Oxygen-18 (0/00)	1	1 %	0.18

## Table 3. Summary Results of Split Sample between Test America /USGS Laboratories

All units are mg/L except as noted <sup>34</sup>

Constituents	Number of Split Sites	Difference in Percent	Difference in Concentration
	Physical P	arameters and General Mineral	Characteristics
Alkalinity, total	2	10/3%	38 / 10
SC (µS/cm)	2	2/0%	70/0
Hardness	2	2/1%	8 / 5
pH (su)	2	6/4%	0.09 / 0.07
TDS	2	1/0%	10/0
		Major Ions	
Calcium	2	3/4%	2.9 / 2.5
Magnesium	2	2/2%	1 / 0.8
Sodium	2	3/5%	18 / 24
Potassium	2	0/5%	0/0.53
Chloride	2	10/7%	40 / 29
Sulfate	2	6/6%	28 / 28
		Nutrients	
Nitrate as N	2	3/1%	1.6 / 0.6
		<b>Trace Elements</b>	
Arsenic	1	4 %	0.0003
Barium	2	3/2%	0.006 / 0.0005
Chromium	2	1 / 2 % 0.0003 / 0.0	
Fluoride	2	16 / 11 %	0.8 / 0.5
Selenium	1	16 %	0.0017

## Table 4. Summary Results of Split Samples between Accutest/Test America Laboratories

All units are mg/L except as noted  $^{36}$ 

**SC** – The SC measured in the field at the time of sampling was significantly correlated with the SC measured by contract laboratories (regression analysis, r = 0.99,  $p \le 0.01$ ).

**pH** – The pH values measured in the field using a YSI meter at the time of sampling were significantly correlated with laboratory pH values (regression analysis, r = 0.87,  $p \ge 0.01$ ).

Based on the results of blank, duplicate, and split samples collected for this study, no significant QA/QC problems were apparent with the study.

#### **Statistical Considerations**

Various statistical analyses were used to examine the groundwater quality data of the study. All statistical tests were conducted using SYSTAT software.<sup>37</sup>

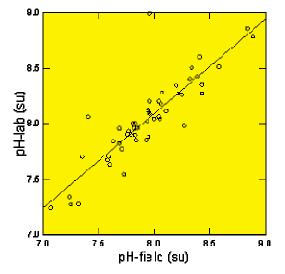
**Data Normality:** Data associated with 27 constituents were tested for non-transformed normality using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.<sup>10</sup> Results of this test revealed that 8 of the 27 constituents examined were normally distributed including oxygen-18, deuterium, temperature, pH-field, pH-lab, sodium, total alkalinity, and bicarbonate.

**Spatial Relationships:** The non-parametric Kruskal-Wallis test using untransformed data was applied to investigate the hypothesis that constituent concentrations from groundwater sites having different aquifers were the same. The Kruskal-Wallis test uses the differences, but also incorporates information about the magnitude of each difference.<sup>37</sup> The null hypothesis of identical mean values for all data sets within each test was rejected if the probability of obtaining identical means by chance was less than or equal to 0.05.

If the null hypothesis was rejected for any of the tests conducted, the Tukey method of multiple comparisons on the ranks of data was applied. The Tukey test identified significant differences between constituent concentrations when compared to each possibility with each of the tests.<sup>37</sup> Both the Kruskal-Wallis and Tukey tests are not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.<sup>19</sup>

**Correlation Between Constituents:** In order to assess the strength of association between constituents, their concentrations were compared to each other using the non-parametric Kendall's tau-b test. Kendall's correlation coefficient varies between -1 and +1; with a value of +1 indicating that a variable can be predicted perfectly by a positive linear function of the other, and vice versa. A value of -1 indicates a perfect inverse or negative relationship.

The results of the Kendall's tau-b test were then subjected to a probability test to determine which of the individual pair wise correlations were significant.<sup>37</sup> The Kendall's tau-b test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.<sup>19</sup>



**Diagram 1** – The graph illustrates a positive correlation between two constituents; as pH-field values increase, pH-lab values also increase. This relationship is described by the regression equation: y = 0.88x + 0.83 (r = 0.87). The pH value is closely related to the environment of the water and is likely to be altered by sampling and storage. <sup>9</sup> Still, the pH values measured in the field using a YSI meter at the time of sampling were significantly correlated with laboratory pH values.

#### **GROUNDWATER SAMPLING RESULTS**

#### Water Quality Standards/Guidelines

The ADEQ ambient groundwater program characterizes regional groundwater quality. An important determination ADEQ makes concerning the collected samples is how the analytical results compare to various drinking water quality standards. ADEQ used three sets of drinking water standards that reflect the best current scientific and technical judgment available to evaluate the suitability of groundwater in the basin for drinking water use:

- Federal SDW Primary Maximum Contaminant Levels (MCLs). These enforceable health-based standards establish the maximum concentration of a constituent allowed in water supplied by public systems.<sup>32</sup>
- State of Arizona Aquifer Water Quality Standards. These apply to aquifers that are classified for drinking water protected use. All aquifers within Arizona are currently classified and protected for drinking water use. These enforceable State standards are identical to the federal Primary MCLs except for arsenic which is at 0.05 mg/L compared with the federal Primary MCL of 0.01 mg/L.<sup>4</sup>
- Federal SDW Secondary MCLs. These nonenforceable aesthetics-based guidelines define the maximum concentration of a constituent that can be present without imparting unpleasant taste, color, odor, or other aesthetic effects on the water.<sup>32</sup>

Health-based drinking water quality standards (such as Primary MCLs) are based on the lifetime consumption (70 years) of two liters of water per day and, as such, are chronic rather than acute standards.<sup>32</sup> Exceedances of specific constituents for each groundwater site is found in Appendix B.

**Overall Results** – Of the 51 sites sampled in the Harquahala study, two sites (four percent) met all health-based and aesthetics-based, water quality standards (excluding the proposed radon standard discussed below).

Of the 51 sites sampled in the Harquahala study, health-based water quality standards were exceeded at 36 sites (71 percent). Constituents above Primary MCLs include nitrate (24 sites), arsenic (19 sites), fluoride (5 sites), and 1 site each for gross alpha and uranium.

**Inorganic Constituent Results** - Of the 51 sites sampled for the full suite of inorganic constituents (excluding radionuclide sample results) in the Harquahala study, 2 sites (4 percent) met all healthbased and aesthetics-based, water quality standards.

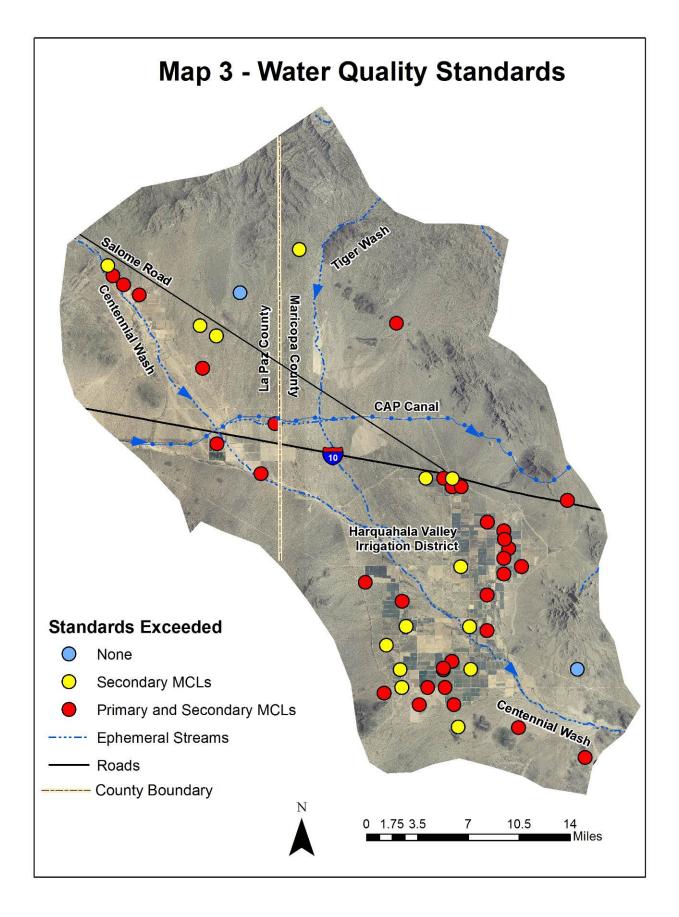
Health-based Primary MCL water quality standards were exceeded at 36 sites (71 percent) of the 51 sites (Map 3; Table 5). Constituents above Primary MCLs include nitrate (24 sites), arsenic (19 sites), and fluoride (5 sites). Potential impacts of these Primary MCL exceedances are given in Table 5.

Aesthetics-based Secondary MCL water quality guidelines were exceeded at 48 of 51 sites (94 percent; Map 3; Table 6). Constituents above Secondary MCLs include TDS (48 sites), fluoride (38 sites), sulfate (19 sites), chloride (17 sites), pH-field (2 sites), and iron (1 site). Potential impacts of these Secondary MCL exceedances are given in Table 6.

**Radon Results** - Of the 31 sites sampled for radon, none exceeded the <u>proposed</u> 4,000 picocuries per liter (pCi/L) standard that would apply if Arizona establishes an enhanced multimedia program to address the health risks from radon in indoor air. Twenty-five (25) sites exceeded the proposed 300 pCi/L standard (Table 5) that would apply if Arizona doesn't develop a multimedia program.<sup>38</sup>

#### Analytical Results

Analytical inorganic and radiochemistry results of the Harquahala sample sites are summarized (Table 7) using the following indices: MRLs, number of sample sites over the MRL, upper and lower 95 percent confidence intervals (CI<sub>95%</sub>), median, and mean. Confidence intervals are a statistical tool which indicates that 95 percent of a constituent's population lies within the stated confidence interval.<sup>37</sup> Specific constituent information for each sampled groundwater site is in Appendix B.



Constituent	Primary MCL	Number of Sites Exceeding Primary MCL	Highest Concentration	Potential Health Effects of MCL Exceedances *
		Nutr	ients	
Nitrite (NO <sub>2</sub> -N)	1.0	0	-	-
Nitrate (NO <sub>3</sub> -N)	10.0	24	79	methemoglobinemia
		Trace F	lements	
Antimony (Sb)	0.006	0	-	-
Arsenic (As)	0.01	19	0.0855	dermal and nervous system toxicity
Arsenic (As)	0.05	0	-	-
Barium (Ba)	2.0	0	-	-
Beryllium (Be)	0.004	0	-	-
Cadmium (Cd)	0.005	0	-	-
Chromium (Cr)	0.1	0	-	-
Copper (Cu)	1.3	0	-	-
Fluoride (F)	4.0	5	9.9	skeletal damage
Lead (Pb)	0.015	0	-	-
Mercury (Hg)	0.002	0	-	-
Nickel (Ni)	0.1	0	-	-
Selenium (Se)	0.05	0	-	-
Thallium (Tl)**	0.002	0	-	-
		Radiochemist	y Constituents	
Gross Alpha	15	1	30	cancer
Ra-226+Ra-228	5	0	-	-
Radon **	300	25	1,861	cancer
Radon **	4,000	0	-	-
Uranium	30	1	38.1	cancer and kidney toxicity

## Table 5. Sampled Sites Exceeding Health-based Water Quality Standards or Primary MCLs

All units are mg/L except gross alpha, radium-226+228 and radon (pCi/L), and uranium (ug/L). \* Health-based drinking water quality standards are based on a lifetime consumption of two liters of water per day over a 70-year life span.<sup>32</sup>

\*\* Proposed EPA Safe Drinking Water Act standards for radon in drinking water. <sup>32</sup>

Constituents	Secondary MCL	Number of Sites Exceeding Secondary MCLs	Concentration Range of Exceedances	Aesthetic Effects of MCL Exceedances
		Physical Par	ameters	
pH - field	< 6.5	0	-	-
pH - field	> 8.5	2	-	slippery feel; soda taste; deposits
		General Mineral C	Characteristics	
TDS	500	48	825	hardness; deposits; colored water; staining; salty taste
		Major I	ons	
Chloride (Cl)	250	17	-	salty taste
Sulfate (SO <sub>4</sub> )	250	19	-	salty taste
		Trace Ele	ments	
Fluoride (F)	2.0	38	3.5	tooth discoloration
Iron (Fe)	0.3	1	-	rusty color; sediment; metallic taste, reddish or orange staining
Manganese (Mn)	0.05	0	-	-
Silver (Ag)	0.1	0	-	-
Zinc (Zn)	5.0	0	-	

Table 6. Sampled Sites Exceeding Aesthetics-Based (Secondary MCL) Water Quality Standards

All units mg/L except pH is in standard units (su). Source:  $^{32}$ 

Constituent	Minimum Reporting Limit (MRL)*	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval	
		Phy	sical Paramete	rs			
Temperature (°C)	0.1	50 / 50	29.8	29.0	30.1	31.3	
pH-field (su)	0.01	51 / 51	7.95	7.83	7.94	8.04	
pH-lab (su)	0.01	51 / 51	8.02	7.93	8.04	8.14	
Turbidity (ntu)	0.01 / 0.20 / 0.50	51 / 18		> 50 percent	of data below M	RL	
		General M	Aineral Charac	teristics			
T. Alkalinity	2.0 / 6.0 / 5.0	51 / 51	160	140	160	180	
SC-field (µS/cm)	N/A	51 / 51	1316	1359	1580	1800	
SC-lab (µS/cm)	N/A / 2.0 / 1.0	51 / 51	1300	1371	1606	1842	
Hardness-lab	-	51/31	250	201	242	285	
TDS	10/20/10	51 / 51	770	868	1042	1216	
			Major Ions				
Calcium	1/2/5	51 / 51	35	43	60	77	
Magnesium	1.0 / 0.25 / 5.0	51 / 49	17	18	25	32	
Sodium	5/2/0.5	51 / 51	210	205	240	275	
Potassium	0.5 / 2.0 / 0.5	51 / 47	4.5	3.7	5.3	6.9	
Bicarbonate	2.0 / 6.0 / 5.0	51 / 51	171	166	190	213	
Carbonate	2.0 / 6.0 / 5.0	51/6	> 50 percent of data below MRL				
Chloride	1 / 20 / 0.5	51 / 51	170	182	229	277	
Sulfate	10/20/0.5	51 / 51	190	197	270	343	
			Nutrients				
Nitrate (as N)	.02 /0.1 / .25	51/51	8	12	16	21	
Nitrite (as N)	.02 /0.1 / .25	51/0	> 50% of data below MRL				
TKN	.05 / 1.3 / .2	51 / 1	> 50% of data below MRL				
Ammonia	.02 / 0.5 / 1.0	51/8	> 50% of data below MRL				
T. Phosphorus	.02 / 0.1 / .02	51/13	> 50% of data below MRL				

