Ambient Groundwater Quality of the San Rafael Basin: A 2002 Baseline Study

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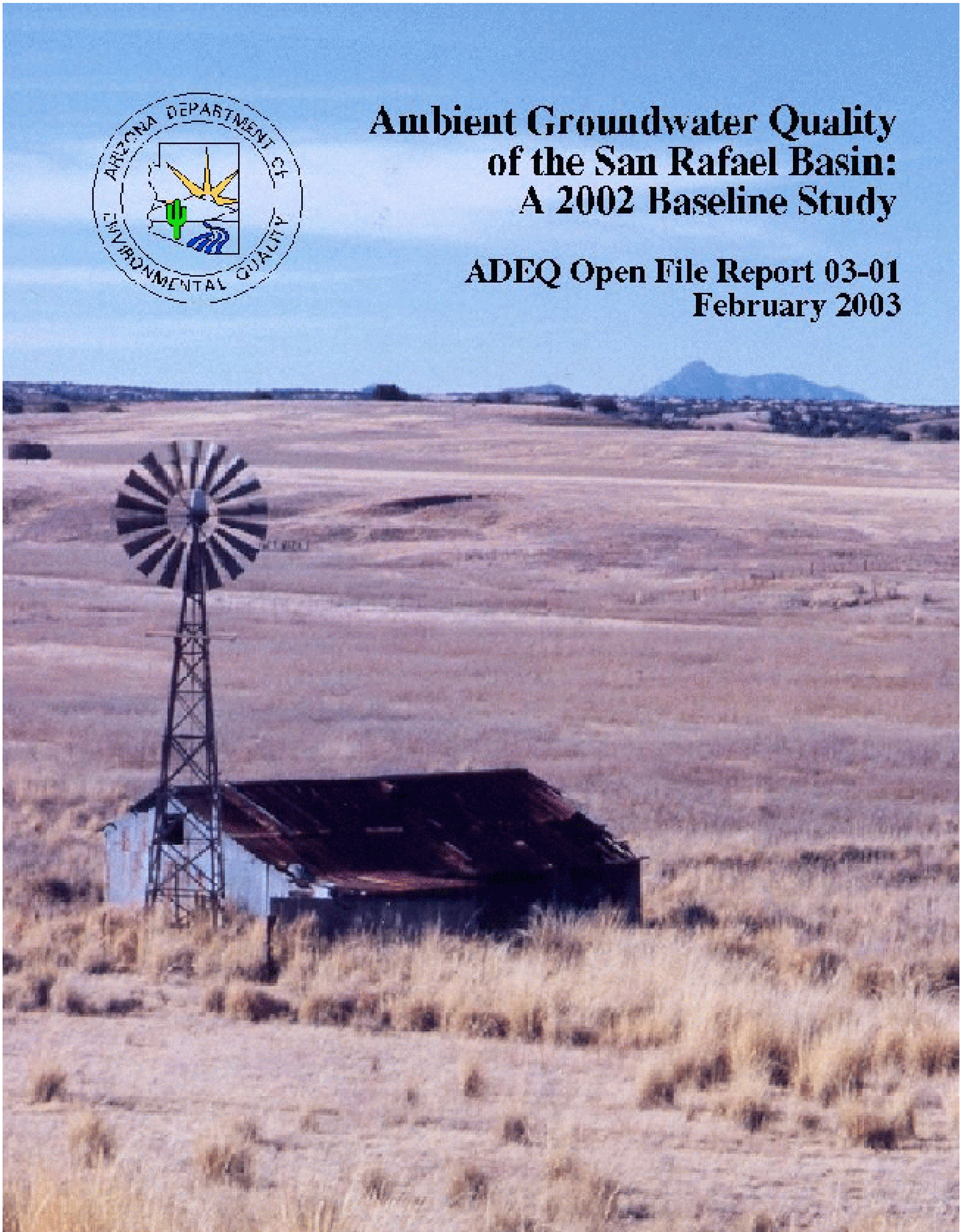

