# Ambient Groundwater Quality of the Aravaipa Canyon Basin A 2003 Baseline Study

By Douglas C. Towne Maps by Jean Ann Rodine

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### **Arizona Department of Environmental Quality Open File Report 13-01**

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#### Thanks:

Field Assistance:	Elizabeth Boettcher and Angela Lucci. 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:	ADEQ Monitoring Unit and Douglas Towne
Report Cover:	A perennial reach of Araviapa Creek is created by groundwater being brought to the surface by bedrock in Aravaipa Canyon. This segment of Aravaipa Creek was named one of Arizona's Heritage Waters in 2007 based on the stream's cultural, historical, political, scientific and social significance. <sup>6</sup>

# Other Publications of the ADEQ Ambient Groundwater Monitoring Program

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

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: www.azdeq.gov/environ/water/assessment/ambient.html



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# Abbreviations

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
ARA	Aravaipa Canyon Groundwater Basin
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 pesticide
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
uS/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
$\mathrm{SO}_4$	sulfate
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
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

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#### Ambient Groundwater Quality of the Aravaipa Canyon Basin: A 2003 Baseline Study

**Abstract** - In 2003, the Arizona Department of Environmental Quality (ADEQ) conducted a baseline groundwater quality study of the Aravaipa Canyon basin located approximately 120 miles southeast of Phoenix in southeastern Arizona. The basin comprises 517 square miles within Graham and Pinal counties and had an estimated 135 residents in 2000.<sup>5</sup> Low-intensity livestock grazing is the predominant land use although there are some small parcels of irrigated pasture and orchards along Aravaipa Creek. Historic mining has resulted in the creation of the Klondyke Tailings Water Quality Assurance Revolving Fund (WQARF) site in 1998.<sup>2</sup> Land ownership in the basin consists of federal lands (47 percent) managed by the U.S. Forest Service (26 percent) and the Bureau of Land Management (21 percent). The remainder of the basin consists of State Trust lands (38 percent), private land (14 percent), and Indian land (1 percent) owned by the San Carlos Apache Tribe.<sup>4,5</sup>

The basin is drained by Aravaipa Creek, which runs north until turning west to exit into the Lower San Pedro groundwater basin. The creek is intermittent in its upper reach but becomes perennial where groundwater is brought to the surface by bedrock at Aravaipa Spring.<sup>5</sup> Perennial flow usually lasts for about 17 miles until the surface water infiltrates into the streambed alluvium about five miles above the creek's confluence with the San Pedro River.<sup>5</sup> The perennial segment of Aravaipa Creek was named one of Arizona's Heritage Waters in 2007 based on the stream's cultural, historical, political, scientific and social significance.<sup>6</sup>

Groundwater occurs primarily in two aquifers: recent stream alluvium and basin-fill alluvium. Stream alluvium is the main aquifer and yields up to 1,500 gallons per minute.<sup>5</sup> Fine-grained, lake-bed sediments separate the stream alluvium from the basin-fill alluvium, which causes confined conditions in the latter aquifer. Well yields in the basin-fill are variable but tend to be much less than the streambed alluvium.<sup>5</sup> Minor amounts of groundwater are found in the surrounding bedrock, especially along faults, fracture zones, and/or localized perched aquifers. Most groundwater is used for irrigation, only minor amounts are used for stock or domestic purposes.<sup>5</sup>

Fifteen sites (13 wells and 2 springs) were sampled for the study. Inorganic constituents, radon, and isotopes (oxygen and deuterium) were collected from each site. The samples appear to consist of water from the streambed alluvium aquifer or fractured and/or faulted bedrock rather than the confined, basin-fill aquifer. Field data indicated none of the wells were flowing and well log information was not available for most sites.<sup>5</sup>

Health-based, Primary Maximum Contaminant Levels (MCLs) were not exceeded at any site. 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>26</sup> Aesthetics-based, Secondary MCLs were exceeded at 4 of the 15 sites (27 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>26</sup> Constituents exceeding Secondary MCLs include fluoride (3 sites) and manganese (1 site).

Groundwater in the basin is typically *slightly-alkaline*, *fresh*, and *moderately hard* to *hard*, based on pH levels along with TDS and hardness concentrations.<sup>10, 14</sup> Calcium was the dominant cation in half the samples while bicarbonate was the dominant anion composition in most samples. Oxygen and deuterium isotope values at most sites appear to consist of recently recharged winter precipitation. Two sites with more enriched isotope values appear to consist of recently recharged summer precipitation.<sup>11</sup>

Groundwater constituent concentrations were influenced by recharge source and geology.<sup>11, 18</sup> Constituents such as temperature, specific conductivity (SC), TDS, bicarbonate, oxygen-18, and deuterium had significantly greater concentrations in recent summer precipitation than in recent winter precipitation (Kruskal-Wallis test,  $p \le 0.05$ ). Constituents such as SC, TDS, calcium, bicarbonate, chloride, and oxygen-18 had significantly greater concentrations in sites located in consolidated rock than in unconsolidated alluvium (Kruskal-Wallis test,  $p \le 0.05$ ).

Groundwater in the basin is suitable for drinking water use based on the results of this ADEQ study. This conclusion is supported by limited data from prior studies conducted by the U.S. Geological Survey in 1975 and ADEQ's WQARF program in 2001.<sup>2, 12</sup> In the latter study, 15 wells sampled in the vicinity of the Klondyke WQARF site by ADEQ had "very good groundwater quality" although the report noted that mine tailings may be impacting surface water in Aravaipa Creek.<sup>2</sup>

#### INTRODUCTION

#### **Purpose and Scope**

The Araviapa Canyon basin (ARA) comprises approximately 517 square miles within Graham and Pinal counties in southeastern Arizona (Map 1).<sup>5</sup> The remote basin, located roughly 120 miles southeast of Phoenix, had an estimated population of 135 in 2000 with many living in the community of Klondyke.<sup>5</sup> The basin is drained by Aravaipa Creek, which runs to the north until turning west and eventually exiting into the Lower San Pedro River basin. Groundwater is used for all domestic use within the basin and most irrigation, and stock water supply. The vast majority of water pumped in the basin is used for irrigation.<sup>5</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>3</sup>

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

- A characterization of regional groundwater quality conditions in the Araviapa Canyon basin identifying water quality variations between groundwater from different sources.
- A process for evaluating potential groundwater quality impacts arising from mineralization, mining, 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 Araviapa Canyon basin is a northwest-trending alluvial valley surrounded by block-faulted mountains within the Basin and Range physiographic province. Vegetation is primarily semidesert grassland with small areas of chaparral and woodland. Riparian vegetation includes cottonwood, willow, mesquite and mixed broadleaf trees.<sup>5</sup> Most of the land is used for low-intensity livestock grazing although there are small parcels of irrigated fields along Araviapa Creek. Retirees and commuters are increasingly relocating to the basin, attracted by its scenic qualities.

The basin is bounded on the north by the Turnbull Mountains, on the northeast by the Santa Theresa and Pinaleno Mountains, and the Galiuro Mountains on the southwest. To the southeast, a subtle ridge forms the boundary between the Aravaipa Canyon and Willcox groundwater basins. Elevations in the basin range from a high of 7,540 feet above mean sea level (amsl) at Kennedy Peak in the Galiuro Mountains to a low of approximately 2,400 feet where Aravaipa Creek exits the basin into the Lower San Pedro groundwater basin.

The Araviapa Canyon basin consists of federal land (47 percent) managed by the U.S. Forest Service (USFS) (26 percent) Bureau of Land Management (BLM) (21 percent). The remainder of the basin is composed of State Trust land (38 percent), private land (14 percent), and Indian land (1 percent) owned by the San Carlos Apache Tribe.<sup>4,5</sup> Generally, tribal land is at the northernmost basin fringes, BLM lands are in the northwest portion, USFS lands are along the eastern and western portions, and State Trust and private land is interspersed throughout especially along Aravaipa Creek (Map 1).