## Table 7. Summary Statistics for Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)*	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
			Trace Elements	1		
Aluminum	0.5 / 0.2 / 0.2	51/0		> 50% of data	below MRL	
Antimony	0.005 / 0.003 / 0.004	51/0		> 50% of data	below MRL	
Arsenic	0.005 / 0.001 / 0.004	51/48	0.008	0.008	0.012	0.016
Barium	0.1 / 0.01 / 0.002	51/44	0.019	0.19	0.25	0.31
Beryllium	0.0005 / 0.001 / 0.005	51 / 1		> 50% of data	below MRL	
Boron	0.1 / 0.2 / 0.1	51/49	0.52	0.51	0.70	0.89
Cadmium	0.005 / 0.001 / 0.002	51/1		> 50% of data	below MRL	
Chromium	0.01 / 0.01 / 0.002	51/49	0.028	0.024	0.029	0.034
Copper	0.01 / 0.01 / 0.004	51/33	0.003	0.003	0.004	0.006
Fluoride	0.2/0.4/0.1	51/51	2.3	2.2	2.7	3.2
Iron	0.1 / 0.05 / 0.2	51/2		> 50% of data	below MRL	
Lead	0.005 / 0.001 0.002	48 / 3		> 50% of data	below MRL	
Manganese	0.05 / 0.01 / 0.15	51/2		> 50% of data	below MRL	
Mercury	0.0002	51/0		> 50% of data	below MRL	
Nickel	0.1 / 0.01 / 0.005	51 / 1	> 50% of data below MRL			
Selenium	0.005 / 0.002 / 0.004	51/38	0.004	0.005	0.007	0.008
Silver	0.001 / 0.01 / 0.002	51/0		> 50% of data	below MRL	
Strontium	0.1 / 0.1 / 0.01	51/49	0.83	0.79	1.10	1.41
Thallium	0.002 / 0.001 / 0.002	51/0		> 50% of data	below MRL	
Zinc	0.05 / 0.005 / 0.02	51/19		> 50% of data	below MRL	
			Radiochemical			
Gross Alpha**	Varies	10/5		> 50% of data	below MRL	
Uranium**	Varies	10/10	11.8	5.9	13.4	20.8
Radon **	Varies	31/29	658	535	697	859
			Isotopes			
Oxygen-18 ***	Varies	51/51	-9.1	-9.3	-9.1	-9.0
Deuterium ***	Varies	51/51	-67.0	-68.3	-67.1	-65.9

## Table 7. Summary Statistics for Groundwater Quality Data—Continued

\* = ADHS / Test America / Accutest MRL All units mg/L except where noted: \*\* - (pCi/L) or \*\*\* - 0/00

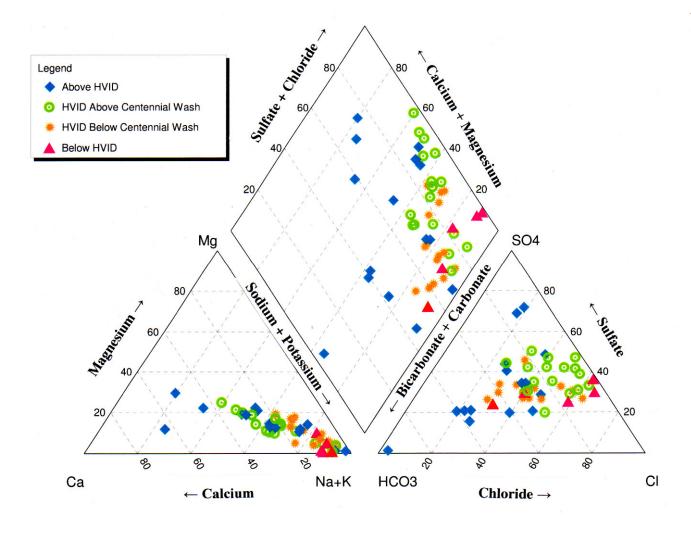
#### **GROUNDWATER COMPOSITION**

#### **General Summary**

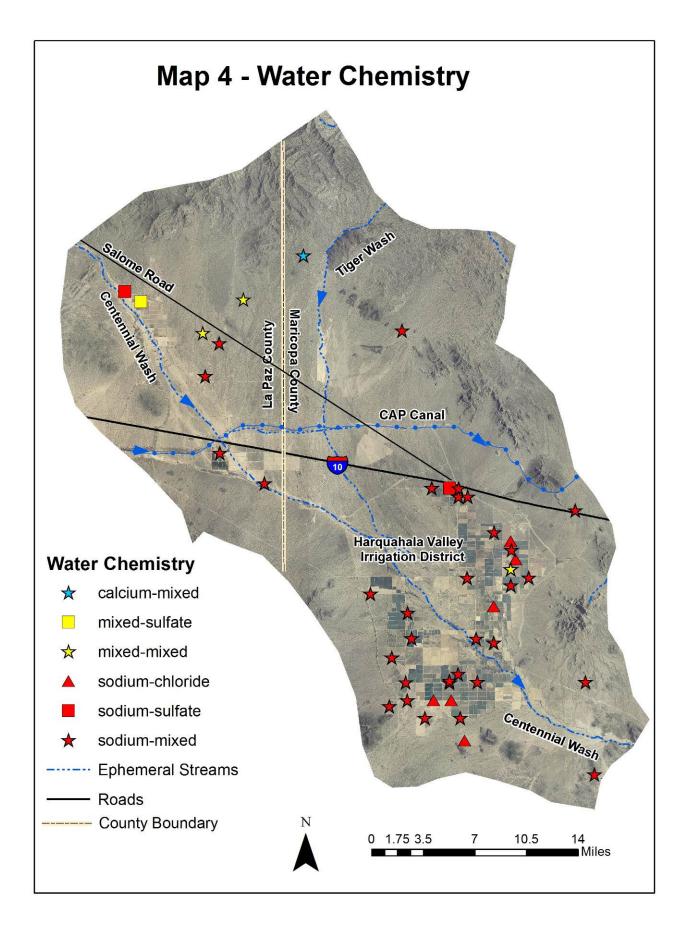
The water chemistry at the 51 sample sites in the Harquahala basin (in decreasing frequency) include sodium-mixed (32 sites), sodium-chloride (seven sites), sodium-bicarbonate and mixed-mixed (four sites apiece), sodium-sulfate (two sites), and mixed-sulfate and calcium-mixed (one site apiece) (Diagram 2 -middle figure) (Map 4).

The dominant cation was sodium at 45 sites and calcium at one site. At five sites the composition was mixed as there was no dominant cation (Diagram 2 - left figure).

The dominant anion was chloride at seven sites, bicarbonate at four sites, and sulfate at three sites. At 37 sites, the composition was mixed as there was no dominant anion (Diagram 2 - right figure).



**Diagram 2** – Samples collected in the Harquahala basin are predominantly sodium-mixed chemistry which is reflective of older groundwater that has was recharged long ago. No sample sites had a calciumbicarbonate chemistry which is characteristic of the most recent recharged groundwater.<sup>25</sup>



At all 51 sites, levels of pH-field were *slightly alkaline* (above 7 su) and 20 sites were above 8 su.<sup>17</sup>

TDS concentrations were considered *fresh* (below 999 mg/L) at 29 sites and slightly saline (1,000 to 3,000 mg/L) at 22 sites (Map 5).<sup>17</sup>

Hardness concentrations were *soft* (below 75 mg/L) at 13 sites, *moderately hard* (75 – 150 mg/L) at 13 sites, *hard* (150 – 300 mg/L) at 11 sites, *very hard* (301 - 600 mg/L) at seven sites, and *extremely hard* (above 601 mg/L) at seven sites (Map 6).<sup>12</sup>

Nitrate (as nitrogen) concentrations at most sites may have been influenced by human activities according to a prominent nationwide USGS study.<sup>22</sup> Nitrate concentrations were divided into natural background (no sites at < 0.2 mg/L), may or may not indicate human influence (one site at 0.2 – 3.0 mg/L), may result from human activities (26 sites at 3.0 – 10 mg/L), and probably result from human activities (24 sites > 10 mg/L).<sup>22</sup> This general classification system, however, may not appear to apply to Sonoran desert areas. Further analysis of nitrate concentrations is provided in the nitrogen isotope analysis section.

Most trace elements such as aluminum, antimony, beryllium, cadmium, iron, lead, manganese, mercury, nickel, silver, and thallium were rarely – if ever - detected. Only arsenic, barium, boron, chromium, copper, fluoride, selenium, strontium, and zinc were detected at more than 33 percent of the sites.

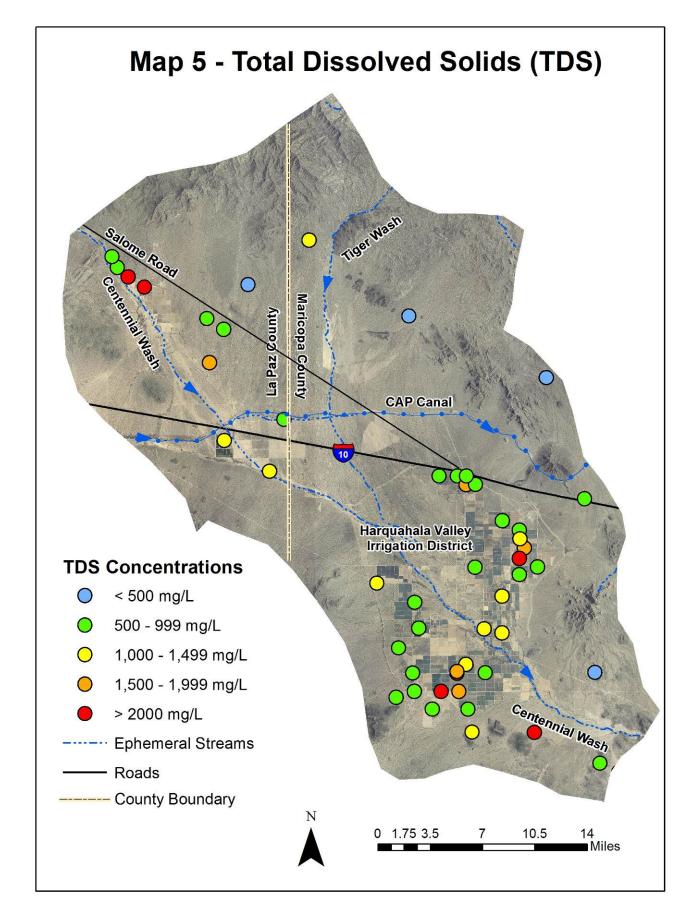
The groundwater at each sample site was assessed as to its suitability for irrigation use based on salinity and sodium hazards. Excessive levels of sodium are known to cause physical deterioration of the soil and vegetation. Irrigation water may be classified using SC and the Sodium Adsorption Ratio (SAR) in conjunction with one another.<sup>35</sup>

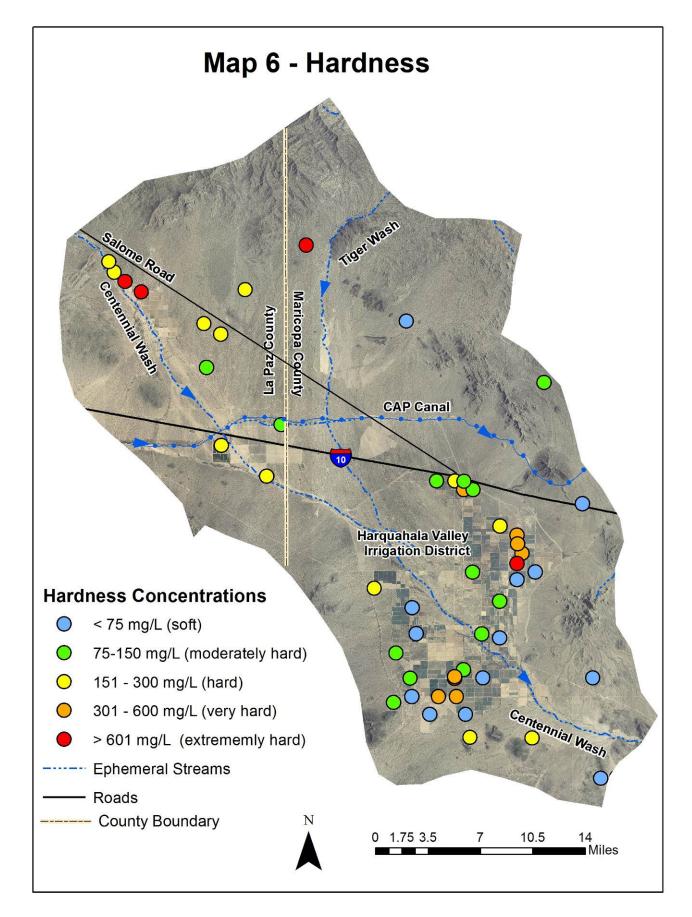
Groundwater sites in the Harquahala basin display a narrow range of irrigation water classifications. Samples predominantly had a "low to medium" sodium hazard and a "high to very high" salinity hazard (Table 8).

Hazard	<b>Total Sites</b>	Low	Medium	High	Very High
		Sodium	n Hazard		
Sodium Adsorption Ratio (SAR)		0 - 10	10- 18	18 - 26	> 26
Sample Sites	51	15	27	6	3
		Salinity	/ Hazard		
Specific Conductivity (µS/cm)		100–250	250 - 750	750-2250	>2250
Sample Sites	51	0	4	36	11

 Table 8. Sodium and Salinity Hazards for Sampled Sites

Source: 35





#### **Constituent Co-Variation**

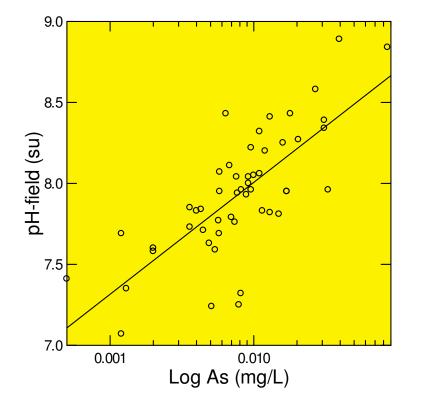
The correlations between different chemical parameters were analyzed to determine the relationship between the constituents that were sampled. The strength of association between the chemical constituents allows for the identification of broad water quality patterns within a basin.