Ambient Groundwater Quality of the San Rafael Basin: A 2002 Baseline Study

By Douglas C. Towne
Maps by Larry W. Stephenson

Arizona Department of Environmental Quality (ADEQ)
Open File Report 2003-01
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Photo Credits: Douglas Towne

Report Cover: The abundant charm of the San Rafael Valley is aided by the many stunning rural landscapes relatively untouched by modern development. This photo shows the windmill, barn, and pristine rolling grasslands of one of Arizona's newest state parks, the San Rafael Ranch, located on a terrace overlooking the Santa Cruz River a few miles north of the border with Mexico. In 1998, the Arizona State Parks Board purchased this property and is refurbishing the ranch house in preparation to open the park to the public. The historic three-story, brick French Colonial style structure is considered the best preserved territorial brick ranch in Arizona.".[7]

Other Publications of the ADEQ Ambient Groundwater Monitoring Program

ADEQ Ambient Groundwater Quality Open-File Reports (OFR) :

Lower San Pedro Basin	OFR 02-01, July 2002, 74 p.
Willcox Basin	OFR 01-09, November 2001, 55 p.
Sacramento Valley Basin	OFR 01-04, June 2001, 77 p.
Upper Santa Cruz Basin	OFR 00-06, September 2000, 55 p. (With the U.S. Geological Survey)
Prescott Active Management Area	OFR 00-01, May 2000, 77 p.
Upper San Pedro Basin	OFR 99-12, July 1999, 50 p. (With the U.S. Geological Survey)
Douglas Basin	OFR 99-11, June 1999, 155 p.
Virgin River Basin	OFR 99-04, March 1999, 98 p.
Yuma Basin	OFR 98-07, September, 1997, 121 p.

ADEQ Ambient Groundwater Quality Factsheets (FS):

San Rafael Basin	FS 03-03, February 2003, 4 p.
Lower San Pedro Basin	FS 02-09, August 2002, 4 p.
Willcox Basin	FS 01-13, October 2001, 4 p.
Sacramento Valley Basin	FS 01-10, June 2001, 4 p.
Yuma Basin	FS 01-03, April 2001, 4 p.
Virgin River Basin	FS 01-02, March 2001 4 p.
Prescott Active Management Area	FS 00-13,December 2000, 4 p.
Douglas Basin	FS 00-08, September 2000, 4 p.
Upper San Pedro Basin	FS 97-08, August 1997, 2 p. (With the U.S. Geological Survey)

ADEQ Targeted Groundwater Quality Open-File Reports (OFR) :

The Impacts of Septic Systems on Water Quality of Shallow Perched Aquifers: A Case Study of Fort Valley, Arizona. ADEQ Open File Report 97-7, February 1997, 70 p.