**Climate** – The Araviapa Canyon has an arid climate characterized by hot, dry summers and mild winters. Precipitation, which ranges annually from 14 inches in Araviapa Canyon to 28 inches in the Galiuro Mountains, occurs predominantly as rain in either late summer, localized monsoon thunderstorms or, less often, as widespread, low intensity winter rain that occasionally includes snow at higher elevations.<sup>5</sup>

#### **Surface Water Characteristics**

The basin is drained by Aravaipa Creek, a tributary to the San Pedro River which flows from the southeast to the northwest. The creek is intermittent in its upper reach but has perennial flow where groundwater is brought to the surface by bedrock at Araviapa Spring.

Perennial flow lasts for approximately 17 miles until the surface water completely infiltrates into the streambed alluvium about five miles above its confluence with the San Pedro River. The creek has a mean annual flow of over 26,000 acre-feet. Surface water diversions for agriculture average 97 acre-feet per year (af/yr).<sup>5</sup>



# Map 1 - Aravaipa Canyon Basin

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The perennial segment of Aravaipa Creek was named an Arizona's Heritage Water based on the cultural, historical, political, scientific, and social significance.<sup>6</sup> The segment is located within the 19,700-acre Aravaipa Canyon Wilderness Area, designated in 1984 and administered by the BLM. The 9,000-acre Aravaipa Canyon Preserve managed by the Nature Conservancy also helps maintain stream flows. The Nature Conservancy and the BLM have instream-flow rights that are used to maintain base flows for conservation purposes.<sup>5</sup> Portions of three tributaries also have perennial flows: Parsons Creek, Turkey Creek and Virgus Canyon.<sup>5</sup>

#### **Groundwater Characteristics**

Groundwater occurs primarily in two aquifers: recent stream alluvium and basin-fill alluvium under confined conditions. Limited groundwater may also be found in the surrounding bedrock. Total estimated recoverable groundwater in storage in the basin-fill sediments to a depth of 1,200 feet below land surface (bls) is estimated at 5.0 million acre-feet (af).<sup>5</sup>

**Streambed Alluvium Aquifer** - The main aquifer is the streambed alluvium which varies in width from 0.5 to 1 mile, ranges in thickness from 25 to 300 feet deep, and is very permeable yielding up to 1,500 gallons per minute (gpm) in irrigation wells. Depth to water varies between less than 10 feet to 100 feet bls. <sup>5</sup>

**Basin-fill Aquifer** - The lower, basin-fill aquifer is confined by fine-grained, lake-bed sediments that are continuous across the entire valley. There are additional deeper confining layers that are only continuous along the eastern and northern parts of the valley, yet some upward leakage into the streambed aquifer has been reported. Well yields from the basin-fill aquifer are dependable but tend to be small. Depth to water ranges from 25 to 500 feet bls.<sup>5</sup>

**Bedrock Complex** – Only minor amounts of groundwater are found in the surrounding bedrock and the Hell Hole Conglomerate. Most water produced from the complex consists of springs located along faults that drain fracture zones of consolidated rocks or localized perched water tables. <sup>5</sup> The U.S. Geological Survey (USGS) has identified 87 springs in the basin, 7 of which have a discharge rate of greater than 10 gpm.<sup>5</sup> Springs support perennial flow in Aravaipa Creek and several streams tributary to it. A few low-yield stock wells have been drilled in the bedrock complex, tapping localized alluvial deposits or fractured consolidated rocks. <sup>5</sup>

**Groundwater Movement** – Groundwater flow direction is generally from the surrounding mountains to the valley floor and then northwest towards Aravaipa Canyon. There, the valley narrows and bedrock brings groundwater to the surface at Aravaipa Spring. Through the gorge, Aravaipa Creek is perennial before becoming ephemeral upon exiting the canyon. <sup>5</sup>

**Groundwater Recharge** – Total recharge in the basin is estimated to range from 7,000 to 16,700 af/yr.<sup>5</sup> This occurs through two major components: streambed infiltration of runoff which is the primary source of recharge for the streambed aquifer and mountain-front recharge which chiefly replenishes the basin-fill aquifer. Direct infiltration of rainfall is considered an insignificant contributor to recharge in the basin.<sup>5</sup>

**Groundwater Development** – Groundwater discharge from the basin is estimated to be 16,700 af/yr. Base flow exiting the basin via Aravaipa Creek is estimated to be 11,000 af/yr. Groundwater pumping averages 3,100 af/yr; 2,400 af/yr from the streambed alluvium aquifer and 700 af/yr from the basin-fill aquifer. Most groundwater use is for irrigating small fields located along Aravaipa Creek. Only minor amounts are used for stock watering (45 af/yr) and domestic use (15 af/yr). <sup>5</sup> As of 2005, there has been modest groundwater development in the basin with 192 wells registered with a pumping capacity of less than 35 gpm and 50 wells with a pumping capacity greater than 35 gpm. <sup>5</sup>

Historic mining in the basin has resulted in the creation of the Klondyke Tailings Water Quality Assurance Revolving Fund (WQARF) site in 1998. Fifteen wells sampled by ADEQ WQARF program in the vicinity of the Klondyke site had "very good groundwater quality" although the report noted that mine tailings may be impacting surface water in Aravaipa Creek.<sup>2</sup>

#### **INVESTIGATION METHODS**

ADEQ collected samples from 15 sites to characterize regional groundwater quality in the Aravaipa Canyon basin (Map 2). Specifically, the following types of samples were collected:

- oxygen and deuterium isotopes at 15 sites
- inorganic suites at 15 sites
- radon at 15 sites

In addition, one isotope sample was collected from Aravaipa Creek. 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>13</sup>

Map 2 - Sample Sites







**Figure 1** – The Aravaipa Canyon groundwater basin is shown above Araviapa Canyon from Klondyke Road. In this portion of the basin, Aravaipa Creek is an intermittent stream. Generally private land is found along the floodplain, State Trust lands are found higher up the slopes, and U.S. Forest Service manages lands at the highest elevations. The Galiuro Mountains, with snow remnants, are across the valley.



**Figure 2** – Above Aravaipa Canyon, groundwater is used to irrigate small fields along the floodplain to raise crops mainly for livestock feed. Groundwater pumping averages 3,100 acre-feet per year with the majority of water used for irrigation. <sup>5</sup>



**Figure 3** – Above Araviapa Canyon, a well formerly powered by a windmill now produces water via a submersible pump. The well is located in the floodplain of Aravaipa Creek.



**Figure 4** – ADEQ's Elizabeth Boettcher stands alongside the perennial flow of Aravaipa Creek as it exits Aravaipa Canyon.



**Figure 5** – ADEQ's Elizabeth Boettcher examines a domestic well drilled in the floodplain just outside the Araviapa Canyon Wilderness Area.



**Figure 6** – A domestic well completed in the floodplain of Aravaipa Creek has its casing extended almost four feet above surface to lessen the threat of contamination from flood flows.



**Figure 7** – Access to the groundwater basin below Aravaipa Canyon is via the Aravaipa Road turnoff from Arizona Highway 77 which parallels the Lower San Pedro River.



**Figure 8** – Small orchards are found along in the lower reaches of Aravaipa Creek before it exits the basin to enter the Lower San Pedro groundwater basin. The lower elevations allow fruit trees such as apricots and citrus to grow in this part of the Aravaipa Canyon groundwater basin.



**Figure 9** – A domestic well located just upgradient of the floodplain in the lower reaches of the basin is used to supply water to a horse property.



**Figure 10** – Aravaipa Creek is photographed from a bridge where the channel makes a hard bend near Brandenburg Mountain downstream of Aravaipa Canyon.



**Figure 11** – A kiosk at the west entrance to the Aravaipa Canyon Wilderness explains the ecologic importance of the perennial flow of Aravaipa Creek. A permit system limits visitation to the wilderness area to 50 people per day.