The results of each combination of constituents were examined for statistically-significant positive or negative correlations. A *positive correlation* occurs when, as the level of a constituent increases or decreases, the concentration of another constituent also correspondingly increases or decreases. А negative correlation occurs when. as the concentration of a constituent increases, the concentration of another constituent decreases, and vice-versa. A positive correlation indicates a direct relationship between constituent concentrations; a correlation indicates negative an inverse relationship.37

Several significant correlations occurred among the 51 sample sites (Table 9, Kendall's tau-b test,  $p \le 0.05$ ). Three groups of correlations were identified:

- TDS was positively correlated with hardness, strontium, and all the major cations (calcium, magnesium, sodium, potassium, chloride, and sulfate) except bicarbonate.
- Fluoride had a negative correlation with hardness, calcium, magnesium, oxygen-18, and deuterium.
- Arsenic, chromium, and pH-field (Diagram 3) were positively correlated with one another and both were mostly negatively correlated with hardness, calcium, bicarbonate, chloride, sulfate, and strontium.

TDS concentrations are best predicted among major ions by sodium concentrations (standard coefficient = 0.78), among cations by sodium concentrations (standard coefficient = 0.60) and among anions, by sulfate concentrations (standard coefficient = 0.60) (multiple regression analysis,  $p \le 0.01$ ).



**Diagram 3** – The graph illustrates a positive correlation between two constituents; as arsenic (log) concentrations increase, pH-field values also increase. Elevated arsenic concentrations have been found to be influenced by factors including long aquifer residence time, which also tends to increase pH values.<sup>25</sup>

Constituent	Temp	pH-f	TDS	Hard	Ca	Mg	Na	K	Bic	Cl	SO <sub>4</sub>	NO <sub>3</sub>	As	Cr	F	Str	<b>O-18</b>	D
							Phy	sical Pa	aramete	rs								
Temperature		**							++				+			+		
pH-field			+	++	++	++		+	++		+	+	**	**		++		
						Ge	eneral N	<b>1ineral</b>	Charac	teristi	cs							
TDS				**	**	**	**	**		**	**	**				**		+
Hardness					**	**	*	**		**	**	**	++		+	**		
								Major	· Ions									
Calcium						**	*	**		**	**	**	++		+	**		
Magnesium							*	**		**	**	**	++		+	**		
Sodium								**		**	**	**				**		++
Potassium										**	**	**	++			**		
Bicarbonate													++			*		
Chloride											**	**				**		
Sulfate												**	+			**		
								Nutri	ents									
Nitrate																**		
							Т	race El	lements									
Arsenic														*		++		
Chromium																+	+	+
Fluoride																	+	+
Strontium																		
								Isoto	pes									
Oxygen-18																		**
Deuterium																		

## Table 9. Correlation Among Groundwater Quality Constituent Concentrations

Blank cell = not a significant relationship between constituent concentrations

\* = Significant positive relationship at  $p \le 0.05$ \*\* = Significant positive relationship at  $p \le 0.01$ 

+ = Significant negative relationship at  $p \le 0.05$ 

++ = Significant negative relationship at  $p \le 0.01$ 

#### **Oxygen and Hydrogen Isotopes**

Isotope samples were collected from 51 sites in the Harquahala basin roughly conforms to what would be expected in an arid environment, having a slope of 7.1, with the Local Meteoric Water Line (LMWL) described by the linear equation:

$$\delta D = 7.1^{18} O - 2.0$$

The LMWL for the Harquahala basin (Diagram 4) is similar to other basins in Arizona such as Aravaipa Canyon (4.1), Dripping Springs Wash (4.4), Upper Hassayampa (5.0), Detrital Valley (5.2), Agua Fria (5.3), Bill Williams (5.3), Sacramento Valley and Tonto Basin (5.5), Big Sandy (6.1), Butler Valley (6.4), Pinal Active Management Area (6.4), Gila Valley (6.4), San Simon (6.5), San Bernardino Valley (6.8), McMullen Valley (7.4), Lake Mohave (7.8), and Ranegras Plain (8.3).<sup>29</sup>

Oxygen and deuterium isotopes values at most sites are lighter and more depleted than would be expected from recharge occurring at elevations within the basin. This suggests that much of the groundwater was recharged long ago (8,000 to 12,000 years) during cooler climatic conditions.<sup>14</sup> Isotope values did, however, have some variability that allowed them to be divided into three groups. Seven samples that experienced the most evaporation were characterized as younger, enriched water and were collected mostly from wells in or near bedrock areas (Map 7). At the other end of the spectrum were eight older, depleted samples that showed little evaporation (Diagram 4). Most samples (36 wells) appear to be a mixture of these younger and older recharge ages but still appear to reflect groundwater recharged during cooler climatic conditions.<sup>14</sup>

#### Nitrogen Isotopes

Sources of nitrate in groundwater may be distinguished by measuring two stable isotopes of nitrogen, nitrogen-14 and nitrogen-15, often represented as  $\delta^{15}$ N. Although the percentage of the two isotopes is nearly constant in the atmosphere, certain chemical and physical processes preferentially utilize one isotope, causing a relative enrichment of the other isotope in the remaining reactants. Because of these isotopic fractionation processes, nitrate from various nitrogen sources has been shown to have different nitrogen isotope ratios. The  $\delta^{15}$ N values have been cited as ranging from +2 to +9 per mil (0/00) for natural soil organic matter, -3 to +3 for inorganic fertilizer, and +10 to +20 per mil for animal waste. <sup>26, 28</sup>

#### **Oxygen and Hydrogen Isotopes**

Groundwater characterizations using oxygen and hydrogen isotope data may be made with respect to the climate and/or elevation where the water originated, residence within the aquifer, and whether or not the water was exposed to extensive evaporation prior to collection.<sup>11</sup> This is accomplished by comparing oxygen-18 isotopes ( $\delta^{18}$ O) and deuterium ( $\delta$  D), an isotope of hydrogen, data to the Global Meteoric Water Line (GMWL). The GMWL is described by the linear equation:

$$\delta D = 8 \delta^{18} O + 10$$

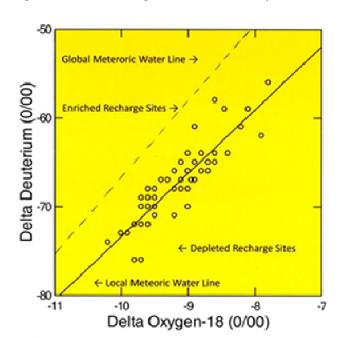
where  $\delta D$  is deuterium in parts per thousand (per mil,  ${}^{0}/_{00}$ ), 8 is the slope of the line,  $\delta {}^{18}O$  is oxygen-18  ${}^{0}/_{00}$ , and 10 is the y-intercept.<sup>11</sup> The GMWL is the standard by which water samples are compared and is a universal reference standard based on worldwide precipitation without the effects of evaporation.

Isotopic data from a region may be plotted to create a Local Meteoric Water Line (LMWL) which is affected by varying climatic and geographic factors. When the LMWL is compared to the GMWL, inferences may be made about the origin or history of the local water.<sup>14</sup> The LMWL created by  $\delta^{18}$ O and  $\delta$  D values for samples collected at sites in the Harquahala basin plot mostly to the right of the GMWL.

Meteoric waters exposed to evaporation are enriched and characteristically plot increasingly below and to the right of the GMWL. Evaporation tends to preferentially contain a higher percentage of lighter isotopes in the vapor phase and causes the water that remains behind to be isotopically heavier. In contrast, meteoric waters that experience little evaporation are depleted and tend to plot increasing to the left of the GMWL and are isotopically lighter.<sup>11</sup>

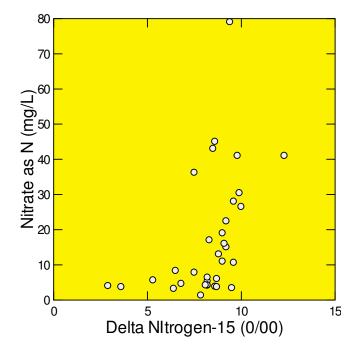
Groundwater from arid environments is typically subject to evaporation, which enriches  $\delta$  D and  $\delta$ <sup>18</sup>O, resulting in a lower slope value (usually between 3 and 6) as compared to the slope of 8 associated with the GMWL.<sup>11</sup>

Groundwater samples for  $\delta^{15}$ N analysis were collected at 34 wells in the basin. The  $\delta^{15}$ N values ranged from +2.9 to +12.3 0/00 while nitrate values ranged at these 34 sites ranged from 1.3 to 79 mg/L (Diagram 5). Based on these results, it appears that the nitrogen source is predominantly natural soil organic matter<sup>26,28</sup> This general classification system,

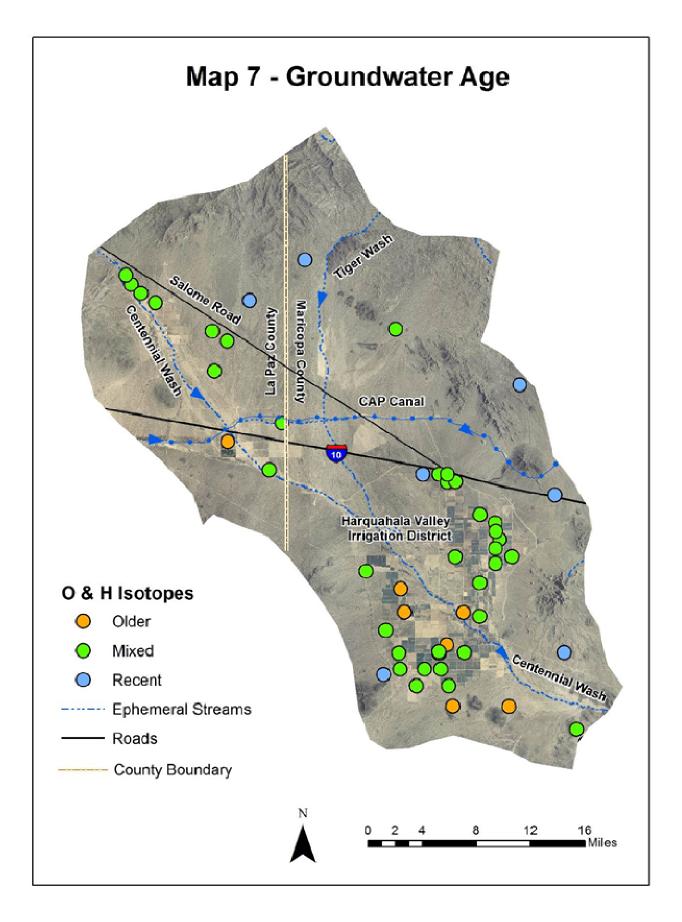


however, may not appear to apply to Sonoran desert areas where there is a statistical correlation between nitrate concentrations and irrigated agriculture. Further analysis of nitrate concentrations is provided in the land use analysis section.

> Diagram 4 – The 51 isotope samples are plotted according to their oxygen-18 and deuterium values and form the Local Meteoric Water Line. The most enriched samples in the basin (upper right of graph) consist of younger water recharged from lower-elevation precipitation that has undergone the most evaporation prior to sampling. The most depleted samples (lower left of graph) consist of older recharge from higher-elevation precipitation that has undergone less evaporation prior to sampling. Most samples appear to be a mixture but still appear to reflect groundwater recharged during cooler climatic conditions.<sup>14</sup>



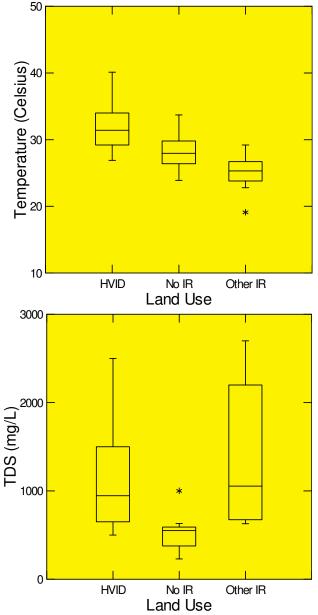
**Diagram 5** – The graph illustrates the relationship between  $\delta^{15}$ N values and nitrate (as nitrogen) concentrations in the 34 wells at which nitrogen isotope samples were collected. Most  $\delta^{15}$ N values are between +2 to +9 per mil which corresponds to the range commonly associated with naturally occurring soil organic matter.<sup>26,28</sup> This finding, however, does not agree with the statistical correlation between nitrate concentrations and areas of irrigated agriculture.



#### **Groundwater Quality Variation**

**Between Three Land Use Groups** – Twenty-four (24) groundwater quality constituents were compared between three broad land use categories: samples collected from sites predominantly in the HVID (34 sites), from sites predominantly in other irrigation areas (eight sites), and from sites where there is no large-scale irrigation (nine sites).

Significant concentration differences were found with 16 constituents: temperature (Diagram 6), pH-field, pH-lab, SC-field, SC-lab, TDS (Diagram 7), sodium, bicarbonate, chloride, sulfate, nitrate (Diagram 8 and

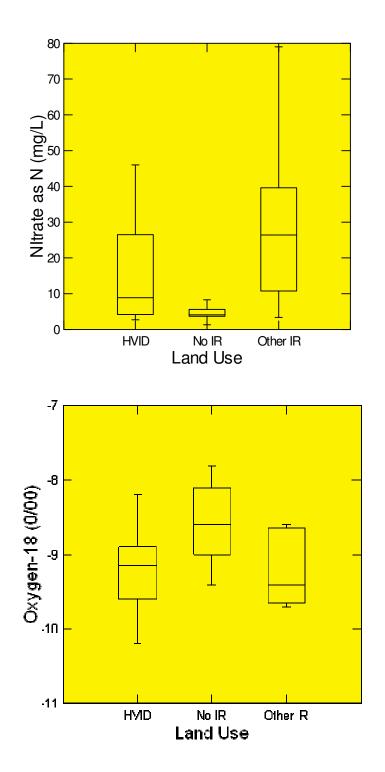


Map 8), barium, chromium, strontium, oxygen-18 (Diagram 9), and deuterium (Kruskal-Wallis and Tukey tests,  $p \le 0.05$ ). In many of these instances, sites located in the HVID had significantly higher constituent concentrations than sites in other irrigation areas or sites with no irrigation.

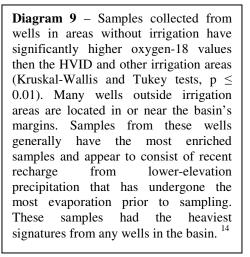
Complete statistical results are in Table 10 and 95 percent confidence intervals for significantly different land use groups are in Table 11.