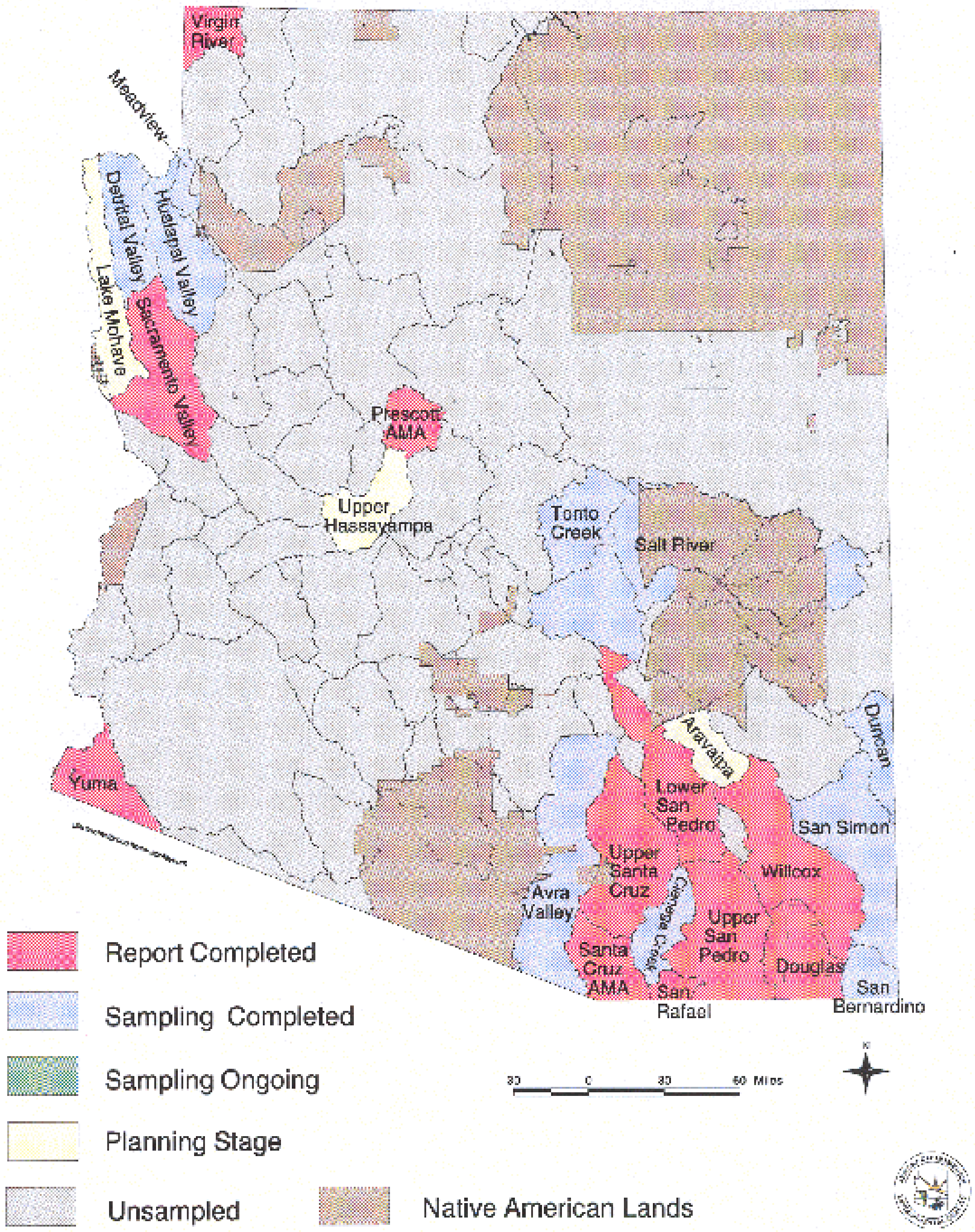
Most of these publications are available on-line.
Visit the ADEQ Ambient Groundwater Monitoring Program at:

http://www.adeq.state.az.us/environ/water/assess/ambient.html#studies

http://www.adeq.state.az.us/environ/water/assess/target.html#studies

Status of GW Basins in the Ambient Monitoring Program

December 2002



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ABBREVIATIONS

amsl	above mean sea level
af	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
As	arsenic
bls	below land surface
BLM	U.S. Department of the Interior Bureau of Land Management
^{o}C	degrees Celsius
$CI_{0.95}$	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
HCl	hydrochloric acid
LLD	Lower Limit of Detection
Mn	manganese
MCL	Maximum Contaminant Level
ml	milliliter
msl	mean sea level
Fg/l	micrograms per liter
Fm	micron
FS/cm	microsiemens per centimeter at 25E Celsius
mg/l	milligrams per liter
MRL	Minimum Reporting Level
MTBE	Methyl tertiary-Butyl Ether
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
SRF	San Rafael Groundwater Basin
su	standard pH units
SO4	sulfate
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound

"....the stream (the Santa Cruz River) crosses the border (into the U.S.) as barely a rivulet east of Lochiel. Least changed in appearance over the ten millennia or so of human presence is the San Rafael Valley in the upper basin. The hills forming the river's watershed have escaped the most severe woodcutting and the grassland in the valley the most severe overgrazing during the periodic crashes in the cattle industry. The river is merely a stream in the San Rafael Valley, but the terrain remains remarkably pristine compared to other vistas along the river's course.