**Figure 12** – Perennial flow in Aravaipa Creek continues for approximately 17 miles until the surface water completely infiltrates into the streambed alluvium about five miles above its confluence with the San Pedro River. The creek has a mean annual flow of over 26,000 acre-feet.<sup>5</sup>

Wells pumping groundwater for domestic, stock, and irrigation 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>1,7</sup>

For this study, ADEQ personnel sampled 13 wells all served by submersible pumps except for one windmill. Of the 13 wells sampled, their primary purposes were domestic (6 wells), stock (5 wells), irrigation (1 well), and wildlife (1 well). Two springs were also sampled for the study, one primarily used for domestic purposes and the other used for stock watering.

Additional information on groundwater sample sites is compiled from the Arizona Department of Water Resources (ADWR) well registry in Appendix A.<sup>5</sup>

#### Sample Collection

The sample collection methods for this study conformed to the *Quality Assurance Project Plan* (QAPP)<sup>1</sup> and the *Field Manual for Water Quality Sampling*.<sup>7</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 onsite information. Physical parameters—temperature, pH, and specific conductivity—were monitored at least every five minutes using either a Hach or 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 filled in the following order:

3. Isotopes

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 subsequently sealed so that no headspace remained.<sup>7,</sup> <sup>21</sup>

The inorganic constituents were collected in three, one-liter polyethylene bottles: samples to be analyzed for dissolved metals were delivered to the laboratory unfiltered and unpreserved where they were subsequently 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 parameters were unpreserved.<sup>7, 19, 21</sup>

Oxygen and hydrogen isotope samples were collected in a 250 ml polyethylene bottle with no preservative.<sup>7, 25</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>7,19,23</sup> Chain of custody procedures were followed in sample handling. Samples for this study were collected during three field trips conducted during 2003.

#### Laboratory Methods

The inorganic analyses for all inorganic samples, except three split samples, were conducted by the Arizona Department of Health Services (ADHS) Laboratory in Phoenix, Arizona.

The inorganic analyses for the three split samples (ARA-7, ARA-11S, and ARA-16S) were conducted by Test America Laboratory in Phoenix, Arizona. A complete listing of inorganic parameters, including laboratory method, and Minimum Reporting Level (MRL) for each laboratory is provided in Table 1.

Radon samples were submitted to Test America Laboratory and analyzed by Radiation Safety Engineering, Inc. Laboratory in Chandler, Arizona.

All isotope samples were analyzed by the Department of Geosciences, Laboratory of Isotope Geochemistry located at the University of Arizona in Tucson, Arizona.

<sup>1.</sup> Radon

<sup>2.</sup> Inorganics

Constituent	ituent Instrumentation ADHS / Test Water Me		ADHS / Test America Minimum Reporting Level				
Physical Parameters and General Mineral Characteristics							
Alkalinity	Electrometric Titration	SM 2320B / M 2320 B	2/6				
SC (µS/cm)	Electrometric	EPA 120.1/ M 2510 B	/ 2				
Hardness	Titrimetric, EDTA	SM 2340 C / SM 2340B	10 / 1				
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	0.01 / 0.2				
		Major Ions					
Calcium	ICP-AES	EPA 200.7	1/2				
Magnesium	ICP-AES	EPA 200.7	1/0.25				
Sodium	ICP-AES EPA 200.7		1/2				
Potassium	Flame AA	EPA 200.7	0.5 / 2				
Bicarbonate	Calculation	Calculation / M 2320 B	2				
Carbonate	Calculation	Calculation / M 2320 B	2				
Chloride	Potentiometric Titration	SM 4500 CL D / E 300	5/2				
Sulfate	Colorimetric	EPA 375.4 / E 300	1/2				
		Nutrients					
Nitrate as N	Colorimetric	EPA 353.2	0.02 / 0.1				
Nitrite as N	Colorimetric	EPA 353.2	0.02 / 0.1				
Ammonia	Colorimetric	EPA 350.1/ EPA 350.3	0.02 / 0.5				
TKN	Colorimetric	EPA 351.2 / M 4500- NH3	0.05 / 1.3				
Total Phosphorus	Colorimetric	EPA 365.4 / M 4500-PB	0.02 / 0.1				

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

All units are mg/L except as noted Source <sup>19, 21</sup>

Constituent	Instrumentation ADHS / Test America Water Method		ADHS / Test America Minimum Reporting Level				
Trace Elements							
Aluminum	ICP-AES	EPA 200.7	0.5 / 0.2				
Antimony	Graphite Furnace AA	EPA 200.8	0.005 / 0.003				
Arsenic	Graphite Furnace AA	EPA 200.9 / EPA 200.8	0.005 / 0.001				
Barium	ICP-AES	EPA 200.8 / EPA 200.7	0.005 to 0.1 / 0.01				
Beryllium	Graphite Furnace AA	EPA 200.9 / EPA 200.8	0.0005 / 0.001				
Boron	ICP-AES	EPA 200.7	0.1 / 0.2				
Cadmium	Graphite Furnace AA	EPA 200.8	0.0005 / 0.001				
Chromium	Graphite Furnace AA	EPA 200.8 / EPA 200.7	0.01 / 0.01				
Copper	Graphite Furnace AA	EPA 200.8 / EPA 200.7	0.01 / 0.01				
Fluoride	Ion Selective Electrode	SM 4500 F-C	0.1 / 0.4				
Iron	ICP-AES	EPA 200.7	0.1 / 0.05				
Lead	Graphite Furnace AA	EPA 200.8	0.005 / 0.001				
Manganese	ICP-AES	EPA 200.7	0.05 / 0.01				
Mercury	Cold Vapor AA	SM 3112 B / EPA 245.1	0.0002				
Nickel	ICP-AES	EPA 200.7	0.1 / 0.01				
Selenium	Graphite Furnace AA	EPA 200.9 / EPA 200.8	0.005 / 0.002				
Silver	Graphite Furnace AA	EPA 200.9 / EPA 200.7	0.001 / 0.01				
Strontium	ICP-AES	EPA 200.7	0.1 / 0.1				
Thallium	Graphite Furnace AA	EPA 200.9 / EPA 200.8	0.002 / 0.001				
Zinc	ICP-AES	EPA 200.7	0.05				
		Radionuclides					
Radon	Liquid scintillation counter	EPA 913.1	varies				

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

All units are mg/L Source <sup>19, 21</sup>

#### 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 Aravaipa Canyon 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>1,7</sup> Types and numbers of QC samples collected for this study are as follows:

- Inorganic: (3 duplicates, 3 splits, and 2 equipment blanks).
- Radon: (none)
- Isotopes: (none)

Based on the QA/QC results, sampling procedures and laboratory equipment did not significantly affect the groundwater quality samples.

**Blanks** – Two equipment blanks for inorganic analyses were collected and delivered to the ADHS laboratory 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>7</sup> Equipment blank samples for major ion and nutrient analyses were collected by filling unpreserved and sulfuric acid preserved bottles with de-ionized water. Equipment blank samples for trace element analyses were collected with de-ionized water that had been filtered into nitric acid preserved bottles.

Systematic contamination was judged to occur if more than 50 percent of the equipment blank samples contained measurable quantities of a particular groundwater quality constituent. The equipment blanks contained specific conductivity (SC)-lab contamination at levels expected due to impurities in the source water used for the samples. Turbidity and nitrate were also each detected in one sample.

For SC, the two equipment blanks had a mean value (3.7 uS/cm) which was less than 1 percent of the SC mean concentration for the study and was not considered to be significantly affecting the sample results. The SC detections may be explained in two ways: water passed through a de-ionizing exchange unit will normally have an SC value of at least 1 uS/cm, and carbon dioxide from the air can dissolve in de-ionized water with the resulting bicarbonate and hydrogen ions imparting the observed conductivity.<sup>19</sup>

For turbidity, one blank had a level of 0.02 nephelometric turbidity units (ntu) less than 1 percent of the turbidity mean level for the study. Testing indicates turbidity is present at 0.01 ntu in the deionized water supplied by the ADHS laboratory, and levels increase with time due to storage in ADEQ carboys.<sup>19</sup>

For nitrate, one blank had a concentration of 0.10 mg/L that is less than 1 percent of the nitrate mean level for the study.