**Diagram 6** – Samples collected from wells in the HVID have significantly higher temperatures than samples collected from wells in other irrigation areas or where there is no irrigation; there was no significant difference between the latter two groups (Kruskal-Wallis and Tukey tests,  $p \le 0.01$ ). These differences are likely related to depths at which water is produced by wells. Groundwater temperature increases with depth, approximately 3 degrees Celsius with every 100 meters or 328 feet.<sup>9</sup>

**Diagram 7** – Samples collected from wells in the HVID and other irrigated areas have significantly higher TDS concentrations than samples collected from wells where there is no irrigation (Kruskal-Wallis and Tukey tests,  $p \le 0.01$ ). This pattern is likely the result of excess irrigation water containing a large salt load recharging groundwater in agricultural areas.<sup>25</sup>



**Diagram 8** – Samples collected from wells in other irrigated areas have significantly higher nitrate concentrations than samples collected from wells without any irrigation. Nitrate concentrations in the HVID are not significantly different from the other two groups (Kruskal-Wallis and Tukey tests,  $p \leq$ 0.01). Nitrogen isotope values suggest the nitrate source is natural soil organic matter that is transported to groundwater by recharge from irrigated agriculture or dedicated recharge facilities. <sup>26, 28</sup> Elevated nitrate concentrations that are significantly correlated with areas of irrigated agriculture suggest that farming practices may also contribute to nitrate concentrations in groundwater.



Constituent	Sites Sampled	Significance	Significant Differences Between Three Land Use Groups
Temperature - field	51	**	HVID > Other IR & No IR
pH – field	51	**	HVID & No IR > Other IR
pH – lab	51	**	HVID & No IR > Other IR
SC - field	51	**	HVID & Other IR > No IR
SC - lab	51	**	HVID & Other IR > No IR
TDS	51	**	HVID & Other IR > No IR
Hardness	51	ns	-
Calcium	51	ns	-
Magnesium	51	ns	-
Sodium	51	**	HVID & Other IR > No IR
Potassium	51	ns	-
Bicarbonate	51	**	Other IR > HVID & No IR
Chloride	51	**	HVID > No IR
Sulfate	51	**	Other IR > HVID & No IR
Nitrate (as N)	51	**	Other IR > No IR
Arsenic	51	*	-
Barium	51	**	Other IR > HVID & No IR
Boron	51	*	-
Chromium	51	*	HVID > Other IR
Copper	51	ns	-
Fluoride	51	*	-
Selenium	51	ns	-
Strontium	51	**	Other IR > HVID & No IR
Radon	29	ns	-
Oxygen	51	*	No IR > HVID & Other IR
Deuterium	51	*	No IR > HVID & Other IR

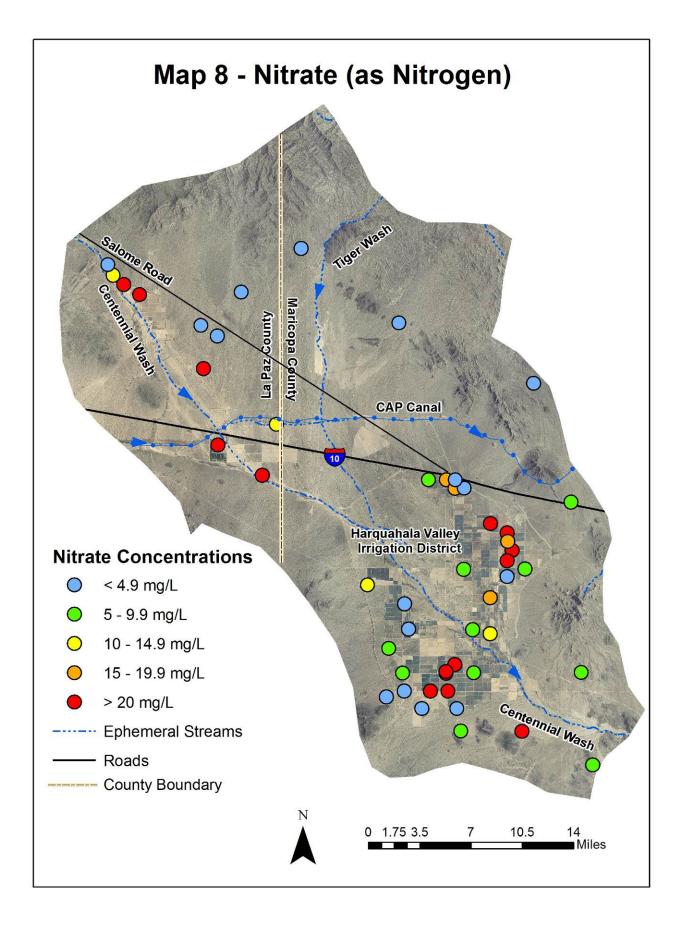
## Table 10. Variation in Groundwater Quality Constituent Concentrations among Three Land Use Groups

 $\begin{array}{ll} ns &= not \ significant \\ * &= significant \ at \ p \leq 0.05 \ or \ 95\% \ confidence \ level \\ ** &= significant \ at \ p \leq 0.01 \ or \ 99\% \ confidence \ level \\ \end{array}$ 

Constituent	Significance	HVID	Other IR	No IR
Temperature - field	**	30.7 to 32.9	22.4 to 27.5	25.7 to 30.7
pH – field	**	7.90 to 8.09	7.33 to 7.71	7.61 to 8.56
pH – lab	**	8.03 to 8.22	7.37 to 7.79	7.70 to 8.51
SC - field	**	1452 to 1959	1123 to 2657	541 to 1116
SC - lab	**	1451 to 1991	1196 to 2831	525 to 1092
TDS	**	903 to 1289	688 to 2108	342 to 697
Hardness	ns	-	-	-
Calcium	ns	-	-	-
Magnesium	ns	-	-	-
Sodium	**	225 to 308	182 to 372	70 - 141
Potassium	ns	-	-	-
Bicarbonate	**	139 to 192	244 to 348	138 to 235
Chloride	**	211 to 337	-	34 to 165
Sulfate	**	210 to 306	50 to 955	45 to 171
Nitrate (as N)	**	11-21	9 to 3.9	3 to 6
Arsenic	*	-	-	-
Barium	**	0.016 to 0.028	0.029 to 0.077	0.001 to 0.027
Boron	*	-	-	-
Chromium	*	0.027 to 0.038	0.011 to 0.022	-
Copper	ns	-	-	-
Fluoride	*	-	-	-
Selenium	ns	-	-	-
Strontium	**	0.70 to 1.21	0.85 to 3.9	0.03 to 0.96
Radon	ns	-	-	-
Oxygen	*	-9.4 to -9.1	-9.64 to -8.79	-9.1 to -8.2
Deuterium	*	-69.1 to -66.6	-71.9 to -65.4	-66.9 to -58.9

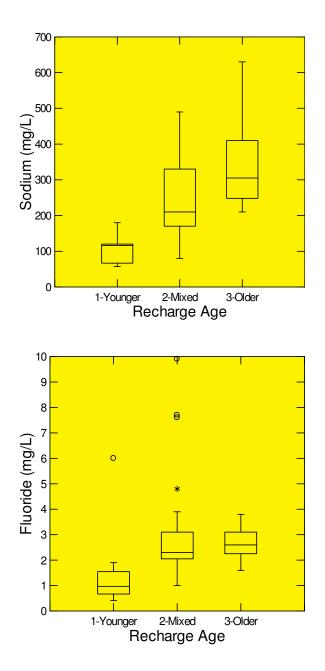
## Table 11. Summary Statistics for Three Land Use Groups with Significant Constituent Differences

 $\begin{array}{l} ns &= not \ significant \\ * = significant \ at \ p \leq 0.05 \ or \ 95\% \ confidence \ level \\ ** &= significant \ at \ p \leq 0.01 \ or \ 99\% \ confidence \ level \\ All units \ are \ mg/L \ except \ where \ indicated. \end{array}$ 



**Between Three Recharge Groups** – Twenty-six groundwater quality constituents were compared between three recharge types: younger (seven sites), mixed (36 sites), and older (eight sites).<sup>14</sup>

Significant concentration differences were found with seven constituents: SC-field, SC-lab, TDS, sodium (Diagram 10), chloride, oxygen-18, and deuterium (Kruskal-Wallis and Tukey test,  $p \le 0.05$ ). Sulfate, nitrate, boron, and fluoride (Diagram 11, Map 9) also

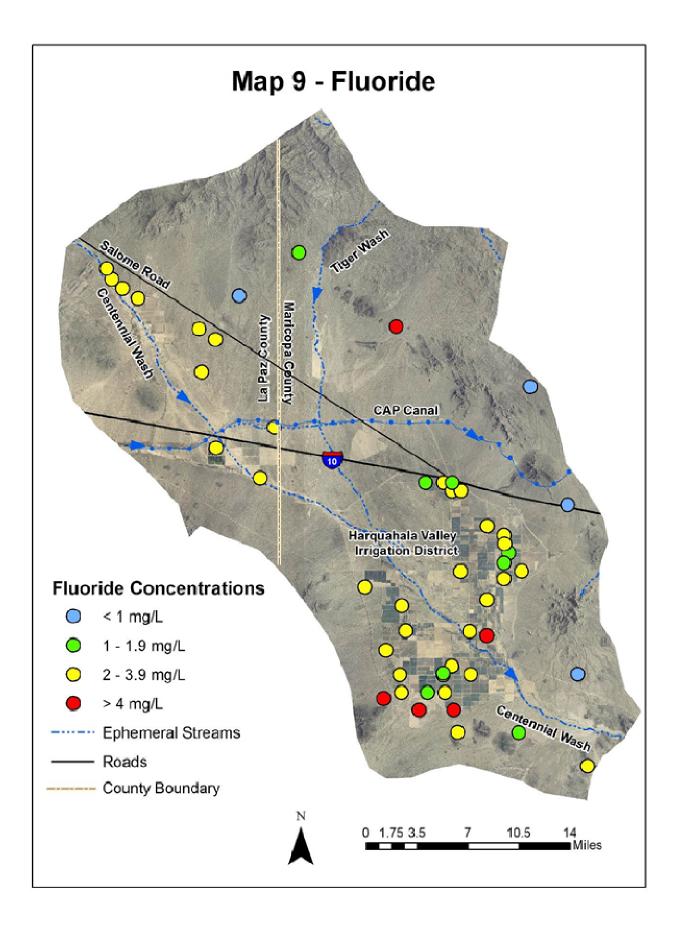


had significant differences using the Kruskal-Wallis test but the Tukey test did not reveal any significant differences between recharge types. In these instances, older samples had significantly higher constituent concentrations than younger samples.

Complete statistical results are in Table 12 and 95 percent confidence intervals for significantly different groups based on recharge groups are in Table 13.

**Diagram 10** – Samples collected from older recharged sites have significantly higher sodium concentrations than mixed and younger sample sites. Samples collected from mixed sites also have significantly higher sodium concentrations than younger sample sites (Kruskal-Wallis and Tukey tests,  $p \le 0.01$ ). Low concentrations of sodium typically occur in recently recharged water and increases downgradient as the result of silicate weathering and halite dissolution along with ion exchange.<sup>25</sup>

**Diagram 11** – Samples collected from older, mixed, and younger age sites have significantly different fluoride concentrations (Kruskal-Wallis test,  $p \leq 0.01$ ). However, when compared by recharge group, none of the differences were significant (Tukey test, 0.05). The highest р <fluoride concentrations tended to be in samples collected from the southeast part of the basin, which confirms the results of previous studies. <sup>12</sup>



Constituent	Sites Sampled	Significance	Significant Differences Among Three Recharge Groups
Temperature - field	51	ns	-
pH – field	51	ns	-
pH – lab	51	ns	-
SC - field	51	**	Older & Mixed > Younger
SC - lab	51	**	Older & Mixed > Younger
TDS	51	**	Older & Mixed > Younger
Hardness	51	ns	-
Calcium	51	ns	-
Magnesium	51	ns	-
Sodium	51	**	Older > Mixed > Younger
Potassium	51	ns	-
Bicarbonate	51	ns	-
Chloride	51	**	Older > Younger
Sulfate	51	*	-
Nitrate (as N)	51	*	-
Arsenic	51	ns	-
Barium	51	ns	-
Boron	51	*	-
Chromium	51	ns	-
Copper	51	ns	-
Fluoride	51	**	-
Selenium	51	ns	-
Strontium	51	ns	-
Radon	29	ns	-
Oxygen	51	**	Younger > Mixed > Older
Deuterium	51	**	Younger > Mixed > Older

## Table 12. Variation in Groundwater Quality Constituent Concentrations Among Three Recharge Groups

 $\begin{array}{ll} ns &= not \ significant \\ * &= significant \ at \ p \leq 0.05 \ or \ 95\% \ confidence \ level \\ ** &= significant \ at \ p \leq 0.01 \ or \ 99\% \ confidence \ level \\ \end{array}$ 

Constituent	Significance	Younger	Mixed	Older
Temperature - field	ns	-	-	-
pH – field	ns	-	-	-
pH – lab	ns	-	-	-
SC - field	**	501 to 1209	1379 to 1895	1280 to 2632
SC - lab	**	472 to 1175	1400 to 1947	1230 to 2745
TDS	**	310 to 739	881 to 1314	770 to 1713
Hardness	ns	-	-	-
Calcium	ns	-	-	-
Magnesium	ns	-	-	-
Sodium	**	64 to 144	206 to 279	231 to 461
Potassium	ns	-	-	-
Bicarbonate	ns	-	-	-
Chloride	**	20 to 191	-	131 to 507
Sulfate	*	-	-	-
Nitrate (as N)	*	-	-	-
Arsenic	ns	-	-	-
Barium	ns	-	-	-
Boron	*	-	-	-
Chromium	ns	-	-	-
Copper	ns	-	-	-
Fluoride	**	-	-	-
Selenium	ns	-	-	-
Strontium	ns	-	-	-
Radon	ns	-	-	-
Oxygen	**	-8.6 to -7.9	-9.2 to -9.0	-10.0 to -9.68
Deuterium	**	-61.3 to -57.5	-67.9 to -66.4	-75.0 to -72.1

## Table 13. Summary Statistics for Three Recharge Groups with Significant Constituent Differences

 $\begin{array}{l} ns &= not \ significant \\ * = \ significant \ at \ p \leq 0.05 \ or \ 95\% \ confidence \ level \\ ** &= \ significant \ at \ p \leq 0.01 \ or \ 99\% \ confidence \ level \\ All units \ are \ mg/L \ except \ where \ indicated. \end{array}$ 

### DISCUSSION

Groundwater in the Harquahala basin is generally unsuitable for drinking water uses without proper treatment based on the sampling results from this ADEQ ambient study. However, the quality of water is generally suitable for irrigation use, which is the predominant water use in the basin.