Moving up the San Rafael valley from south to north, the low Canelo Hills rise as blue swells in the distance. The river still begins in those hills, little more than a seep and ooze at first, growing quickly into a modern stream. Although the start of the river's journey remains largely unchanged, and the stretch through the high valley greatly resembles the scene from centuries gove by, most of the river's course is a testament to change. Human society has wrought many of those changes, but natural cases of climate and hydrology have influenced the river's circumstances as well. The river has never stood still, even as it has disappeared through most of its reaches downstream. The river will continue to flow, aboveground or underflow, through periods of ebb and flow, as the forces of change act upon it."

Michael F. Logan
in
The Lessening Stream: An Environmental History of the Santa Cruz River [25]

Ambient Groundwater Quality of the San Rafael Basin: A 2002 Baseline Study

By Douglas C. Towne

Abstract - The San Rafael groundwater basin (SRF) baseline groundwater quality study was conducted by the Arizona Department of Environmental Quality (ADEQ) in 2002. Located between Sierra Vista and Nogales along the Mexican border in southeastern Arizona, this semiarid basin is relatively untouched by modern development. It contains some of the most pristine desert grasslands in the Southwest. The basin consists of the San Rafael Valley and the surrounding slopes of the Patagonia and Huachuca Mountains and the Canelo Hills. The local economy was originally based on mining and livestock grazing, but mining operations have long been inactive.[19]

Hydrologically, the SRF is most noted as the headwaters of the Santa Cruz River. This watercourse, perennial in stretches, flows into Mexico and later reenters the U.S. near Nogales, Arizona. Groundwater from the *alluvial aquifer* is the principle water source though, where sufficiently fractured and faulted, mountain *hardrock* provides limited supplies.[28] For this study, 20 groundwater sites were sampled for inorganic constituents as well as oxygen and hydrogen isotopes. In addition, samples were also collected at selected sites for radiochemistry (5), radon gas (5), and Volatile Organic Compounds (2) analyses.

Two of the 20 sampled sites (10 percent) had concentrations of at least one constituent that exceeded a health-based, Federal or State water-quality standard. These enforceable standards define the maximum concentrations of constituents allowed in water supplied to the public.[34] Constituents that exceeded these standards included antimony (1 site), lead (1 site), gross alpha (1 site), and uranium (1 site). In addition, 3 of the 20 sampled sites (15 percent) had concentrations of at least one constituent that exceeded an aesthetics-based, Federal water-quality guideline. These are unenforceable guidelines that define the maximum concentration of a constituent that can be present in drinking water without an unpleasant taste, color, odor, or other aesthetic effect occurring.[34] Constituents that exceeded these guidelines included iron (1 site), manganese (2 sites), sulfate (2 sites), and total dissolved solids or TDS (2 sites). No Volatile Organic Compounds were detected.

Interpretation of the analytical results of the groundwater quality samples indicates that groundwater in the SRF generally meets drinking water standards and is suitable for domestic, municipal, irrigation, and stock purposes. Samples collected from two sites in the Patagonia Mountains contained all the health-based standard exceedances and the aesthetics-based guideline exceedances (except one) that occurred in the SRF. The elevated sulfate, TDS, and trace element concentrations found at these sites suggests impacts from the historic mining conducted in the area.[23] The elevated radiochemsitry concentrations found at one of these sites also suggest additional impacts from the granitic geology found in the area.[26]

Groundwater in the SRF is generally *fresh*, *slightly alkaline*, and *hard* based on TDS, pH, and hardness concentrations.[20] The majority of sites had a *calcium-bicarbonate* chemistry. The two previously mentioned sites in the Patagonia Mountains exhibited a *calcium-sulfate* chemistry. Nutrient concentrations were low with the exception of one site near the center of the basin whose nitrate concentration approached the health-based water standard. Barium, fluoride, and zinc were the only trace elements detected at more than ten percent of sites. Antimony, arsenic, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium were rarely, if ever, detected. Groundwater quality constituent concentrations were compared among aquifers, watersheds, and geologic types; few significant differences were found in any of the groupings (Kruskal-Wallis test in conjunction with the Tukey test, p#0.05).