**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>7</sup> Duplicate samples were collected from sampling sites that were believed to have elevated or unique constituent concentrations as judged by SC-field and pH-field values.

Two duplicate samples were collected and submitted to the ADHS laboratory for this study. Analytical results indicate that of the 40 constituents examined, 20 had concentrations above the MRL. The duplicate samples had an excellent correlation as the maximum variation between constituents was less than 4 percent except for turbidity (15 percent) and TDS (7 percent) (Table 2).

**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>7</sup> Three inorganic split samples were collected and distributed between the ADHS and Test America labs. However, only one of the split sample results was available; the other two split sample results were missing and had not been entered into the ADEQ groundwater quality database. Partial split results entered into a spreadsheet accompanying the laboratory 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 36 constituents examined, 16 had concentrations above MRLs for both ADHS and Test America laboratories (Table 3). The maximum variation between constituents was 12 percent; over half of the constituents had maximum variations below 5 percent. Split samples were also evaluated using the non-parametric Sign test to

	Number	Difference in Percent			Difference in Concentrations				
Parameter	of Dup. Sites	Minimum	Maximum	Median	Minimum	Maximum	Median		
Physical Parameters and General Mineral Characteristics									
Alk., Total	2	0 %	2 %	-	0	1	-		
SC (µS/cm)	2	1 %	4 %	-	10	10	-		
Hardness	2	0 %	3 %	-	0	2	-		
pH (su)	2	1 %	1 %	-	0.1	0.1	-		
TDS	2	0 %	7 %	-	0	11	-		
Turb. (ntu)	2	8 %	15 %	-	0.04	0.4	-		
			Major	Ions					
Calcium	2	0 %	3 %	-	0	3	-		
Magnesium	2	0 %	3 %	-	0	1	-		
Sodium	2	0 %	0 %	-	0	0	-		
Potassium	2	2 %	3 %	-	0.02	0.1	-		
Bicarbonate	2	0 %	4 %	-	0	2	-		
Chloride	2	0 %	1 %	-	0	0.1	-		
Sulfate	2	0 %	0 %	-	0	0	-		
			Nutri	ients					
Nitrate (as N)	2	1 %	2 %	-	0.1	0.01	-		
Phosphorus, T.	1	0 %	0 %	-	0	0	-		
TKN *	1	-	-	3 %	-	-	0.1		
	Trace Elements								
Barium	1	-	-	0 %	-	-	0		
Copper	1	-	-	14 %	-	-	0.004		
Fluoride	2	0 %	2 %	-	0	0.1	-		
Zinc	1	-	-	13 %	-	-	0.17		

### Table 2. Summary Results of Duplicate Samples from ADHS Laboratory

All concentration units are mg/L except as noted with certain physical parameters. \* = TKN was detected in one sample (ARA-11D) at a concentration of 0.078 mg/L and not detected in the duplicate (ARA-11)

a	Number of	Difference in Percent		Difference in Levels		<i>a</i> t 1 <b>0</b>			
Constituents	Split Sites	Minimum	Maximum	Minimum	Maximum	Significance			
	Physical Parameters and General Mineral Characteristics								
Alkalinity, total	3	0 %	2 %	0	10	ns			
SC (µS/cm)	3	0 %	2 %	0	10	ns			
Hardness	3	4 %	9 %	20	30	ns			
pH (su)	3	1 %	2 %	0.1	0.31	ns			
TDS	3	1 %	9 %	10	30	ns			
Turbidity (ntu)	1	9 %	9 %	1.1	1.1	ns			
			Major Ions						
Calcium	3	0 %	5 %	2	9	ns			
Magnesium	3	2 %	7 %	1	1.4	ns			
Sodium	3	1 %	5 %	0	1	ns			
Potassium	3	4 %	12 %	0.2	0.9	ns			
Chloride	3	1 %	10 %	0.1	2.1	ns			
Sulfate	3	0 %	3 %	0	1	ns			
			Nutrients						
Nitrate as N	1	1 %	1 %	0.58	0.58	ns			
Phosphorus, T.	1	8 %	8 %	0.12	0.12	ns			
Trace Elements									
Fluoride	3	0 %	2 %	0	0.01	ns			
Zinc	1	4 %	4 %	0.01	0.01	ns			

### Table 3. Summary Results of Split Samples between ADHS / Test America Labs

ns = No significant (p  $\Box \le 0.05$ ) difference All units are mg/L except as noted

determine if there were any significant differences between ADHS laboratory and Test America laboratory analytical results.<sup>15</sup> There were no significant differences in constituent concentrations between the labs (Sign test,  $p \le 0.05$ ).

Based on the results of blanks, duplicate, and split 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>16</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>16</sup>

Overall, cation/anion meq/L balances of Aravaipa Canyon basin samples were significantly correlated (regression analysis,  $p \le 0.01$ ). Of the 15 samples, all were within +/-2 percent except for one sample with a 23 percent variation. Five samples had low cation/high anion sums; 10 samples had high cation/low anion sums.

SC/TDS - The SC and TDS concentrations measured by contract laboratories were significantly correlated as were SC-field and TDS concentrations (regression analysis, r = 0.99, p  $\leq$  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. $^{16}$ 

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>16</sup>

**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 = 0.94,  $p \le 0.01$ ).

**pH** - The pH value is closely related to the environment of the water and is likely to be altered

by sampling and storage.<sup>16</sup> The pH values measured in the field using a YSI meter at the time of sampling were not significantly correlated with laboratory pH values (regression analysis, r = 0.41,  $p \ge 0.05$ ).

#### **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>28</sup>

**Data Normality:** Data associated with 23 constituents were tested for non-transformed normality using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.<sup>8</sup> Results of this test revealed that 17 of the 23 constituents (temperature, pH-field, SC-field, SC-lab, TDS, hardness, hardness-calculated, calcium, magnesium, sodium, potassium, total alkalinity, bicarbonate, chloride, sulfate, nitrate, and radon) examined were normally distributed.

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>28</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. The Kruskal-Wallis test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.<sup>15</sup>

**Correlation Between Constituents:** In order to assess the strength of association between constituents, their concentrations were compared to each other using the Pearson Correlation Coefficient test. The Pearson 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 Pearson Correlation Coefficient test were then subjected to a probability test to determine which of the individual pair wise correlations were significant.<sup>28</sup> The Pearson test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.<sup>15</sup>

#### **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 Safe Drinking Water (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>26</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>3</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>26</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 not acute standards.<sup>26</sup> Exceedances of specific constituents for each groundwater site is found in Appendix B.

**Inorganic Constituent Results** - Health-based Primary MCL water quality standards and State aquifer water quality standards were not exceeded at any of the 15 sites. Aesthetics-based Secondary MCL water quality guidelines were exceeded at 4 of 15 sites (27 percent; Map 3; Table 4). Constituents above Secondary MCLs include fluoride (3 sites), and manganese (1 site). Potential impacts of these Secondary MCL exceedances are given in Table 4.

**Radon Results** - Of the 15 sites sampled for radon none exceeded the proposed 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. Seven (7) sites exceeded the proposed 300 pCi/L standard (Map 4) that would apply if Arizona doesn't develop a multimedia program.<sup>26</sup>

#### **Suitability for Irrigation**

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>27</sup>

Groundwater sites in the Aravaipa Canyon basin display a narrow range of irrigation water classifications. Samples from all 15 sites were within the "low" to "medium" for both alkalinity and salinity hazard categories (Table 5).

#### **Analytical Results**

Analytical inorganic and radiochemistry results of the Aravaipa Canyon basin sample sites are summarized (Table 6) 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>28</sup> Specific constituent information for each sampled groundwater site is in Appendix B.