Of the 51 sites sampled, only two sites met all health and aesthetic drinking water quality standards. Health-based, Primary MCLs such as nitrate, arsenic, fluoride, gross alpha, and uranium were exceeded at 71 percent of sites.<sup>32</sup> These are the constituents that most commonly exceed health-based water quality standards in Arizona.<sup>30</sup> These constituents are likely naturally occurring in the basin though nitrate concentrations may be exacerbated by percolating groundwater from irrigation applications or recharge projects.

These results generally substantiate earlier water quality studies in the basin. In ADWR's water atlas, using historical data the agency identified 82 wells in the basin with constituent concentrations exceeding health-based Primary MCLs.<sup>7</sup> Most of these exceedances were for nitrate, arsenic, and fluoride, though noted isolated exceedances of lead, chromium, and mercury occurred that were not found in this ADEQ study.<sup>7</sup> Groundwater characteristics such as recharge that occurred long ago suggest chromium may occasionally occur in concentrations exceeding its Primary MCL. Based on the ADEQ study results, however, it's likely that lead and mercury exceedances were caused by sample contamination or lab error.

Previous studies have noted that concentrations of some constituents, particularly TDS and nitrate, are elevated in wells which draw water from, or partially from, perched aquifers in the HVID.<sup>15, 18</sup> Field observations suggested that this conclusion was correct, though positively identifying which wells had contributions of water from perched aquifers was problematic as well logs were generally not available and/or the wells were constantly running during the growing season. Previous ADEQ baseline studies in irrigated agricultural areas have found percolating irrigation water laden with salts and nitrate impact shallow perched aquifers.<sup>29</sup> Thus, within the HVID, many constituent concentrations may be controlled more by whether the irrigation well is screened in the perched aquifer than by its location.

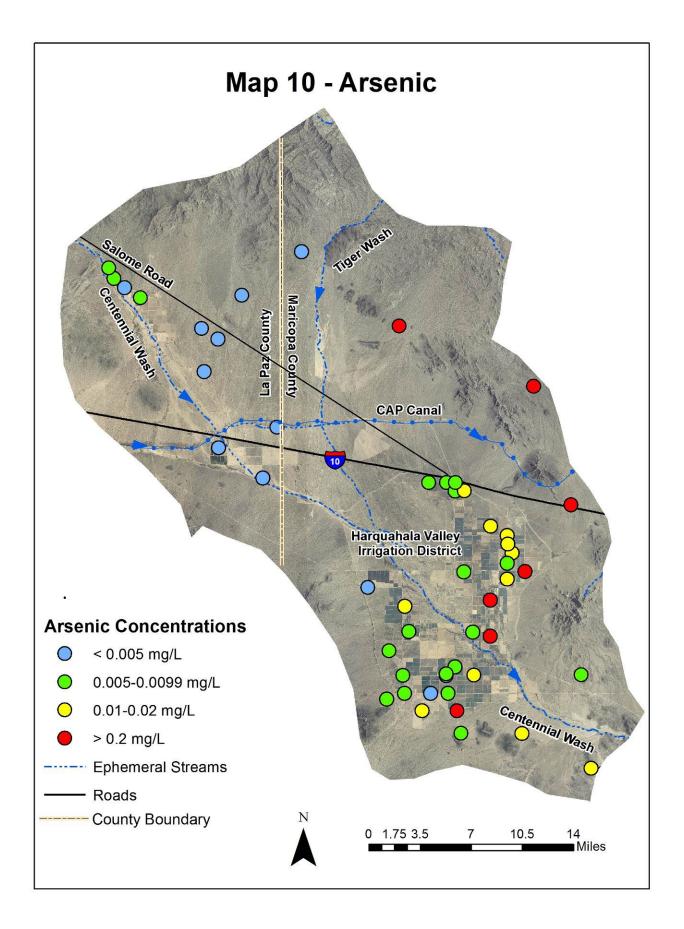
**Nitrate** - Nitrate exceeded health-based, water quality standards in samples collected from 24 wells.

Nitrate concentrations were as high as 79 mg/L, which is almost eight times the 10.0 mg/L nitrate (as nitrogen) standard. Nitrogen isotopes suggest the predominant source of nitrate is naturally occurring soil organic matter.<sup>26, 28</sup> Percolating groundwater such as which occurs underneath irrigated fields or recharge projects likely helps transport the nitrogen. The significant correlation between elevated nitrate concentrations and irrigation areas, however, suggests that farming practices also contribute to this water quality problem. The possibility of anthropomorphic sources contributing to groundwater nitrate concentrations is also supported by previous U.S. Geological Survey research.<sup>22</sup> More research on these topics in Sonoran desert areas is needed to definitively determine the relative contributions of nitrate from different sources.

Arsenic - Arsenic exceeded health-based, water quality standards in samples collected from 19 wells, with concentrations as high as 0.0855 mg/L, over eight times the 0.01 mg/L standard. Arsenic concentrations are affected by reactions with hydroxyl ions and are influenced by factors such as an oxidizing environment, lithology, and aquifer residence time.<sup>25</sup> These factors are present in the basin to produce elevated arsenic concentrations, especially aquifer residence time as oxygen and hydrogen isotope values suggest that groundwater was recharged long ago during cooler climatic conditions.<sup>14</sup> Arsenic concentrations tend to be lowest in the northwest and western portions of the basin and highest in the eastern portions especially in and adjacent to the Big Horn Mountains (Map 10).

**Fluoride** - Fluoride exceeded health-based, water quality standards in samples collected from 5 wells, with concentrations as high as 9.9 mg/L, more than double the 4.0 mg/L standard. The frequency of fluoride exceedances in this study is much less than that cited in previous reports. In 115 samples collected by ADWR in the basin between 1984 and 1989, 49 (or 43 percent) exceeded the 4.0 mg/L Primary MCL.<sup>18</sup> This high frequency may be due to older studies using 1.4 mg/L as the health-based water quality standard, based partially on an outmoded method that factors in the annual average maximum daily air temperature.<sup>15</sup>

Fluoride concentrations in groundwater are often controlled by calcium through precipitation or dissolution of the mineral fluorite. In a chemically closed hydrologic system, calcium is removed from solution by precipitation of calcium carbonate and the formation of smectite clays. Concentrations exceeding 5 mg/L of dissolved fluoride may occur in



groundwater depleted in calcium if a source of fluoride ions is available for dissolution.<sup>25</sup> Andesite and basalt in the mountains surrounding the Harquahala Plain can contribute large amounts of fluoride to the groundwater, particularly in the southern part of the basin.<sup>8</sup>

Sites only partially depleted in calcium may be controlled by processes other than fluorite dissolution. Hydroxyl ion exchange or sorption-desorption reactions have also been cited as providing controls on lower (< 5 mg/L) levels of fluoride. As pH values increase downgradient, greater levels of hydroxyl ions may affect an exchange of hydroxyl for fluoride ions thereby increasing fluoride in solution.<sup>25</sup>

**Gross alpha and Uranium** - Of the 10 radionuclide samples collected, gross alpha and uranium exceeded health-based, water quality standards at only one site, Big Horn windmill. The windmill is located in granitic geology, which is associated with elevated radionuclide concentrations in groundwater.<sup>21, 23</sup>

**TDS** – In the ADEO study, 48 of the 51 sample sites (or 94 percent) exceeded the Secondary MCL of 500 Previous studies estimating mg/L. TDS concentrations from specific conductivity had similar results. Of the 118 samples analyzed between 1984 and 1989, 102 samples (or 86 percent) exceeded the Secondary MCL. Previous studies indicated that groundwater in the northeast part of the HVID generally had the lowest TDS concentrations, including many wells below 500 mg/L. This area, which coincided with the deepest part of the cone of depression, may indicate water at greater depth, is of better quality.<sup>13</sup>

#### REFERENCES

- <sup>1</sup> Accutest, 2014, Personal communication from Test America staff.
- <sup>2</sup> Arizona Department of Environmental Quality, 1991, Quality Assurance Project Plan: Arizona Department of Environmental Quality Standards Unit, 209 p.
- <sup>3</sup> Arizona Department of Environmental Quality, 2013, Personal message from John Calkins, Manager, ADEQ Safe Drinking Water Section, September 13.
- <sup>4</sup> Arizona Department of Environmental Quality, 2013-2014, Arizona Laws Relating to Environmental Quality: St. Paul, Minnesota, West Group Publishing, §49-221-224, p 134-137.

- <sup>5</sup> Arizona State Land Department, 1997, "Land Ownership - Arizona" GIS coverage: Arizona Land Resource Information Systems, downloaded, 4/7/07.
- <sup>6</sup> Arizona Department of Water Resources website, 1991, Water service organizations in Arizona, p. 21.
- <sup>7</sup> Arizona Department of Water Resources website, 2014, <u>www.azwater.gov/azdwr/default.aspx</u>, accessed 05/14/14.
- <sup>8</sup> Arizona Water Resources Research Center, 1995, Field Manual for Water-Quality Sampling: Tucson, University of Arizona College of Agriculture, 51 p.
- <sup>9</sup> Bitton, G. and Gerba, C.P., 1994. *Groundwater Pollution Microbiology*: Malabar, FL: Krieger Publishing Company, 377 p.
- <sup>10</sup> Brown, S.L., Yu, W.K., and Munson, B.E., 1996, The impact of agricultural runoff on the pesticide contamination of a river system - A case study on the middle Gila River: Arizona Department of Environmental Quality Open File Report 96-1: Phoenix, Arizona, 50 p.
- <sup>11</sup> Craig, H., 1961, Isotopic variations in meteoric waters. *Science*, 133, pp. 1702-1703.
- <sup>12</sup> Crockett, J.K., 1995. Idaho statewide groundwater quality monitoring program–Summary of results, 1991 through 1993: Idaho Department of Water Resources, Water Information Bulletin No. 50, Part 2, p. 60.
- <sup>13</sup> Dennis, E.E., 1971. Ground-water conditions in the Harquahala Plains, Maricopa and Yuma Counties, Arizona: Arizona State Land Department Water-Resources Report 45, 44 p.
- <sup>14</sup> Earman, Sam, et al, 2003, An investigation of the properties of the San Bernardino groundwater basin, Arizona and Sonora, Mexico: Hydrology program, New Mexico Institute of Mining and Technology, 283 p.
- <sup>15</sup> Graf, C. G., 1980, Maps showing ground-water conditions in the Harquahala Plains area, Maricopa and Yuma Counties, Arizona—1980; Arizona Department of Water Resources Hydrologic Map Series Report Number 1, 3 sheets, scale, 1:250,000.
- <sup>16</sup> Graf, Charles, 1990, An overview of groundwater contamination in Arizona: Problems and principals: Arizona Department of Environmental Quality seminar, 21 p.
- <sup>17</sup> Heath, R.C., 1989, Basic ground-water hydrology: U.S. Geological Survey Water-Supply Paper 2220, 84 p.
- <sup>18</sup> Hedley, J.D., 1990, Maps showing ground-water conditions in the Harquahala Irrigation Non-Expansion area and Tiger Wash basin, Maricopa and La Paz Counties, Arizona—1989; Arizona Department

of Water Resources Hydrologic Map Series Report Number 17, 3 sheets, scale, 1:250,000.

- <sup>19</sup> Helsel, D.R. and Hirsch, R.M., 1992, *Statistical methods in water resources*: New York, Elsevier, 529 p.
- <sup>20</sup> Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water [Third edition]: U.S. Geological Survey Water-Supply Paper 2254, 264 p.
- <sup>21</sup> Lowry, J.D. and Lowry, S.B., 1988, "Radionuclides in Drinking Waters," in *American Water Works Association Journal*, 80 (July), pp. 50-64.
- <sup>22</sup> Madison, R.J., and Brunett, J.O., 1984, Overview of the occurrence of nitrate in ground water of the United States, *in* National Water Summary 1984-Water Quality Issues: U.S. Geological Survey Water Supply Paper 2275, pp. 93-105.
- <sup>23</sup> Richard, S.M., Reynolds, S.J., Spencer, J.E. and Pearthree, Pa, P.A., 2000, Geologic map of Arizona: Arizona Geological Survey Map 35, scale 1:1,000,000.
- <sup>24</sup> Roberts, Isaac, 2008, Personal communication from ADHS staff.
- <sup>25</sup> Robertson, F.N., 1991, Geochemistry of ground water in alluvial basins of Arizona and adjacent parts of Nevada, New Mexico, and California: U.S. Geological Survey Professional Paper 1406-C, 90 p.
- <sup>26</sup> Sustainability of Semi-Arid Hydrology and Riparian Areas website, <u>http://web.sahra.arizona.edu/programs/isotopes/nitrog</u> en.html#2, accessed 6/05/14.
- <sup>27</sup> Test America, 2013, Personal communication from Test America staff.
- <sup>28</sup> Thiros, S.A., Bexfield, L.M., Anning, D.W., and Huntington, J.M., eds., 2010, Conceptual understanding and groundwater quality of selected basin-fill aquifers in the Southwestern United States: U.S. Geological Professional Paper 1781, 288 p.
- <sup>29</sup> Towne, D.C., 2011, Ambient groundwater quality of the McMullen Valley basin: a 2008-2009 baseline study: Arizona Department of Environmental Quality Open File Report 11-02, 94 p.
- <sup>30</sup> Towne, Douglas and Jones, Jason, 2011, Groundwater quality in Arizona: a 15 year overview of the ADEQ ambient groundwater monitoring program (1995-2009): Arizona Department of Environmental Quality Open File Report 11-04, 44 p.
- <sup>31</sup> University of Arizona Environmental Isotope Laboratory, 2013, Personal communication from Christopher Eastoe.

- <sup>32</sup> U.S. Environmental Protection Agency website, <u>www.epa.gov/waterscience/criteria/humanhealth/</u>, accessed 3/05/14.
- <sup>33</sup> U.S. Geological Survey, Arizona Water Use website, <u>http://az.water.usgs.gov/projects/9671-9DW/</u> accessed 6/12/14.
- <sup>34</sup> U.S. Geological Survey, 2014, Personal communication from Kimberly Beisner.
- <sup>35</sup> U.S. Salinity Laboratory, 1954, Diagnosis and improvement of saline and alkali soils: U.S. Department of Agriculture, Agricultural Research Service, Agriculture Handbook No. 60, 160 p.
- <sup>36</sup> Vidler Water Company, 2014, Personal communication from Vidler Water staff.
- <sup>37</sup> Wilkinson, L., and Hill, M.A., 1996. Using Systat 6.0 for Windows, Systat: Evanston, Illinois, p. 71-275.
- <sup>38</sup> U.S. Environmental Protection Agency website, <u>http://water.epa.gov/lawsregs/rulesregs/sdwa/radon/regulations.cfm</u>, accessed 6/18/14.

Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Recharge Age Well Use
			1 <sup>st</sup> Field	Frip, June 3-4	l, 2009 – Towne				
HAR-1	B(1-9)17bba turbine	33°26'05.401" 113°12'41.464"	616570	17012	Courthouse Well #1	Inorganic 2 Isotopes	1973'	520'	Older Irrigation
HAR-2	B(1-9)20bdc turbine	33°24'50.433" 113°12'27.216"	616572	17022	Courthouse Well #3	Inorganic 2 Isotopes	1500'	520'	Older Irrigation
HAR-3	B(2-8)30aaa turbine	33°29'36.391" 113°06'37.234"	608452	17602	Bighorn Well #2	Inorganic 2 Isotopes	1180'	-	Mixed Irrigation
HAR-4	B(2-8)19cbb turbine	33°30'02.914" 113°07'36.300"	608454	17585	Bighorn Well #1	Inorganic 2 Isotopes	1080'	-	Mixed Irrigation
		2 <sup>nd</sup> F	ield Trip, Sep	tember 14, 20	11 – Towne &	Boettcher			
HAR-5/6 duplicate	B(2-8)15dad submersible	33°31.120" 113°04.161"	573621	006219	Burnt Well Rest Area	Inorganic, Radon Radiochem, 2 Isotopes	770'	440'	Younger Public Suppl
HAR-7	B(2-9)11bbb turbine	33°32.213" 113°09.683"	611126	17623	C1-1	Inorganic, Radon 2 Isotopes	1355'	-	Mixed Irrigation
HAR-8	B(1-9)34add turbine	33°23.088" 113°09.727"	627798	17049	Shepherd Well #1	Inorganic, Radon 2 Isotopes	1000'	500'	Older Irrigation
HAR-9	B(1-9)34dcc turbine	33°22.749" 113°10.232"	627799	17051	Shepherd Well #2	Inorganic, Radon 2 Isotopes	1000'	560'	Mixed Irrigation
HAR-10	B(1-9)34dcc submersible	33°22.660" 113°10.227"	627805	17052	Shepherd Dm Well	Inorganic, Radon 2 Isotopes	1000'	520'	Older Domestic
HAR-11	C(1-9)03dcc turbine	33°23.088" 113°09.727"	626958	23144	W13-6	Inorganic, Radon 2 Isotopes	1000'	578'	Mixed Irrigation
		3 <sup>rd</sup> Field Trip, Oct	tober 6, 2011 -	- Towne & D	<b>etermann</b> (Equi	pment Blank – HAR-21)			
HAR-12	B(1-9)30bcb submersible	33°23'53.048" 113°13'37.688"	209743	77305	Eagletail Rn House	Inorganic, Radon Radiochem, 3 Isotopes	600'	450'	Mixed Domestic
HAR-13	C(1-10)12ada submersible	33°21'30.116" 113°13'46.879"	601285	23176	Shipping Pen Well	Inorganic, Radon 3 Isotopes	600'	450'	Younger Stock
HAR-14/15 duplicate	B(1-9)32ccc turbine	33°22'39.887" 113°12'48.808"	626952	17048	W12-1	Inorganic, Radon 3 Isotopes	1200'	550'	Mixed Irrigation
HAR-16	C(1-9)11ccc turbine	33°20'54.764" 113°09'36.078"	627800	23158	W14-4	Inorganic, 3 Isotopes	690'	590'	Mixed Irrigation
HAR-17	B(1-9)23cbb turbine	33°24'49.050" 113°08'40.069"	635438	17033	C9.5-1	Inorganic, Radon 3 Isotopes	1000'	460'	Older Irrigation
HAR-18	B(1-9)02baa turbine	33°27'48.294" 113°09'12.011"	614408	16982	C6-2	Inorganic, Radon 3 Isotopes	1510'	460'	Mixed Irrigation
HAR-19/42 resample	B(2-8)31daa turbine	33°28'13.802" 113°06'37.017"	612560	17607	#2	Inorganic, Radon Radiochem, 3 Isotopes	1200'	-	Mixed Irrigation
		4 <sup>th</sup> F	ield Trip, Dec	ember 19, 201	11 – Towne & D	etermann			
HAR-20	B(4-11)29acb submersible	33°39'49.669" 113°24'45.670"	587195	77543	Pancho's Well	Inorganic, Radon 3 Isotopes	680'	530'	Mixed Domestic
		5 <sup>ti</sup>	<sup>1</sup> Field Trip, I	March 8, 2012	– Towne & Bo	ettcher			
HAR-22	B(4-11)15ad windmill	33°41'28.174" 113°22'21.903"	612688	18097	Carmelita Windmill	Inorganic 3 Isotopes	650'	615'	Younger Stock
			<sup>th</sup> Field Trip,	April 9, 2012	– Towne & Boe	•			
HAR-24	B(4-12)14cbb submersible	33°41'21.373" 113°28'23.958"	603143	18103	Farm Camp Well	Inorganic 3 Isotopes	1059'	370'	Mixed Domestic
HAR-25	B(4-11)28cda submersible	33°39'18.972" 113°23'47.913"	575971	78061	Hunter Well	Inorganic 3 Isotopes	685'	550'	Mixed Domestic
HAR-26	B(3-11)05dbc submersible	33°37'42.731" 113°24'36.878"	205647	78062	Caudell Well	Inorganic, Radiochem 3 Isotopes	632'	491'	Mixed

# Appendix A. Data for Sample Sites, Harquahala Basin, 2009 -2014

Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Recharge Ag
		7	<sup>th</sup> Field Trip,	April 10, 201	2 – Towne & R	hyner			
HAR-27	B(2-9)10abb turbine	33°32'13.110" 113°10'13.116"	611125	17619	W1-3	Inorganic 3 Isotopes	1398'	470'	Mixed Irrigation
HAR-28	B(2-9)09abb turbine	33°32'13.050" 113°11'16.030"	611123	17617	W1-1	Inorganic 3 Isotopes	1540'	-	Younger Irrigation
HAR-29	B(1-10)01ccc submersible	33°27'01.739" 113°14'53.575"	624935	17058	Farm Camp Well	Inorganic 3 Isotopes	917'	486'	Mixed Domestic
HAR-30	B(1-9)36ccc turbine	33°22'41.037" 113°08'35.505"	614410	17055	W12-8	Inorganic 3 Isotopes	1190'	-	Mixed Irrigation
HAR-31	B(1-8)19cbc turbine	33°24'37.072" 113°07'37.449"	605786	16976	C97-1	Inorganic 3 Isotopes	1000'	-	Mixed Irrigation
HAR-32/23 isotope dup	B(4-11)15ad windmill	33°43'37.438" 113°18'49.569"	216701	18404	Alaska Mn Windmill	Inorganic, Radon Radiochem, 3 Isotopes	540'	174'	Younger Stock
		8 <sup>th</sup>	Field Trip, A	pril 10, 2013	– Towne & Bo	ettcher			
HAR-33/34 duplicate	B(4-9)30aac windmill	33°39'56.755" 113°13'02.068"	612687	18096	Big Horn Windmill	Inorganic, Radon Radiochem, 3 Isotopes	700'	340'	Mixed Stock
HAR-35	B(2-9)11cbb turbine	33°31'47.624" 113°09'42.139"	611128	17624	-	Inorganic, Radon 3 Isotopes	1505'	-	Mixed Irrigation
HAR-36	B(2-9)11acc turbine	33°31'48.080" 113°09'09.808"	611130	17621	-	Inorganic, Radon 3 Isotopes	-	434'	Mixed Irrigation
		9 <sup>th</sup> Field Trip,	July 2, 2013 –	Towne & Boo	ettcher & USGS	(Beisner & Sanger)			
HAR-37 USGS split	C(1-9)05ccc submersible	33°21'47.162" 113°12'43.262"	602826	23148	Eagletail Water Co.	Inorganic, Radon Radiochem, 3 Isotopes	1140'	600'	Mixed Public Supp
HAR-38	C(1-9)09ccc turbine	33°20'54.887" 113°11'40.481"	602825	23155	W-14-2	Inorganic, Radon 3 Isotopes	1425'	527'	Mixed Irrigation
HAR-39	C(1-9)04dcc turbine	33°21'47.145" 113°11'09.461"	626960	23146	W-13-4	Inorganic, Radon 3 Isotopes	900'	610'	Mixed Irrigation
		10 <sup>tt</sup>	<sup>1</sup> Field Trip, A	August 1, 201.	3 – Towne & B	oettcher			
HAR-40	B(1-8)04bbb submersible	33°27'49.303" 113°05'33.230"	802143	16959	Rosemont Water Co.	Inorganic, Radon Radiochem, 3 Isotopes	1000'	220'	Mixed Public Supp
HAR-41	B(2-8)32bba turbine	33°28'43.536" 113°06'19.410"	614430	17610	E-5-3	Inorganic 3 Isotopes	1720'	280'	Mixed Irrigation
HAR-19/42 resample	B(2-8)31daa turbine	33°28'13.720" 113°06'36.870"	612560	17607	#2	Inorganic, Radon 3 Isotopes	1200'	-	Mixed Irrigation
HAR-43	B(2-8)29cbb turbine	33°29'10.375" 113°06'35.269"	586640	17600	E-4, 5-2	Inorganic, Radon 3 Isotopes	900'	-	Mixed Irrigation
HAR-44	B(1-8)06daa turbine	33°27'26.159" 113°06'36.849"	612567	16962	-	Inorganic 3 Isotopes	1200'	-	Mixed Irrigation
HAR-45	B(1-8)07cbb turbine	33°26'24.498" 113°07'37.565"	085118	16971	E-7-4	Inorganic, Radon 3 Isotopes	1008'	-	Mixed Irrigation
HAR-46	C(1-9)23bdb submersible	33°19'48.478" 113°09'20.821"	807638	23174	Aussie Well	Inorganic, Radon 3 Isotopes	1311'	336'	Mixed Irrigation
HAR-47	C(1-8)08bbb turbine	33°21'44.739" 113°06'31.224"	606842	23092	Stevens Well	Inorganic, Radon 3 Isotopes	800'	370'	Older Irrigation
		11 <sup>th</sup> 1	Field Trip, No	vember 13, 20	)13 – Towne &	Boettcher			
HAR-48	C(1-8)20adb submersible	33°19'46.837" 113°05'44.409"	806998	23118	Davis Well	Inorganic, Radon 3 Isotopes	400' 50'		Older Domestic
HAR-49	C(1-7)31acc windmill	33°17'51.782" 113°00'49.585"	614952	78661	Chimney Windmill	Inorganic, Radon 3 Isotopes	600'	-	Mixed Stock

## Appendix A. Data for Sample Sites, Harquahala Basin, 2009-2014---Continued

Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Recharge Age
		12 <sup>th</sup> Field Trip, J	anuary 22, 20	14 – Towne &	<b>Turner</b> (Equip	ment Blank – HAR-56)			
HAR-50 Vidler split	B(2-11)01ccb monitoring	33°32'26.638" 113°21'07.790"	579335	78881	Vidler AE-2	Inorganic 3 Isotopes	560'	356'	Mixed Monitoring
HAR-51 Vidler split	B(3-11)33baa submersible	33°33'56.335" 113°23'45.512"	579336	78882	Vidler UG-1	Inorganic 3 Isotopes	570'	420'	Older Monitoring
HAR-52	B(3-11)24ddb submersible	33°34'56.988" 113°20'17.585"	-	78883	ABCO Well	Inorganic 3 Isotopes	-	-	Mixed Domestic
HAR-53/54 duplicate	B(4-12)09acc turbine	33°42'18.800" 113°29'58.154"	602987	18101	La Paz IR Well#11	Inorganic, Radon Radiochem, 3 Isotopes	1340'	500'	Mixed Irrigation
HAR-55	B(4-12)10ccc submersible	33°41'51.238" 113°29'20.524"	603142	18102	La Paz Dm Well	Inorganic, Radon 3 Isotopes	900'	-	Mixed Irrigation
HAR-57	B(4-12)04cca turbine	33°42'49.314" 113°30'16.587"	603141	18098	La Paz IR Well #10	Inorganic, Radon 3 Isotopes	1018'	420'	Mixed Irrigation
		13 <sup>th</sup>	Field Trip, Fe	ebruary 3, 201	4 – Towne & 1	Boettcher			
HAR-58	B(1-8)36c submersible	33°22'41.484" 113°02'13.902"	614406	16978	Rattlesnake Well	Inorganic, Radon Radiochem, 3 Isotopes	442'	252'	Younger Stock
		14 <sup>th</sup>	' Field Trip, F	ebruary 19, 2	014 – Towne &	Turner			
HAR-59	B(3-8)9db windmill	33°36'58.584" 113°05'03.375"	612696	48007	Wallace Windmill	Inorganic, 3 Isotopes	405'	205'	Younger Stock