Deuterium and oxygen isotope data formed a *Local Meteoric Water Line* whose slope of 4.6 conformed to the range of slopes (3 to 6) normally found in arid environments.[13] The most *depleted*, or isotopically lighter, sites tended to be in the highest mountains and may be from recent local precipitation less subject to evaporation. In contrast, the most *enriched*, or isotopically heaviest, sites tended to be at lower elevations within the central part of the basin. The levels of these two groups were found to be significantly differ (Kruskal-Wallis test, p#0.01).

INTRODUCTION

The San Rafael (SRF) groundwater basin, located in southeastern Arizona, is a rural landscape mainly composed of public lands and extensive cattle ranches. The SRF is renown for the beauty of its oak-dotted, rolling hills that contain some of the most pristine remnants of shortgrass prairie in the Southwest (**Figure 1**). Groundwater is the primary source for water uses in the SRF (**Figure 2**). From a hydrology perspective, the basin is most noteworthy as the headwaters of the Santa Cruz River which flows into Sonora, Mexico for a 32-mile loop only to later reenter the U.S. five miles east of the city of Nogales, Arizona.

Figure 1. John Russell Bartlett toured the San Rafael Valley in 1851 as part of the U.S. Boundary Commission and wrote that "this valley was covered with the most luxuriant herbage, and thickly studded with live oaks; not like a forest, but rather resembling a cultivated park."[25] This description is still appropriate today.

The Arizona Department of Environmental Quality (ADEQ) Groundwater Monitoring Unit designed a study to characterize the current (2002) groundwater quality conditions in the SRF. Sampling by ADEQ was completed as part of the Ambient Groundwater Monitoring Program, which is based on the legislative mandate in the Arizona Revised Statutes §49-225 that authorizes:[3]

Figure 2. The remoteness of the San Rafael Valley results in ranchers often depending on springs such as Captain Spring (which ADEQ hydrologist Elizabeth Boettcher samples) for much of their water supply.

"*...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.*"

The ADEQ ambient groundwater monitoring program examines regional groundwater quality in Arizona basins such as the SRF to:

- Provide a comprehensive baseline study of the SRF in preparation for potential bi-national watershed issues effecting the Santa Cruz River.
- Determine if there are any areas where groundwater does not currently meet U.S. Environmental Protection Agency (EPA) Safe Drinking Water Act (SDWA) water quality standards.
- Examine for water quality differences among the various aquifers, watersheds and/or rock types found within the SRF.
- Further explore the relationship between various SRF groundwater sites and the Santa Cruz River.

Purpose and Scope

ADEQ collected samples from 20 sites for this groundwater quality assessment of the SRF. Types and numbers of samples collected and analyzed include inorganics (physical parameters, major ions, nutrient constituents, and trace elements) (20 sites), oxygen and hydrogen isotopes (20 sites), radiochemistry (5 sites), radon gas (5 sites), and Volatile Organic Compounds (VOCs) (2 sites).

Reasons for Study - The SRF was selected for study for the following reasons:

< Support the ADEQ watershed program by expanding the hydrologic information available on the Santa Cruz watershed. County and local governments can also benefit from this study.

< Add to the groundwater quality data available for the SRF, a basin which an ADEQ report noted the lack of groundwater quality data collection alternatives as well as a high dependence of the population on the groundwater supply.[24]

< Provide support to the ADEQ Border Program, especially concerning the many bi-national issues coming to the forefront involving the Santa Cruz River.

< Provide a more comprehensive baseline study than was possible in the past because of recent population growth and a subsequent increase in the number of wells providing greater access to groundwater.

Benefits of Study - This groundwater quality study was undertaken with the purpose of developing a reproducible, scientific report utilizing statistical analysis to investigate the groundwater quality in the SRF. The report's conclusions concerning groundwater quality is anticipated to provide the following three benefits:

#1 - Residents in the SRF obtain domestic supplies from private wells whose water is seldom tested for a wide variety of possible pollutants. Arizona statutes only require well drilling contractors to disinfect, for potential bacteria contamination, new wells which are used for human consumption. Many wells are not tested for other groundwater quality concerns. Thus, contamination affecting groundwater pumped from private wells may go undetected for years and have adverse health effects on users of this resource. Testing all private wells for a wide variety of groundwater quality concerns would be prohibitively expensive. An affordable alternative is this type of statistically-based groundwater study characterizing regional groundwater quality conditions and identifying areas with impaired groundwater.