Map 4 - Radon





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	0	-	-					
		General Mineral C	Characteristics						
TDS	500	0	2,100	hardness; deposits; colored water; staining; salty taste					
Major Ions									
Chloride (Cl)	250	0	800	salty taste					
Sulfate (SO <sub>4</sub> )	250	0	670	salty taste					
		Trace Ele	ments						
Fluoride (F)	2.0	3	5.0	tooth discoloration					
Iron (Fe)	0.3	0	-	-					
Manganese (Mn)	0.05	1	0.10	black staining; bitter metallic taste					
Silver (Ag)	0.1	0	-	-					
Zinc (Zn)	5.0	0	-	-					

Table 4. Sampled Sites Exceeding Aesthetics-Based (Secondary MCL) Water Quality Standards

All units mg/L except pH is in standard units (su). Source:  $^{26}$ 

### Table 5. Alkalinity and Salinity Hazards for Sampled Sites

Hazard	<b>Total Sites</b>	Low	Medium	High	Very High					
Alkalinity Hazard										
Sodium Adsorption Ratio (SAR)		0 - 10	10- 18	18 - 26	> 26					
Sample Sites	15	15	0	0	0					
		Salinity	/ Hazard							
Specific Conductivity (µS/cm)		100–250	250 - 750	750-2250	>2250					
Sample Sites	15	2	13	0	0					

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	15 / 15	21.2	19.6	21.8	24.1
pH-field (su)	0.01	15 / 15	7.65	7.48	7.66	7.83
pH-lab (su)	0.01	15 / 15	7.65	7.45	7.64	7.84
Turbidity (ntu)	0.01 / 0.20	15 / 15	0.29	0.11	1.06	2.01
		General N	Mineral Charac	teristics		
T. Alkalinity	2.0 / 6.0	15 / 15	190	148	186	224
Phenol. Alk.	2.0 / 6.0	15/0		> 50% of	data below MRL	
SC-field (µS/cm)	N/A	15 / 15	455	348	432	515
SC-lab (µS/cm)	N/A / 2.0	15 / 15	410	348	434	520
Hardness-lab	10/6	15 / 15	180	121	159	197
TDS	10/20	15 / 15	260	216	264	312
			Major Ions			
Calcium	5/2	15 / 15	53	35	48	60
Magnesium	1.0 / 0.25	15 / 15	11.0	8.3	11.3	14.3
Sodium	5/2	15 / 15	28	22	30	39
Potassium	0.5 / 2.0	15 / 15	2.1	1.7	2.4	3.0
Bicarbonate	2.0 / 6.0	15 / 15	230	177	221	265
Carbonate	2.0 / 6.0	15/0		> 50% of	data below MRL	
Chloride	1 / 20	15 / 15	6.8	5.2	8.4	11.7
Sulfate	10/20	15 / 15	20	15	25	36
			Nutrients			
Nitrate (as N)	0.02 / 0.20	15 / 14	0.6	0.3	0.6	0.9
Nitrite (as N)	0.02 / 0.20	15/0		> 50% of	data below MRL	
TKN	0.05 / 1.0	15/6		> 50% of	data below MRL	
Ammonia	0.02 / 0.05	15 / 1		> 50% of	data below MRL	
T. Phosphorus	0.02 / 0.10	15/7		> 50% of	data below MRL	

# Table 6. 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					
Aluminum	0.5 / 0.2	15/0		> 50% of dat	a below MRL			
Antimony	0.005 / 0.003	15/0		> 50% of dat	a below MRL			
Arsenic	0.01 / 0.001	15/0		a below MRL				
Barium	0.1 / 0.001	15/2		a below MRL				
Beryllium	0.0005 / 0.001	15 / 1		> 50% of dat	a below MRL			
Boron	0.1 / 0.2	15 / 1		> 50% of dat	a below MRL			
Cadmium	0.001	15/0		> 50% of dat	a below MRL			
Chromium	0.01 / 0.001	15/0		> 50% of dat	a below MRL			
Copper	0.01 / 0.001	15/2		> 50% of dat	a below MRL			
Fluoride	0.2 / 0.4	15/15	0.5	0.4	1.0	1.6		
Iron	0.1 / 0.05	15 / 1		> 50% of dat	a below MRL			
Lead	0.005 / 0.001	15/0		> 50% of dat	a below MRL			
Manganese	0.05 / 0.01	15 / 1		> 50% of dat	ata below MRL			
Mercury	0.0005 / 0.0002	15/0		> 50% of dat	a below MRL			
Nickel	0.1 / 0.01	15/0		> 50% of dat	a below MRL			
Selenium	0.005 / 0.002	15/0		>50% of data	a below MRL			
Silver	0.001	15/0		> 50% of dat	a below MRL			
Thallium	0.002 / 0.001	15/0		> 50% of dat	a below MRL			
Zinc	0.05	15/5		> 50% of dat	a below MRL			
			Radiochemical					
Radon (pCi/L)	Varies	15/15	264	184	307	430		
			Isotopes					
Oxygen-18 **	Varies	15/15	- 9.2	- 9.4	- 8.9	- 8.5		
Deuterium **	Varies	15 / 15	- 65.0	- 66.7	- 64.7	- 62.6		

### Table 6. Summary Statistics for Groundwater Quality Data—Continued

\* = ADHS MRL / Test America MRL

All units mg/L except where noted or \*\* = 0/00

#### **GROUNDWATER COMPOSITION**

#### **General Summary**

The water chemistry at the 15 sample sites in the Aravaipa Canyon basin (in decreasing frequency) include calcium-bicarbonate (8 sites), mixed-bicarbonate (4 sites), sodium-bicarbonate (2 sites), and mixed-mixed (1 site) (Diagram 1 – middle diagram) (Map 5).

Of the 15 sample sites in the Aravaipa Canyon basin, the dominant cation was calcium at 8 sites and sodium at 2 sites; at 5 sites, the composition was mixed as there was no dominant cation (Diagram 1 -left diagram).

The dominant anion was bicarbonate at 14 sites; at 1 site the composition was mixed as there was no dominant anion (Diagram 1 -right diagram).



**Diagram 1 –** Groundwater in the Aravaipa Canyon basin is predominantly a calcium-bicarbonate chemistry which is reflective of recent local recharge occurring from both winter and summer precipitation.

# Map 5 - Water Chemistry





At all 15 sites, levels of pH-field were all *slightly alkaline* (above 7 su) and 3 sites were above 8 su.<sup>14</sup>

TDS concentrations were considered *fresh* (below 999 mg/L) at all 15 sites (Map 6).<sup>14</sup>

Hardness concentrations were *soft* (below 75 mg/L) at 1 site, *moderately hard* (75 – 150 mg/L) at 6 sites, *hard* (150 – 300 mg/L) at 8 sites, *very hard* (300 - 600 mg/L) at 0 sites (Diagram 2 and Map 7).<sup>10</sup>

Nitrate (as nitrogen) concentrations at most sites may have been influenced by human activities according to one source often cited. Nitrate concentrations were divided into natural background (3 sites at < 0.2 mg/L), may or may not indicate human influence (12 sites at 0.2 - 3.0 mg/L), may result from human activities (0 sites at 3.0 - 10 mg/L), and probably result from human activities (0 sites > 10 mg/L).<sup>17</sup>

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



**Diagram 2 –** In the Aravaipa Canyon basin hardness concentrations vary from 35 to 270 mg/L. The highest hardness concentrations tend to occur in samples collected from sites in consolidated bedrock and in downgraident areas along Aravaipa Creek.



### Map 6 - Total Dissolved Solids (TDS)

Map 7 - Hardness





#### **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 negative correlation indicates inverse an relationship.28

Several significant correlations occurred among the 15 sample sites (Table 7, Pearson Correlation Coefficient test,  $p \le 0.05$ ). Four groups of correlations were identified:

- Fluoride was positively correlated with sodium; pH-field was negatively correlated with calcium (Diagram 3).
- TDS was positively correlated with calcium, magnesium, sodium, bicarbonate, chloride, and sulfate.
- Sodium was positively correlated with bicarbonate and chloride.

TDS concentrations are best predicted among major ions by bicarbonate concentrations (standard coefficient = 0.84), among cations by calcium concentrations (standard coefficient = 0.65) and among anions, by bicarbonate concentrations (standard coefficient = 0.86) (multiple regression analysis,  $p \le 0.01$ ).