Appendix A. Data for Sample Sites, Harquahala Basin, 2009–2014---Continued

Site #	MCL Exceedances	Temp (°C)	<b>pH-field</b> (su)	<b>pH-lab</b> (su)	SC-field (µS/cm)	SC-lab (µS/cm)	TDS (mg/L)	Hard (mg/L)	Hard - cal (mg/L)	<b>Turb</b> (ntu)
HAR-1	TDS, As, F	35.6	8.32	8.4	1156	1000	680	57	58	0.76
HAR-2	TDS, F	39.5	7.96	8.2	1291	1200	750	69	70	0.030
HAR-3	TDS, Cl, NO <sub>3</sub> , As, F	33.7	7.81	8.0	1615	1600	940	330	330	0.05
HAR-4	TDS, NO <sub>3</sub> , As, F	31.2	7.95	8.1	1314	1300	820	200	210	0.32
HAR-5/6	TDS, pH-f, As	33.7	8.89	8.78	935	875	550	-	ND	0.21
HAR-7	TDS	35.1	8.00	8.04	884	810	500	-	140	ND
HAR-8	TDS, Cl, NO <sub>3</sub> , F	30.2	8.04	8.06	1642	1700	1000	-	130	ND
HAR-9	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> ,	28.4	7.77	7.93	2200	2300	1500	-	340	ND
HAR-10	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , F	29.2	7.35	7.70	3030	3200	2000	-	610	3.2
HAR-11	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , F	28.3	7.94	8.02	2700	2800	1800	-	440	ND
HAR-12	TDS, F	29.7	8.07	8.28	1210	1200	730	-	85	0.23
HAR-13	TDS, F	34.6	7.79	7.99	819	790	500	-	82	0.22
HAR-14/15	TDS, F	31.2	7.69	7.955	1316	1300	770	-	145	ND
HAR-16	TDS, As, F	33.5	8.39	8.42	1116	1100	650	-	34	ND
HAR-17	TDS, SO <sub>4</sub> , F	28.4	8.22	8.27	1595	1600	1000	-	120	ND
HAR-18	TDS, F	34.8	8.04	8.20	1216	1200	750	-	150	ND
HAR-19/42	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , As	31.45	7.83	7.895	2474	2500	1750	-	655	ND
HAR-20	TDS, F	27.6	7.73	7.54	884	840	590	-	240	0.58
HAR-22	-	26.27	7.41	8.06	742	740	480	-	260	0.61
HAR-24	TDS, Cl, SO <sub>4</sub> NO <sub>3</sub> , F	24.9	7.24	7.34	3126	3400	2700	-	1000	ND
HAR-25	TDS, F	-	7.85	7.96	909	860	560	-	200	2.0
HAR-26	TDS, Cl, SO <sub>4</sub> NO <sub>3</sub> , F	29.2	7.63	7.84	2660	2800	1900	-	150	ND
HAR-27	TDS, Cl, NO <sub>3</sub> , F	29.9	7.76	7.90	1528	1500	950	-	270	ND
HAR-28	TDS	32.1	7.96	8.09	873	780	510	-	130	ND
HAR-29	TDS, SO <sub>4,</sub> NO <sub>3</sub> , F	26.9	7.83	8.00	1875	2000	1200	-	300	0.61
HAR-30	TDS, F, As	28.6	8.20	8.34	1301	1300	760	-	58	ND
HAR-31	TDS, SO <sub>4</sub> , NO <sub>3</sub> , As, <b>F</b>	29.4	7.96	8.99	1675	1600	1000	-	64	ND
HAR-32	TDS, Cl, SO <sub>4</sub>	30.0	7.07	7.24	1621	1600	1000	-	670	2.0

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014

Site #	MCL Exceedances	Temp (°C)	<b>pH-field</b> (su)	<b>pH-lab</b> (su)	SC-field (µS/cm)	SC-lab (µS/cm)	TDS (mg/L)	Hard (mg/L)	Hard - cal (mg/L)	Turb (ntu)
HAR-33/34	pH-f, As, <b>F</b> , Fe, Gross α, U	29.6	8.84	8.855	378	385	230	ND	-	3.15
HAR-35	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , F	27.7	7.59	7.70	2395	2500	1700	420	-	ND
HAR-36	TDS, As, F	31.3	7.82	7.96	823	860	520	140	-	0.90
HAR-37	TDS, F	35.2	7.95	8.12	957	890	640	71	-	ND
HAR-38	TDS, As, F	28.7	8.06	8.18	877	820	570	68	-	0.20
HAR-39	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub>	28.6	7.69	7.82	3254	3000	2100	470	-	ND
HAR-40	pH-f, TDS, F, As	31.4	8.58	8.51	922	970	630	32	-	ND
HAR-41	TDS, Cl, SO4, NO3, As	33.1	8.05	8.04	2138	2200	1500	450	-	ND
HAR-43	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub>	34.0	7.93	7.85	2760	3000	2500	970	-	ND
HAR-44	TDS, SO <sub>4</sub> , NO <sub>3</sub> F, As	31.5	7.95	7.88	1717	1800	1200	320	-	ND
HAR-45	TDS, F, As	40.1	8.43	8.35	963	990	640	54	-	ND
HAR-46	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , As, F	34.0	8.34	8.50	1858	2000	1200	100	-	ND
HAR-47	TDS, Cl, SO <sub>4</sub> , F	31.9	8.11	8.11	2056	2100	1300	180	-	ND
HAR-48	TDS, Cl, SO <sub>4</sub> , NO <sub>3</sub> , As	31.4	8.41	8.60	3343	3500	2200	170	-	ND
HAR-49	TDS, As, F	28.3	8.25	8.26	990	1000	630	52	-	ND
HAR-50	TDS, NO <sub>3</sub> , F	22.8	7.60	7.63	1672	1770	1110	202	-	ND
HAR-51	TDS, NO <sub>3</sub> , F	24.8	7.84	7.85	1534	1600	1000	175	-	ND
HAR-52	TDS, NO <sub>3</sub> , F	27.5	7.71	7.77	1002	1090	629	130	-	0.69
HAR-53/54	TDS, NO <sub>3</sub> , F	25.7	7.32	7.275	1053	1140	672	209.5	-	ND
HAR-55	TDS, SO <sub>4</sub> , NO <sub>3</sub> F	19.1	7.58	7.67	3053	3220	2500	829	-	ND
HAR-57	TDS, F	25.9	7.25	7.27	1022	1090	674	198	-	ND
HAR-58	-	26.5	8.43	8.27	591	609	376	ND	-	ND
HAR-59	As	21.5	8.27	7.98	406	369	258	77.6	-	1.3

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	<b>T. Alk</b> (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
HAR-1	15	5	210	3.3	200	230	3.6	100	160
HAR-2	14	8.7	240	2.7	230	280	ND	120	160
HAR-3	79	32	170	5.1	64	78	ND	270	190
HAR-4	48	21	180	4.0	83	100	ND	160	160
HAR-5/6	3.05	ND	180	ND	170	129	22	110	64.5
HAR-7	31	16	110	4.0	110	134	ND	110	110
HAR-8	29	14	330	4.4	210	256	ND	270	200
HAR-9	77	36	370	5.4	170	207	ND	400	340
HAR-10	120	72	440	6.9	250	305	ND	590	500
HAR-11	82	57	440	5.5	160	195	ND	530	380
HAR-12	14	12	200	2.9	270	317	11	110	140
HAR-13	26	4.1	120	2.2	120	146	ND	93	120
HAR-14/15	30.5	16.5	210	3.15	190	232	ND	190	160
HAR-16	8.7	3.0	210	2.9	130	159	6.4	150	150
HAR-17	33	8.8	280	11	130	159	ND	170	360
HAR-18	35	15	190	4.5	130	159	ND	140	230
HAR-19/42	160	62.5	270	8.0	68.5	83.5	ND	485	485
HAR-20	50	27	100	5.1	140	171	ND	81	190
HAR-22	70	21	57	4.8	180	220	ND	99	68
HAR-24	250	91	440	6.7	210	256	ND	280	1500
HAR-25	43	23	100	6.4	140	171	ND	86	170
HAR-26	150	76	370	8.0	190	232	ND	380	660
HAR-27	77	19	220	4.5	110	134	ND	320	220
HAR-28	31	13	120	3.1	120	146	ND	73	170
HAR-29	51	43	320	5.0	240	293	ND	240	470
HAR-30	11	7.3	270	3.6	230	251	7	180	160
HAR-31	13	7.7	350	ND	230	144	36	220	300
HAR-32	170	59	69	6.8	230	281	ND	300	250

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009--2014--Continued

Site #	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	<b>T. Alk</b> (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
HAR-33/34	4.3	ND	80	ND	86	107	ND	27	32
HAR-35	120	30	380	4.9	110	134	ND	400	470
HAR-36	31	14	120	4.0	120	146	ND	110	110
HAR-37	15	8.2	170	4.2	160	195	ND	110	110
HAR-38	21	3.9	160	2.7	110	134	ND	110	110
HAR-39	88	60	490	5.6	160	195	ND	670	380
HAR-40	12	0.59	180	6.1	120	146	ND	160	82
HAR-41	120	36	270	6.2	50	61	ND	460	330
HAR-43	230	95	280	7.9	43	53	ND	550	700
HAR-44	90	23	240	9.6	110	134	ND	240	380
HAR-45	14	4.7	170	3.0	110	134	ND	130	150
HAR-46	36	2.7	340	4.3	38	46	ND	410	250
HAR-47	32	25	380	4.8	170	207	ND	430	250
HAR-48	63	2.2	630	5.2	24	29	ND	690	540
HAR-49	12	5.4	180	1.4	140	171	ND	130	130
HAR-50	43.11	23	272	4.8	218	266	ND	190	242
HAR-51	28.5	25.2	256	5.27	190	232	ND	181	222
HAR-52	30.2	13.3	177	3.58	279	340	ND	74.3	95.7
HAR-53/54	52.2	19.3	154.5	3.48	296.5	362	ND	94.5	76.1
HAR-55	205	76.9	394	6.05	233	284	ND	203	1120
HAR-57	51.6	16.7	152	2.69	324	395	ND	71.5	104
HAR-58	7.61	ND	116	ND	120	146	ND	58.2	60.9
HAR-59	19.9	6.77	64.6	2.63	232	283	ND	4.7	3.1

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009--2014--Continued

Site #	Nitrate-N (mg/L)	<b>δ</b> <sup>15</sup> N ( <sup>0</sup> / <sub>00</sub> )	Nitrite-N (mg/L)	TKN (mg/L)	Ammonia (mg/L)	<b>T. Phos.</b> (mg/L)	SAR (value)	Irrigation Quality	Alum (mg/L)	Strontium (mg/L)
HAR-1	3.9	-	ND	ND	ND	ND	12.0	C3-S2	ND	0.41
HAR-2	3.8	-	ND	ND	ND	ND	12.4	C3-S2	ND	0.40
HAR-3	24	-	ND	ND	ND	ND	4.1	C3-S1	ND	0.62
HAR-4	32	-	ND	ND	ND	ND	5.5	C3-S1	ND	0.42
HAR-5/6	6.8	-	ND	ND	ND	ND	23.1	C3-S4	ND	ND
HAR-7	2.7	-	ND	ND	ND	ND	4.0	C3-S1	ND	0.45
HAR-8	21	-	ND	ND	ND	ND	12.5	C3-S2	ND	0.95
HAR-9	30	-	ND	ND	ND	ND	8.7	C4-S2	ND	1.7
HAR-10	38	-	ND	ND	ND	ND	7.8	C4-S2	ND	2.7
HAR-11	46	-	ND	ND	ND	ND	9.1	C4-S2	ND	2.5
HAR-12	6.5	-	ND	ND	ND	ND	9.5	C3-S2	ND	0.51
HAR-13	3.5	-	ND	ND	0.059	0.10	5.8	C3-S2	ND	1.3
HAR-14/15	6.85	-	ND	ND	ND	ND	7.4	C3-S2	ND	0.96
HAR-16	3.7	-	ND	ND	ND	ND	15.7	C3-S3	ND	0.45
HAR-17	6.2	-	ND	ND	ND	ND	11.2	C3-S2	ND	0.66
HAR-18	6.4	-	ND	ND	ND	ND	6.8	C3-S2	ND	0.34
HAR-19/42	34	9.8	ND	ND	ND/0.0016	ND/0.00 16	4.4	C4-S2	ND	1.7
HAR-20	4.0	2.9	ND	ND	ND	ND	2.8	C3-S1	ND	1.1
HAR-22	3.2	6.4	ND	ND	ND	ND	1.5	C2-S1	ND	0.82
HAR-24	43	8.5	ND	ND	0.052	ND	6.1	C4-S2	ND	5.2
HAR-25	4.1	8.2	ND	ND	ND	ND	3.1	C3-S1	ND	0.61
HAR-26	79	9.4	ND	ND	ND	ND	6.1	C4-S2	ND	4.0
HAR-27	15	9.2	ND	ND	ND	ND	5.8	C3-S2	ND	0.92
HAR-28	5.3	8.2	ND	ND	ND	ND	4.6	C3-S1	ND	0.23
HAR-29	13	8.8	ND	ND	ND	ND	8.0	C3-S2	ND	2.6
HAR-30	6.0	8.7	ND	ND	ND	ND	15.5	C3-S3	ND	0.38
HAR-31	10	-	ND	ND	ND	ND	19.0	C3-S4	ND	0.27
HAR-32	4.6	6.8	ND	ND	ND	0.21	1.2	C3-S1	ND	1.7

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Nitrate-N (mg/L)	<b>δ</b> <sup>15</sup> N ( <sup>0</sup> / <sub>00</sub> )	Nitrite-N (mg/L)	TKN (mg/L)	Ammonia (mg/L)	<b>T. Phos.</b> (mg/L)	SAR (value)	Irrigation Quality	Alum (mg/L)	Strontium (mg/L)
HAR-33/34	1.3	7.85	ND	ND	ND	ND	9.2	C2-S1	ND	ND
HAR-35	19	9.0	ND	ND	ND	ND	8.0	C4-S2	ND	1.1
HAR-36	3.8	8.6	ND	ND	ND	ND	4.5	C3-S1	ND	0.43
HAR-37	3.7	8.7	ND	ND	ND	ND	8.8	C3-S2	ND	061
HAR-38	4.2	8.2	ND	ND	ND	ND	8.4	C3-S2	ND	0.93
HAR-39	45	8.6	ND	ND	0.073	ND	9.9	C4-S3	ND	2.4
HAR-40	6.4	8.2	ND	ND	ND	0.034	13.7	C3-S3	ND	0.054
HAR-41	28	9.6	ND	ND	ND	ND	5.5	C3-S1	ND	1.1
HAR-43	41	9.8	ND	ND	0.016	0.016	3.9	C4-S2	ND	1.9
HAR-44	17	8.3	ND	ND	ND	0.023	5.8	C3-S2	ND	0.89
HAR-45	4.2	8.1	ND	ND	ND	0.023	10.0	C3-S2	ND	0.14
HAR-46	16	9.1	ND	ND	0.018	0.039	14.7	C3-S3	ND	0.93
HAR-47	7.8	7.5	ND	ND	ND	ND	12.2	C3-S3	ND	1.2
HAR-48	41	12.3	ND	ND	0.019	0.010	21.3	C4-S4	ND	0.57
HAR-49	8.3	6.5	ND	ND	0.020	0.014	10.9	C3-S2	ND	0.046
HAR-50	30.4	9.9	ND	1.6	ND	ND	8.3	C3-S2	ND	1.95
HAR-51	22.4	9.2	ND	ND	ND	ND	8.4	C3-S2	ND	0.504
HAR-52	10.6	9.6	ND	ND	ND	ND	6.8	C3-S2	ND	0.825
HAR-53/54	10.95	9.0	ND	ND/3.3	ND	0.021	4.6	C3-S1	ND	1.15
HAR-55	36.2	7.5	ND	ND	ND	ND	6.0	C4-S1	ND	4.40
HAR-57	3.4	9.5	ND	ND	ND	0.021	4.7	C3-S1	ND	1.10
HAR-58	5.6	5.3	ND	ND	ND	ND	9.3	C2-S2	ND	0.078
HAR-59	3.7	3.6	ND	ND	ND	0.060	3.2	C2-S1	ND	0.0883