#2 - A process for evaluating potential groundwater quality impacts arising from a variety of sources including natural mineralization, mining, agriculture, livestock, septic tanks, and poor well construction.

#3 - A process for identifying future locations of public supply wells and wellhead protection areas.

Physical Setting

The SRF covers approximately 172 square miles in southeastern Arizona, wedged along the border with Mexico between the cities of Nogales and Sierra Vista.[28] The basin consists of the broad, northern-trending San Rafael Valley and the eastern slopes of the Patagonia Mountains, the southern slopes of the Canelo Hills, and portions of the western slopes of the Huachuca Mountains (**Figure 3**). The International Boundary with Mexico forms the basin's southern boundary.

Elevations in the surrounding uplands range from 7,220 feet above mean sea level (amsl) in the Patagonia Mountains to 6,170 feet amsl in the Canelo Hills to approximately 7,900 feet amsl at Peterson Peak in the Huachua Mountains. Elevations along the valley floor range from 5,100 feet amsl near the northern boundary descending to 4,500 feet amsl near where the Santa Cruz River enters Mexico near the community of Lochiel.

Five major soil associations compose the SRF.[29] The central part of the San Rafael Valley is composed of deep gravelly clay loams of the *Bernadino-White House-Hathaway* association. Directly to the east are the deep gravelly loams of the *Caralampi-White House-Hathaway* association. Surrounding these two associations are the deep gravelly sandy loams of the *Casto-Martinez-Canelo* association. In the