**Diagram 3** – The graph illustrates a negative correlation between two constituents; as pH-field values increase, calcium concentrations decrease. This relationship is described by the regression equation: y = -37x + 337 (r = 0.53). The pH-calcium relationship has been found in other Arizona groundwater basins and is likely related to precipitation of calcite in response to increases in pH.<sup>20</sup>

Constituent	Temp	pH-f	pH- lab	SC-f	TDS	Hard	Ca	Mg	Na	K	Bic	Cl	SO <sub>4</sub>	NO <sub>3</sub>	F	Radon	0	D
							DI	· 1D										
Physical Parameters																		
Temperature												*					**	*
pH-field							+											+
pH-lab					*			*	*		**							
SC-field					**	**	**	**	*		**	**	**			*		
	General Mineral Characteristics																	
TDS						**	**	**	*		**	**	**				*	
Hardness							**	**			**	*	*			*		
Major Ions																		
Calcium								*			**	*	**					
Magnesium											**					**		
Sodium											*	**			*			
Potassium																		
Bicarbonate												*				+		
Chloride													**	+			*	
Sulfate														+	*			
								Nutrie	ents									
Nitrate																		
							Т	race El	ements									
Fluoride																		
								Radioac	tivity									
Radon									v									
								Isoto	pes									
Oxygen																		**
Deuterium																		

#### Table 7. 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**

The data for the Aravaipa Canyon basin roughly conforms to what would be expected in an arid environment, having a slope of 4.1, with the Local Meteoric Water Line (LMWL) described by the linear equation:  $\delta D = 4.1 \delta^{18}O - 27.7$  (Diagram 4).

The LMWL for the Aravaipa Canyon basin (4.1) is lower than other basins in Arizona including Dripping Springs Wash (4.4), Detrital Valley (5.2), Agua Fria (5.3), Bill Williams (5.3), Sacramento Valley (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>22</sup>

The most isotope samples plotted in a cluster that suggest much of the groundwater at these wells and springs consists of recent winter recharge stemming from precipitation originating in the Galiuro, Pinaleno, and/or Santa Theresa mountains. Two samples, ARA-12/12S and ARA-15, plot higher on the LWML and appear to consist of recent summer precipitation recharge (Map 8).



**Diagram 4** – The 15 isotope samples are plotted according to their oxygen-18 and deuterium values and form the Local Meteoric Water Line. Most samples consist of recent winter precipitation recharge; two outliers consist of recent summer precipitation recharge.<sup>11</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>9</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>9</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>9</sup> The LMWL created by  $\delta^{18}$ O and  $\delta$  D values for samples collected at sites in the Aravaipa Canyon 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>9</sup>

Groundwater from arid environments is typically subject to evaporation, which enriches  $\delta D$  and  $\delta^{18}O$ , resulting in a lower slope value (usually between 3 and 6) as compared to the slope of 8 associated with the GMWL.<sup>9</sup>



#### **Groundwater Quality Variation**

**Between Two Recharge Sources** – Twenty (20) groundwater quality constituents were compared between two recharge types: recent winter precipitation (13 sites) and recent summer precipitation (2 sites).

Significant concentration differences were found with seven constituents: temperature, SC-field, SC-lab, TDS, bicarbonate (Diagram 5), oxygen-18 and deuterium (Kruskal-Wallis test,  $p \leq 0.05$ ). In



addition, hardness (Diagram 6), calcium, and magnesium just missed having significant differences. In all these instances, sites with recent summer precipitation recharge had significantly higher constituent concentrations than sites with recent winter precipitation recharge.

Complete statistical results are in Table 8 and 95 percent confidence intervals for significantly different groups based on isotope recharge sources are in Table 9.

**Diagram 5** – Sample sites consisting of recharge from recent summer precipitation have significantly higher bicarbonate concentrations than sample sites consisting of recharge from recent winter precipitation (Kruskal-Wallis,  $p \le 0.05$ ). Elevated bicarbonate concentrations are often associated with recharge areas.<sup>20</sup>



Constituent	Significance	Significant Differences Between Recharge Sources
Temperature - field	*	Summer > Winter
pH – field	ns	-
pH – lab	ns	-
SC - field	*	Summer > Winter
SC - lab	*	Summer > Winter
TDS	*	Summer > Winter
Turbidity	ns	-
Hardness	ns	-
Calcium	ns	-
Magnesium	*	-
Sodium	ns	-
Potassium	ns	-
Bicarbonate	*	Summer > Winter
Chloride	ns	-
Sulfate	ns	-
Nitrate (as N)	ns	-
Fluoride	ns	-
Radon	ns	-
Oxygen	*	Summer > Winter
Deuterium	*	Summer > Winter

#### Table 8. Variation in Groundwater Quality Constituent Concentrations between Two 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	Summer Precipitation	Winter Precipitation
Temperature – field (°C)	*	1.8 to 56.5	18.9 to 22.4
pH – field (su)	ns	-	-
pH – lab (su)	ns	-	-
SC - field (µS/cm)	*	320 to 480	-213 to 1489
SC - lab (µS/cm)	*	319 to 483	15 to 1,285
TDS	*	287 to 478	199 to 294
Turbidity	ns	-	-
Hardness	ns	-	-
Calcium	ns	-	-
Magnesium	*	-	-
Sodium	ns	-	-
Potassium	ns	-	-
Bicarbonate	*	217 to 408	161 to 253
Chloride	ns	-	-
Sulfate	ns	-	-
Nitrate (as N)	ns	-	-
Fluoride	ns	-	-
Radon	ns	-	-
Oxygen (0/00)	*	-7.59 to -6.32	-9.41 to -9.08
Deuterium (0/00)	*	-88.3 to -24.7	-66.9 to -65.0

#### Table 9. Summary Statistics for Two Recharge Groups with Significant Constituent Differences

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

**Between Two Geologic Types** - Twenty (20) groundwater quality constituents were compared between two geologic types: consolidated crystalline and sedimentary rocks (6 sites) and unconsolidated sediments (9 sites).<sup>5, 18</sup>

Significant concentration differences were found with seven constituents: SC-field, SC-lab, TDS (Diagram

400 Total Dissolved Solids or TDS (mg/L) Rock Sediment Geology 90 80 70 Calcium (mg/L) b g g 30 20 10 Sediment Rock Geology

7), calcium, bicarbonate, chloride (Diagram 8) and oxygen-18 (Kruskal-Wallis test,  $p \le 0.05$ ).

Complete statistical results are in Table 10 and 95 percent confidence intervals for significantly different groups based on isotope recharge ages are in Table 11.

Diagram 7 – Sample sites collected from bedrock have significantly higher TDS concentrations than sample sites collected from sediment (Kruskal-Wallis,  $p \leq 0.05$ ). Other groundwater basins in Arizona have also been characterized as having more mineralized groundwater in hardrock the valley areas than alluvium. Precipitation reactions could account for the decrease in TDS concentrations as water moves downgradient in the basin.<sup>20</sup>

Constituent	Significance	Significant Differences Between Geologic Types
Temperature - field	ns	-
pH – field	ns	-
pH – lab	ns	-
SC - field	*	Consolidated Rock > Unconsolidated Sediment
SC - lab	*	Consolidated Rock > Unconsolidated Sediment
TDS	*	Consolidated Rock > Unconsolidated Sediment
Turbidity	ns	-
Hardness	ns	-
Calcium	*	Consolidated Rock > Unconsolidated Sediment
Magnesium	ns	-
Sodium	ns	-
Potassium	ns	-
Bicarbonate	**	Consolidated Rock > Unconsolidated Sediment
Chloride	*	Consolidated Rock > Unconsolidated Sediment
Sulfate	ns	-
Nitrate (as N)	ns	-
Fluoride	ns	-
Radon	ns	-
Oxygen	*	Consolidated Rock > Unconsolidated Sediment
Deuterium	ns	-