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Antimony (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Beryllium (mg/L)	Boron (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Fluoride (mg/L)
HAR-1	ND	0.011	ND	ND	0.47	ND	0.042	ND	3.3
HAR-2	ND	0.0069	ND	ND	0.64	ND	0.026	ND	2.8
HAR-3	ND	0.015	ND	ND	0.32	ND	0.028	ND	2.0
HAR-4	ND	0.017	ND	ND	0.43	ND	0.032	ND	2.5
HAR-5/6	ND	0.0395	0.0015	ND	3.05	ND	0.029	0.00205	0.81
HAR-7	ND	0.0092	0.0063	ND	0.43	ND	0.021	0.029	1.2
HAR-8	ND	0.0076	0.035	ND	0.69	ND	0.047	0.0028	2.4
HAR-9	ND	0.0057	0.039	ND	0.72	ND	0.030	0.0031	1.8
HAR-10	ND	0.0013	0.037	ND	2.3	ND	ND	0.0015	2.9
HAR-11	ND	0.0077	0.058	ND	0.60	ND	0.027	0.0043	2.3
HAR-12	ND	0.0058	0.016	ND	0.51	ND	0.023	0.0093	3.3
HAR-13	ND	0.0070	0.062	ND	0.55	ND	0.010	0.0014	6.0
HAR-14/15	ND	0.00575	0.047	ND	0.525	ND	0.021	0.0024	2.7
HAR-16	ND	0.031	ND	ND	0.63	ND	0.042	0.0035	7.6
HAR-17	ND	0.0096	0.016	ND	1.0	ND	0.056	0.0023	2.4
HAR-18	ND	0.0092	0.012	ND	0.85	ND	0.048	0.0036	2.5
HAR-19/42	ND	0.0115	0.0155	ND	0.58	ND	0.043	0.0071	1.45
HAR-20	ND	0.0036	0.013	ND	0.41	ND	0.047	0.0030	2.1
HAR-22	ND	ND	0.040	ND	ND	ND	0.0011	ND	0.41
HAR-24	ND	0.0051	0.032	ND	2.6	ND	0.021	0.0086	3.1
HAR-25	ND	0.0036	0.0070	ND	0.40	ND	0.042	0.0015	2.3
HAR-26	ND	0.0049	0.077	ND	0.43	ND	0.0080	0.0040	2.3
HAR-27	ND	0.0074	0.022	ND	0.37	ND	0.036	0.0018	2.3
HAR-28	ND	0.0082	0.0043	ND	0.29	ND	0.044	0.0010	1.9
HAR-29	ND	0.0040	0.032	ND	0.67	ND	0.050	0.0031	2.7
HAR-30	ND	0.012	0.0031	ND	0.58	ND	0.057	0.0023	3.9
HAR-31	ND	0.033	0.0053	ND	1.2	ND	0.049	0.0028	7.7
HAR-32	ND	0.0012	0.049	ND	ND	ND	ND	0.014	1.2

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Antimony (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Beryllium (mg/L)	Boron (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Fluoride (mg/L)
HAR-33/34	ND	0.0855	ND	ND	0.41	ND	0.0105	ND	9.9
HAR-35	ND	0.0054	0.016	ND	1.4	ND	0.028	ND	2.4
HAR-36	ND	0.013	0.0053	ND	0.43	ND	0.026	ND	2.0
HAR-37	ND	0.0058	0.0058	ND	0.51	ND	0.0087	ND	3.4
HAR-38	ND	0.011	0.029	0.00020	0.54	ND	0.0079	ND	4.8
HAR-39	ND	0.0012	0.044	ND	0.52	ND	0.018	ND	1.4
HAR-40	ND	0.027	0.0043	ND	0.49	ND	0.028	0.0029	3.1
HAR-41	ND	0.010	0.019	ND	0.41	ND	0.026	0.0035	1.4
HAR-43	ND	0.0089	0.029	ND	0.36	ND	0.037	0.016	1.0
HAR-44	ND	0.017	0.047	ND	0.93	ND	0.044	0.0031	2.1
HAR-45	ND	0.018	0.0061	ND	0.53	ND	0.054	0.0024	2.2
HAR-46	ND	0.031	0.0021	ND	0.56	ND	0.0054	0.0058	3.5
HAR-47	ND	0.0068	0.013	ND	0.55	ND	0.058	0.0075	3.8
HAR-48	ND	0.013	0.0031	ND	0.33	ND	0.044	0.0082	1.6
HAR-49	ND	0.016	0.0020	ND	0.59	ND	0.051	0.0036	2.0
HAR-50	ND	ND	0.102	ND	0.515	ND	0.0253	ND	2.1
HAR-51	ND	0.0043	0.0115	ND	0.413	ND	0.023	ND	2.1
HAR-52	ND	0.0046	0.0519	ND	0.435	ND	0.0144	ND	2.2
HAR-53/54	ND	0.00815	0.0623	ND	0.3245	ND	0.0100	ND	2.45
HAR-55	ND	ND	0.0303	ND	3.23	ND	0.0172	0.0055	2.3
HAR-57	ND	0.0079	0.0562	ND	0.377	ND	0.0095	ND	2.9
HAR-58	ND	0.0064	0.0022	ND	0.259	ND	0.0464	ND	0.53
HAR-59	ND	0.0205	ND	ND	ND	ND	0.0066	ND	0.97

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Iron (mg/L)	Lead (mg/L)	Manganese (mg/L)	Mercury (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Thallium (mg/L)	Zinc (mg/L)
HAR-1	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-2	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-3	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-4	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-5/6	ND	ND	ND	ND	0.0105	0.00295	ND	ND	ND
HAR-7	ND	0.0026	ND	ND	ND	0.0023	ND	ND	ND
HAR-8	ND	ND	ND	ND	ND	0.012	ND	ND	ND
HAR-9	ND	ND	ND	ND	ND	0.017	ND	ND	ND
HAR-10	ND	ND	ND	ND	ND	ND	ND	ND	0.18
HAR-11	ND	ND	ND	ND	ND	0.021	ND	ND	ND
HAR-12	ND	ND	ND	ND	ND	0.0052	ND	ND	ND
HAR-13	ND	ND	ND	ND	ND	0.0031	ND	ND	ND
HAR-14/15	ND	ND	ND	ND	ND	0.0051	ND	ND	ND
HAR-16	ND	ND	ND	ND	ND	0.0043	ND	ND	ND
HAR-17	ND	ND	ND	ND	ND	0.0078	ND	ND	ND
HAR-18	ND	ND	ND	ND	ND	0.0060	ND	ND	ND
HAR-19/42	ND	ND	ND	ND	ND	0.0135	ND	ND	ND/0.012
HAR-20	ND	ND	ND	ND	ND	0.0054	ND	ND	ND
HAR-22	ND	ND	0.012	ND	ND	0.0051	ND	ND	1.4
HAR-24	ND	ND	ND	ND	ND	0.023	ND	ND	ND
HAR-25	ND	ND	ND	ND	ND	0.0030	ND	ND	0.35
HAR-26	ND	ND	ND	ND	ND	0.025	ND	ND	0.21
HAR-27	ND	ND	ND	ND	ND	0.0072	ND	ND	ND
HAR-28	ND	ND	ND	ND	ND	0.0026	ND	ND	ND
HAR-29	ND	ND	ND	ND	ND	0.012	ND	ND	ND
HAR-30	ND	ND	ND	ND	ND	0.0045	ND	ND	ND
HAR-31	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-32	ND	ND	ND	ND	ND	0.0085	ND	ND	1.0

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Iron (mg/L)	Lead (mg/L)	Manganese (mg/L)	Mercury (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Thallium (mg/L)	Zinc (mg/L)
HAR-33/34	0.805	0.0014	ND	ND	ND	ND	ND	ND	0.26
HAR-35	ND	ND	ND	ND	ND	0.012	ND	ND	ND
HAR-36	ND	ND	ND	ND	ND	0.0016	ND	ND	ND
HAR-37	ND	-	ND	ND	ND	0.0025	ND	ND	ND
HAR-38	ND	-	ND	ND	ND	0.0025	ND	ND	ND
HAR-39	ND	-	ND	ND	ND	0.0017	ND	ND	ND
HAR-40	0.072	ND	0.0022	ND	ND	0.0024	ND	ND	0.021
HAR-41	ND	ND	ND	ND	ND	0.0092	ND	ND	0.012
HAR-43	ND	ND	ND	ND	ND	0.012	ND	ND	0.015
HAR-44	ND	ND	ND	ND	ND	0.0062	ND	ND	0.012
HAR-45	ND	0.00069	ND	ND	ND	0.017	ND	ND	0.0093
HAR-46	ND	ND	ND	ND	ND	0.0093	ND	ND	0.016
HAR-47	ND	ND	ND	ND	ND	0.0079	ND	ND	0.0098
HAR-48	ND	ND	ND	ND	ND	0.012	ND	ND	0.010
HAR-49	ND	ND	ND	ND	ND	0.0033	ND	ND	0.045
HAR-50	ND	ND	ND	ND	ND	0.0043	ND	ND	ND
HAR-51	ND	ND	ND	ND	ND	ND	ND	ND	0.107
HAR-52	ND	ND	ND	ND	ND	ND	ND	ND	0.774
HAR-53/54	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-55	ND	ND	ND	ND	ND	0.0153	ND	ND	ND
HAR-57	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-58	ND	ND	ND	ND	ND	ND	ND	ND	ND
HAR-59	ND	ND	ND	ND	ND	ND	ND	ND	0.0764

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

Site #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	<b>Ra-226 + Ra-228</b> (pCi/L)	Uranium (µg/L)	* <sup>18</sup> O ( <sup>0</sup> / <sub>00</sub> )	<b>* D</b> ( <sup>0</sup> / <sub>00</sub> )	Type of Chemistry
HAR-1	-	-	-	-	-	- 9.9	- 73	sodium-mixed
HAR-2	-	-	-	-	-	- 9.7	- 72	sodium-mixed
HAR-3	-	-	-	-	-	- 9.2	- 66	sodium-chloride
HAR-4	-	-	-	-	-	- 9.2	- 68	sodium-mixed
HAR-5/6	668	ND	-	ND	3.2	- 8.1	- 59	sodium-mixed
HAR-7	608	-	-	-	-	- 8.8	- 64	sodium-mixed
HAR-8	658	-	-	-	-	- 9.6	- 72	sodium-mixed
HAR-9	708	-	-	-	-	- 9.5	- 71	sodium-mixed
HAR-10	513	-	-	-	-	- 9.8	- 76	sodium-mixed
HAR-11	707	-	-	-	-	- 9.1	- 68	sodium-chloride
HAR-12	32	3.9	ND	ND	11.2	- 9.0	- 64	sodium-mixed
HAR-13	1,340	-	-	-	-	- 8.2	- 61	sodium-mixed
HAR-14/15	830	-	-	-	-	- 9.5	- 68	sodium-mixed
HAR-16	-	-	-	-	-	- 9.5	- 69	sodium-mixed
HAR-17	366	-	-	-	-	-10.0	- 73	sodium-mixed
HAR-18	840	-	-	-	-	- 9.6	- 70	sodium-mixed
HAR-19/42	615	ND	-	ND	16	- 9.05	- 665	mixed-mixed
HAR-20	658	-	-	-	-	- 9.4	- 67	mixed-mixed
HAR-22		-	-	-	-	- 8.6	- 58	mixed-mixed
HAR-24	-	-	-	-	-	- 8.6	- 65	mixed-sulfate
HAR-25	-	-	-	-	-	- 9.3	- 67	sodium-mixed
HAR-26	-	3.8	-	ND	18	- 8.6	- 64	sodium-mixed
HAR-27	-	-	-	-	-	- 9.1	- 65	sodium-sulfate
HAR-28	-	-	-	-	-	- 8.9	- 61	sodium-mixed
HAR-29	-	-	-	-	-	- 8.8	- 66	sodium-mixed
HAR-30	-	-	-	-	-	- 9.5	- 70	sodium-mixed
HAR-31	-	-	-	-	-	- 9.5	- 70	sodium-mixed
HAR-32	1,242	ND	-	ND	18	- 8.45	- 59	calcium-mixed

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

LLD = Lower Limit of Detection *italics* = constituent exceeded holding time **bold** = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Site #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	<b>Ra-226 + Ra-228</b> (pCi/L)	Uranium (µg/L)	* <sup>18</sup> O ( <sup>0</sup> / <sub>00</sub> )	<b>* D</b> ( <sup>0</sup> / <sub>00</sub> )	Type of Chemistry
HAR-33/34	1728	30.0	-	ND	38.1	- 9.0	- 68	sodium-mixed
HAR-35	897	-	-	-	-	- 8.7	- 65	sodium-mixed
HAR-36	712	-	-	-	-	- 8.8	- 64	sodium-mixed
HAR-37	998	1.5	5.4	ND	5.7	- 8.7	- 65	sodium-mixed
HAR-38	561	-	-	-	-	- 8.4	- 64	sodium-mixed
HAR-39	387	-	-	-	-	- 9.2	- 68	sodium-chloride
HAR-40	531	ND	ND	ND	9.6	- 9.1	- 67	sodium-mixed
HAR-41	-	-	-	-	-	- 9.0	- 66	sodium-chloride
HAR-43	441	-	-	-	-	- 8.9	- 65	mixed-mixed
HAR-44	-	-	-	-	-	- 9.0	- 66	sodium-mixed
HAR-45	473	-	-	-	-	- 9.7	- 69	sodium-mixed
HAR-46	1,861	-	-	-	-	- 8.9	- 67	sodium-chloride
HAR-47	690	-	-	-	-	- 9.8	- 72	sodium-chloride
HAR-48	692	-	-	-	-	- 10.2	- 74	sodium-chloride
HAR-49	100	-	-	-	-	- 9.0	- 70	sodium-mixed
HAR-50	-	-	-	-	-	- 9.2	- 71	sodium-mixed
HAR-51	-	-	-	-	-	- 9.7	- 76	sodium-mixed
HAR-52	-	-	-	-	-	- 9.6	- 69	sodium-bicarbonate
HAR-53/54	78	0.3	-	-	12.3	- 9.7	- 70	sodium-bicarbonate
HAR-55	ND	-	-	-	-	- 8.7	- 66	sodium-sulfate
HAR-57	ND	-	-	-	-	- 9.6	- 68	sodium-bicarbonate
HAR-58	271	1.0	-	-	1.6	- 7.9	- 62	sodium-mixed
HAR-59	-	-	-	-	-	- 7.8	- 56	sodium-bicarbonate

Appendix B. Groundwater Quality Data, Harquahala Basin, 2009-2014--Continued

LLD = Lower Limit of Detection *italics* = constituent exceeded holding time **bold** = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level