Figure 3 - San Rafael Groundwater Basin

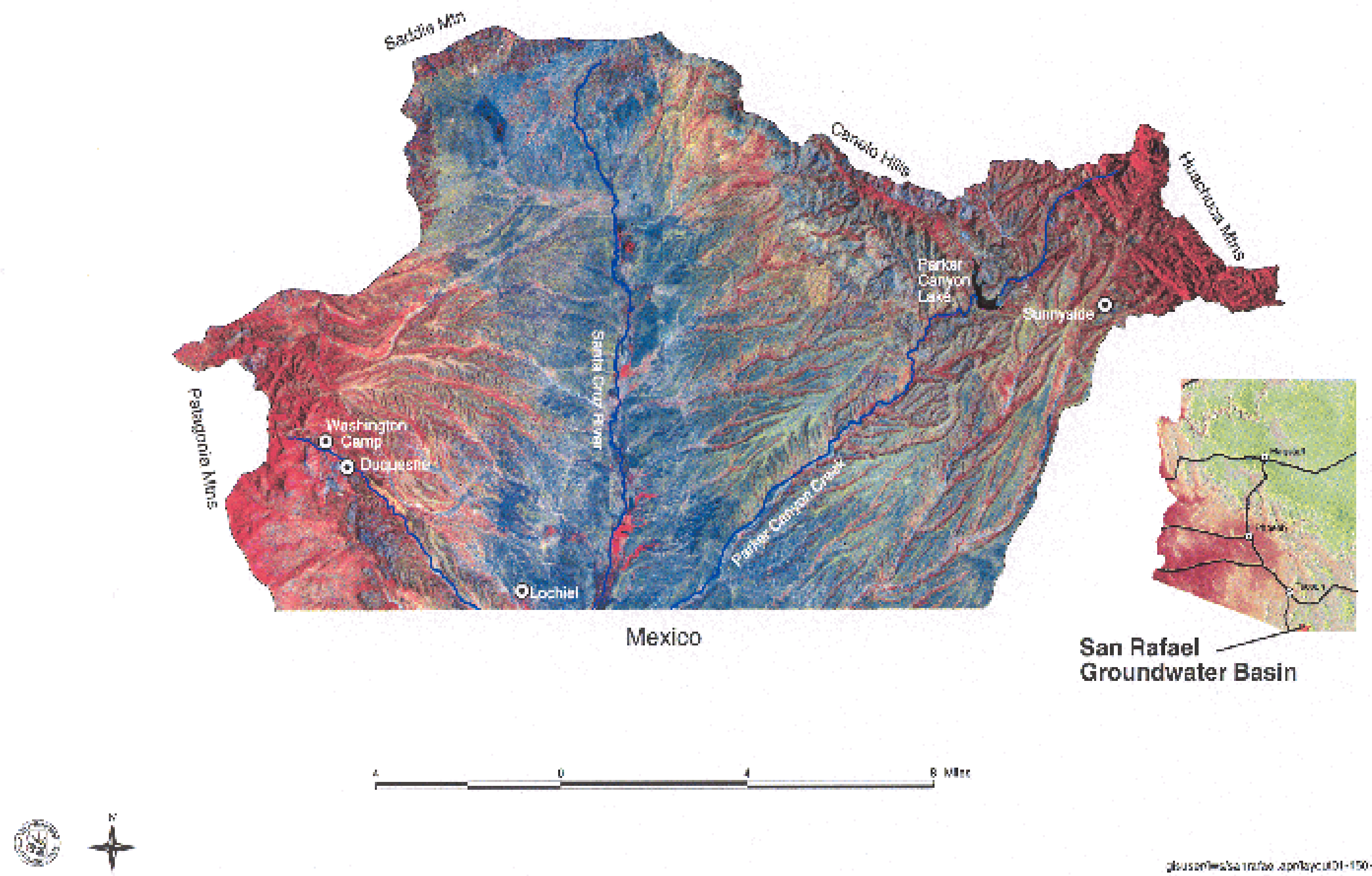


Figure 4. The verdant green cottonwoods of the Santa Cruz River's riparian area cut a linear swath across the dry grasslands of the San Rafael Valley. The evergreen woodlands of the Patagonia Mountains are in the background.

Patagonia Mountains and Canelo Hills are the very shallow sandy loams of the the *Faraway-Rock outcrop-Barkerville* association. Finally, in the Huachuca Mountains are the shallow loams and rock outcrops of the *Tortugas-Rock outcrop* association.[29]

The San Rafael Valley is an area of rolling grasslands extending for over 90,000 acres and is one of the most pristine remnants of shortgrass prairie in Arizona (**Figure 4**). Major vegetation zones include *plains grassland* at 4,500 - 6,000 feet at the center of the valley, *mixed cottonwood riparian habitat* along the Santa Cruz River and major tributaries at 4,500 to 5,500 feet, *evergreen woodland* from 4,500 to 7,000 feet, and *ponderosa pine and mixed-conifer forests* at 7,000 to 9,500 feet.[19] The SRF is part of the *Madrean sky island bioregion* which harbors the greatest diversity of mammal species in North America.[7]

Surface Water - The main drainage in the basin is the Santa Cruz River, whose headwaters are in the Canelo Hills. The Santa Cruz River is one of the few perennial grassland streams found in the Southwest.[25] The river flows south through the SRF, entering Mexico for the next 32 miles before changing course and flowing north back into the United States near Nogales, Arizona. A largely ephemeral watercourse, the Santa Cruz River is perennial for a three-mile reach, five miles north of the international boundary near Lochiel, Arizona (**Figure 5**).[6] Numerous springs and creeks in the SRF contribute to this perennial flow.[33] The Santa Cruz River has an average discharge into Mexico of about 2,910 acre-feet based on data collected between 1949 and 1988 at a U.S. Geological Survey streamgage (#09480000) near Lochiel.[28]

Other major watercourses within the SRF include Parker Canyon to the east and Duquesne Wash to the west. Parker Canyon also has a perennial stretch of about six miles above where it is impounded to form Parker Canyon Lake. This lake, at 5400 feet amsl, averages 125 surface acres and 82 feet in depth and was recently found to have high levels of mercury in the warm-water species of fish.[32] These tributaries to the Santa Cruz River actually enter the watercourse south of the international border with Mexico.