### Table 10. Variation in Groundwater Quality Constituent Concentrations between Two Geologic 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	Consolidated Rock	Unconsolidated Sediments
Temperature – field (°C)	ns	-	-
pH - field (su)	ns	-	-
pH – lab (su)	ns	-	-
$SC - field (\mu S/cm)$	*	402 to 644	260 to 481
SC – lab (µS/cm)	*	402 to 662	260 to 478
TDS	*	258 to 384	162 to 291
Turbidity	ns	-	-
Hardness	ns	-	-
Calcium	*	47 to 73	21 to 59
Magnesium	ns	-	-
Sodium	ns	-	-
Potassium	ns	-	-
Bicarbonate	**	238 to 315	123 to 245
Chloride	*	3.7 to 20.2	4.2 to 7.9
Sulfate	ns	-	-
Nitrate (as N)	ns	-	-
Fluoride	ns	-	-
Radon	ns	-	-
Oxygen (0/00)	*	-9.57 to -7.19	-9.51 to -9.12
Deuterium (0/00)	ns	-	-

#### Table 11. Summary Statistics for Two Geologic Groups with Significant Constituent Differences

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

#### DISCUSSION

Groundwater in Aravaipa Canyon basin appears to be suitable for irrigation, stock, and domestic uses based on the water quality sampling results of the ADEQ ambient study. Samples collected from 15 sites had no health-based standard exceedances and only four aesthetics-based standard exceedances.

This determination is supported by the results of groundwater quality studies conducted by the agency in other southeastern Arizona basins. Groundwater quality in the Cienega Creek, Dripping Springs, Upper San Pedro, and Lower San Pedro basins also generally met water quality standards particularly in samples collected from unconfined aquifers.<sup>23</sup> In addition, the Aravaipa Canyon basin is relatively pristine with minimal irrigation, domestic, and mining development to impact groundwater quality.

In the Aravaipa Canyon basin, there is some tendency for constituent concentrations to be significantly higher in groundwater quality sites collected in bedrock areas and/or which consist of recharge from summer precipitation. These trends however, do not impact the acceptability of these sites for use as a drinking water source.

Groundwater quality samples collected from three sites exceeded the 2.0 mg/L Secondary MCL for fluoride, though none had concentrations above the 4.0 mg/L Primary MCL. 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>20</sup> The three sites however, are not depleted in calcium and appear to 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 the levels of fluoride in solution. <sup>20</sup> The pH levels of only one of the three sampled sites however, appears to follow this pattern so there may be yet other influences causing the elevated fluoride concentrations.

The only other Secondary MCL exceedance was an elevated concentration of manganese in sample ARA-1. Groundwater in the Aravaipa Canyon basin would normally be expected to be oxidizing and have very low manganese concentrations. The sample site, ARA-1, however appears to be have a reducing environment as evidenced by not only the elevated manganese concentrations but also the only detections of iron and ammonia in the basin.<sup>20</sup> Thus, the Secondary MCL for manganese appears to be site specific and not reflective of regional groundwater conditions.

Some aspects of groundwater quality in the Aravaipa Canyon basin are however, still uncharacterized. Radionuclide samples were not collected at any of the sample sites and these constituents are often elevated by mining activity such as which created the Klondyke tailings piles. ADEQ's WQARF program also did not collect radionuclide samples at any wells.<sup>2</sup> Radionuclide constituents, such as gross alpha and uranium, are among the most common groundwater quality exceedances in Arizona.<sup>22</sup>

Another uncharacterized aspect of groundwater quality in the Aravaipa Canyon basin is the confined, basin-fill aquifer. During sample collection, no effort appears to have been made to collect samples from wells known to be producing water from this aquifer. Although some sampled wells may be producing from the confined basin-fill aquifer, it is difficult to make this determination based on field notes and the lack of well logs.<sup>5</sup> Samples from the confined, basin-fill aquifer could potentially have groundwater quality issues as samples collected from wells producing water from confined aquifers in nearby basins often had water quality exceedances for fluoride, arsenic, and TDS.<sup>23</sup>

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Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Geology	
		1 <sup>st</sup> Field Trip, Jan	ıary 28-29, 20	03 – Towne &	& Boettcher (Equ	uipment Blank - ARA-5)				
ARA-1	D(6-17)24cbb submersible	32°53'45.346" 110°34'03.240"	619594	30461	HCN Well	Inorganic, Radon O & H Isotopes	-	-	Consolidated Rock	
ARA-2	D(6-19)28add submersible	32°52'59.000" 110°24'06.076"	619597	49052	HCN OfficeWell	Inorganic, Radon O & H Isotopes	86'	19'	Unconsolidated Sediments	
ARA -3	D(6-19) Aravaipa Creek	-	-	-	Aravaipa Creek	O & H Isotopes	-	-	-	
ARA -4	D(7-20)08cca submersible	32°50'10.720" 110°19'52.200"	577266	49095	Garwood Well	Inorganic, Radon O & H Isotopes	120'	-	Unconsolidated Sediments	
ARA -6/7 Split	D(6-19)12cd submersible	32°55'12.772" 110°21'35.288"	608765	60558	Claridge Well	Inorganic, Radon O & H Isotopes	120'	90'	Unconsolidated Sediments	
ARA -8	D(7-17)09bcb submersible	-	806141	61398	Newton IR Well	Inorganic, Radon O & H Isotopes	65'	18'	Consolidated Rock	
ARA -9	D(7-17)09bcb submersible	-	806142	58652	Newton DM Well	Inorganic, Radon O & H Isotopes	65'	12'	Consolidated Rock	
2 <sup>nd</sup> Field Trip, May 5-6, 2003 –Boettcher & Lucci (Equipment Blank - Unnumbered)										
ARA-10	D(8-21)07abb submersible	32°45'25.648" 110°14'05.105"	624920	60983	Decker Well	Inorganic, Radon O & H Isotopes	120'	40'	Unconsolidated Sediments	
ARA-11/11D Duplicate	D(7-19)26abb spring	32°47'26.274" 110°22'38.832"	-	60985	Lackner Well	Inorganic, Radon O & H Isotopes	-	-	Unconsolidated Sediments	
ARA -12/12S Split	D(8-19)01cad submersible	32°45'51.214" 110°21'15.319"	805043	60984	Holcomb Well	Inorganic, Radon O & H Isotopes	-	128'	Consolidated Rock	
ARA -13	D(9-22)19dcc submersible	32°37'53.438" 110°08'06.034"	627711	33998	ASLD Well #1	Inorganic, Radon O & H Isotopes	278'	90'	Unconsolidated Sediments	
ARA -14	D(9-21)13acb submersible	32°39'17.319" 110°09'08.110"	627728	33993	ASLD Well #2	Inorganic, Radon O & H Isotopes	126'	113'	Unconsolidated Sediments	
		3 <sup>rd</sup>	Field Trip, J	lune 16-17, 20	)03 –Boettcher &	& Lucci				
ARA-15	D(8-22)20 submersible	32°43'48.150" 110°06'54.036"	-	49136	Lindsey Well	Inorganic, Radon O & H Isotopes	-	-	Consolidated Rock	
ARA-16/16S Split	D(8-20)1 submersible	32°46'19.479" 110°15'39.155"	624821	33220	Sollers Well	Inorganic, Radon O & H Isotopes	85'	50'	Unconsolidated Sediments	
ARA -17	D(9-20)10 spring	32°39'55.548" 110°17'08.446"	-	33988	Deer Creek Spring	Inorganic, Radon O & H Isotopes	-	-	Consolidated Rock	
ARA -18/18D duplicate	D(6-20)32 windmill	32°51'47.169" 110°19'47.862"	647920	49061	Dowdle Well	Inorganic, Radon O & H Isotopes	-	-	Unconsolidated Sediments	

# Appendix A. Data for Sample Sites, Aravaipa Canyon Basin, 2003

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)
ARA-1	Mn	21.3	7.95	7.9	562	600	350	210	210	1.2
ARA-2	F	16.8	8.08	7.8	386	410	260	90	87	0.15
ARA -4	-	20.5	7.47	7.6	533	360	220	210	210	4.4
ARA -6/7	-	17.2	7.36	7.75	593	635	375	270	290	5.85
ARA -8	-	19.3	7.71	7.5	465	440	270	190	200	0.24
ARA -9	-	19.0	7.63	7.6	464	490	300	180	180	0.56
ARA-10	-	17.4	7.65	7.6	231	250	180	85	91	0.68
ARA-11/11D	-	21.2	7.27	7.65	455	485	310	190	195	0.25
ARA -12/12S	-	27.0	7.06	7.55	571	600	375	245	250	0.24
ARA -13	-	20.6	7.86	8.0	339	360	230	83	86	0.34
ARA -14	-	25.1	8.01	8.1	349	370	210	140	150	0.13
ARA-15	F	31.3	7.48	7.8	705	700	390	220	240	0.17
ARA-16/16S	-	26.4	7.7	7.45	323	325	175	110	130	0.29
ARA -17	-	22.4	8.18	7.8	372	360	240	130	140	0.08
ARA -18/18D	F	21.6	7.47	6.55	126	125	81.5	35	39	1.3

### Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003

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)
ARA-1	59	16	39	5.5	250	300	ND	13	42
ARA-2	30	2.8	54	1.4	160	195	ND	5.1	32
ARA -4	64	13	32	1.7	150	180	ND	6	16
ARA -6/7	89.5	13.5	17.5	2.05	255	280	ND	10.95	58
ARA -8	60	11	29	3.0	200	244	ND	9.3	34
ARA -9	56	11	28	2.8	210	260	ND	10	28
ARA-10	28	5.2	13	1.9	100	120	ND	3.7	14
ARA-11/11D	52.5	15.5	25	0.64	230	280	ND	6.75	12
ARA -12/12S	75	16.5	34	4.05	290	320	ND	8.15	19.5
ARA -13	22	7.5	46	2.9	160	200	ND	8.5	9.1
ARA -14	24	21	22	2.5	180	220	ND	4.9	4
ARA-15	70	16	64	1.4	250	305	ND	27	70
ARA-16/16S	35	6.6	16.5	2.3	140	155	ND	5.05	15
ARA -17	39	11	28	1.9	190	230	ND	4.3	3.8
ARA -18/18D	11	2.8	7.2	1.55	20.5	25	ND	3.5	21

Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003---Continued

Site #	Nitrate-N (mg/L)	Nitrite-N (mg/L)	TKN (mg/L)	Ammonia (mg/L)	<b>T. Phos</b> (mg/L)	SAR (value)	Irrigation Quality	Aluminum (mg/L)
ARA-1	ND	ND	0.18	0.063	ND	1.2	C2-S1	ND
ARA-2	0.58	ND	ND	ND	ND	2.5	C2-S1	ND
ARA -4	0.73	ND	ND	ND	0.048	1.0	C2-S1	ND
ARA -6/7	0.062	ND	ND	ND	ND	0.4	C2-S1	ND
ARA -8	0.26	ND	ND	ND	0.046	0.9	C2-S1	ND
ARA -9	0.24	ND	0.053	ND	0.021	0.9	C2-S1	ND
ARA-10	1.4	ND	0.05	ND	0.15	0.6	C1-S1	ND
ARA-11/11D	0.245	ND	ND/ 0.078	ND	ND	0.8	C2-S1	ND
ARA -12/12S	1.6	ND	ND	ND	0.037 /ND	0.9	C2-S1	ND
ARA -13	0.87	ND	ND	ND	ND	2.2	C2-S1	ND
ARA -14	0.79	ND	ND	ND	ND	0.8	C2-S1	ND
ARA-15	0.038	ND	0.2	ND	ND	1.8	C2-S1	ND
ARA-16/16S	0.62	ND	ND	ND	0.076	0.6	C2-S1	ND
ARA -17	0.43	ND	0.089	ND	0.032	1.0	C2-S1	ND
ARA -18/18D	0.895	ND	0.145	ND	0.037	0.5	C1-S1	ND

Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003---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)
ARA-1	ND	ND	ND	ND	ND	ND	ND	ND	0.75
ARA-2	ND	ND	ND	ND	ND	ND	ND	ND	3.5
ARA -4	ND	ND	ND	ND	0.12	ND	ND	ND	0.43
ARA -6/7	ND	ND	ND/0.024	ND	ND	ND	ND	ND	1.2
ARA -8	ND	ND	ND	ND	ND	ND	ND	ND	0.86
ARA -9	ND	ND	ND	ND	ND	ND	ND	ND	0.73
ARA-10	ND	ND	ND	0.0016	ND	ND	ND	ND	0.21
ARA-11/11D	ND	ND	0.63	ND	ND	ND	ND	ND	0.245
ARA -12/12S	ND	ND	ND/0.052	ND	ND	ND	ND	ND	0.465
ARA -13	ND	ND	ND	ND	ND	ND	ND	ND	0.32
ARA -14	ND	ND	0.16	ND	ND	ND	ND	ND	0.21
ARA-15	ND	ND	ND	ND	ND	ND	ND	0.011	3.0
ARA-16/16S	ND	ND	ND	ND	ND	ND	ND	ND	0.295
ARA -17	ND	ND	ND	ND	ND	ND	ND	ND	0.29
ARA -18	ND	ND	ND	ND	ND	ND	ND	0.014	2.1

Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003---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)
ARA-1	0.19	ND	0.18	ND	ND	ND	ND	ND	ND
ARA-2	ND	ND	ND	ND	ND	ND	ND	ND	0.083
ARA -4	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -6/7	ND	ND	ND	ND	ND	ND	ND	ND	0.135
ARA -8	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -9	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA-10	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA-11/11D	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -12/12S	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -13	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -14	ND	ND	ND	ND	ND	ND	ND	ND	0.069
ARA-15	ND	ND	ND	ND	ND	ND	ND	ND	0.062
ARA-16/16S	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -17	ND	ND	ND	ND	ND	ND	ND	ND	ND
ARA -18	ND	ND	ND	ND	ND	ND	ND	ND	0.68

Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003---Continued

Site #	Radon-222 (pCi/L)	* <sup>18</sup> O ( <sup>0</sup> / <sub>00</sub> )	* <b>D</b> ( <sup>0</sup> / <sub>00</sub> )	Type of Chemistry	Ion Balance % Difference Pass / Fail
ARA-1	124	-9.5	-67	mixed-bicarbonate	Low cation - 0.65 - Yes
ARA-2	782	-9.2	-68	sodium-bicarbonate	Low cation - 1.42 - Yes
ARA-3	-	-9.6	-68	-	-
ARA -4	214	-9.6	-68	calcium-bicarbonate	Low anion - 22.97 - No
ARA -6/7	188	-9.5	-67	calcium-bicarbonate	Low anion - 0.76 - Yes
ARA -8	306	-9.1	-66	calcium-bicarbonate	Low anion - 1.97 - Yes
ARA -9	338	-9.0	-65	calcium-bicarbonate	Low cation - 1.91 - Yes
ARA-10	123	-9.1	-64	calcium-bicarbonate	Low cation – 0.71 - Yes
ARA-11/11D	132	-8.9	-64	calcium-bicarbonate	Low cation – 1.28 - Yes
ARA -12/12S	264	-6.9	-54	calcium-bicarbonate	Low anion - 0.44 - Yes
ARA -13	327	-9.2	-64	sodium-bicarbonate	Low anion - 0.03 - Yes
ARA -14	117	-9.3	-65	mixed-bicarbonate	Low anion - 0.67 - Yes
ARA-15	<31	-7.0	-59	mixed-bicarbonate	Low anion - 1.68 - Yes
ARA-16/16S	400	-9.7	-68	calcium-bicarbonate	Low anion - 1.32 - Yes
ARA -17	570	-8.8	-65	mixed-bicarbonate	Low anion - 1.23 - Yes
ARA -18	693	-9.3	-66	mixed-mixed	Low anion - 1.46 - Yes

Appendix B. Groundwater Quality Data, Aravaipa Canyon Basin, 2003---Continued

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