Figure 5. The perennial flow of the Santa Cruz River is shown here near the U.S. Geological Survey gaging station several miles north of Mexico. This late May photograph shows that the riparian vegetation ends its winter dormancy before the surrounding grasslands.

Climate - The SRF has a semiarid climate characterized by hot summers and cool, moderate winters. Summer highs are in the mid 90's and winter lows are in the 20's (in Fahrenheit).[19] In the basin, climate becomes warmer and drier with decreasing elevation. Precipitation averages 17inches annually at Lochiel and typically occurs during two periods: as intense rains of short duration produced by thunderstorms from July to September and as gentle, long-duration rains and some snow produced by frontal-type storms during the winter months.[6] May is the driest month while July and August are the wettest months. Runoff from thunderstorms tends to be short-lived and localized.

Figure 6. Picturesque remnants of abandoned homesteads are found throughout the San Rafael Valley such as this residence and windmill in Meadow Valley, located in the northwest part of the basin.

Cultural Setting

The San Rafael Valley has a colorful history with the earliest Spanish explorers of North America, Fray Marcos de Niza (commemorated in a roadside marker near Lochiel) and Francisco Vasquez de Coronado both crossing the area during their journeys. Much of the central part of the SRF was part of an original 1825 Spanish land grant known as San Rafael de la Zinja. As part of the Primeria Alta, the land was under Spanish or Mexican control until obtained by the U.S. in the 1854 Gadsden purchase.[19]

The SRF was the site of significant mining activity for silver, lead, zinc, manganese, copper, and to a much lesser extent, gold beginning around 1880, particularly in the Patagonia Mountains.[19] Over 1.9 million tons of ore were extracted from about 40 large mines mainly located in the districts of Mowry and Duqesne.[33] Associated with mining was extensive logging for fuelwood for both milling purposes and domestic fuel. Most mines were active for only a few years with production ebbing by 1910, but a few were worked until the 1960s.

Figure 7. The official border crossing customs house at Lochiel was closed during the 1980s because of infrequent usage and budget cutbacks. Much of the San Rafael Valley is remote and residents must travel outside the basin to Patagonia, Sonoita, or Nogales for most supplies and services.

Dry farming was practiced in the late 19th and early 20th centuries but had largely faded by World War II. Since then, farming has been largely a subsidiary activity of livestock raising with fields irrigated either from surface water diversions or wells. The multitude of small cattle operations present during the late 19th century had contracted to a few, large ranchers by the 1960s.[19]

Economic activity in the SRF is currently focused on livestock ranching with approximately twenty cattle ranches comprising one of the largest contiguous tracts of privately-owned land in Santa Cruz County. These landowners formed the San Rafael Valley Land Trust in 1994 in an effort to preserve the ranching lifestyle and ecosystem health.[25] With ranchers practicing conservation grazing management, the San Rafael Valley is currently one of the healthiest grassland systems in the Southwest.[33] In particular, the Heady and Ashburn Ranch has been heralded as one of the most successful range restoration programs in Arizona.[25] The ranching industry has been aided by having less pressure from urban development than other areas in southeast Arizona.

Tourism is becoming an increasingly important economic factor in the SRF. Recreational opportunities in the basin abound with the abundance of public lands especially with Parker Canyon Lake as well as the recent establishment of the rustic San Rafael Ranch State Park.[7]

Settlements in the SRF are small and most are former mining camps dating from the late 1800s. Most of the area's schools, post offices, and stores had closed down by 1960.[19] Commercial activity is very limited in these communities and for even the most basic services, residents must travel to towns such as Patagonia, Sonoita, or Nogales.

Communities within the SRF include Lochiel, an official border crossing with Mexico whose port of entry and customs house were closed in the 1980s.[19] Duquesne is a small, rustic settlement in the Patagonia Mountains that formerly supported nearby mines that have long been inactive while nearby Washington Camp was the supply center for the settlements.[17] Sunnyside, a ghost town in the Huachuca Mountains, has a unique history of being a mining community composed of Donellites, followers of a religion founded by Samuel Donnelly. As such, Sunnyside residents were devoted to hymn singing, bible reading, and mining.[17]

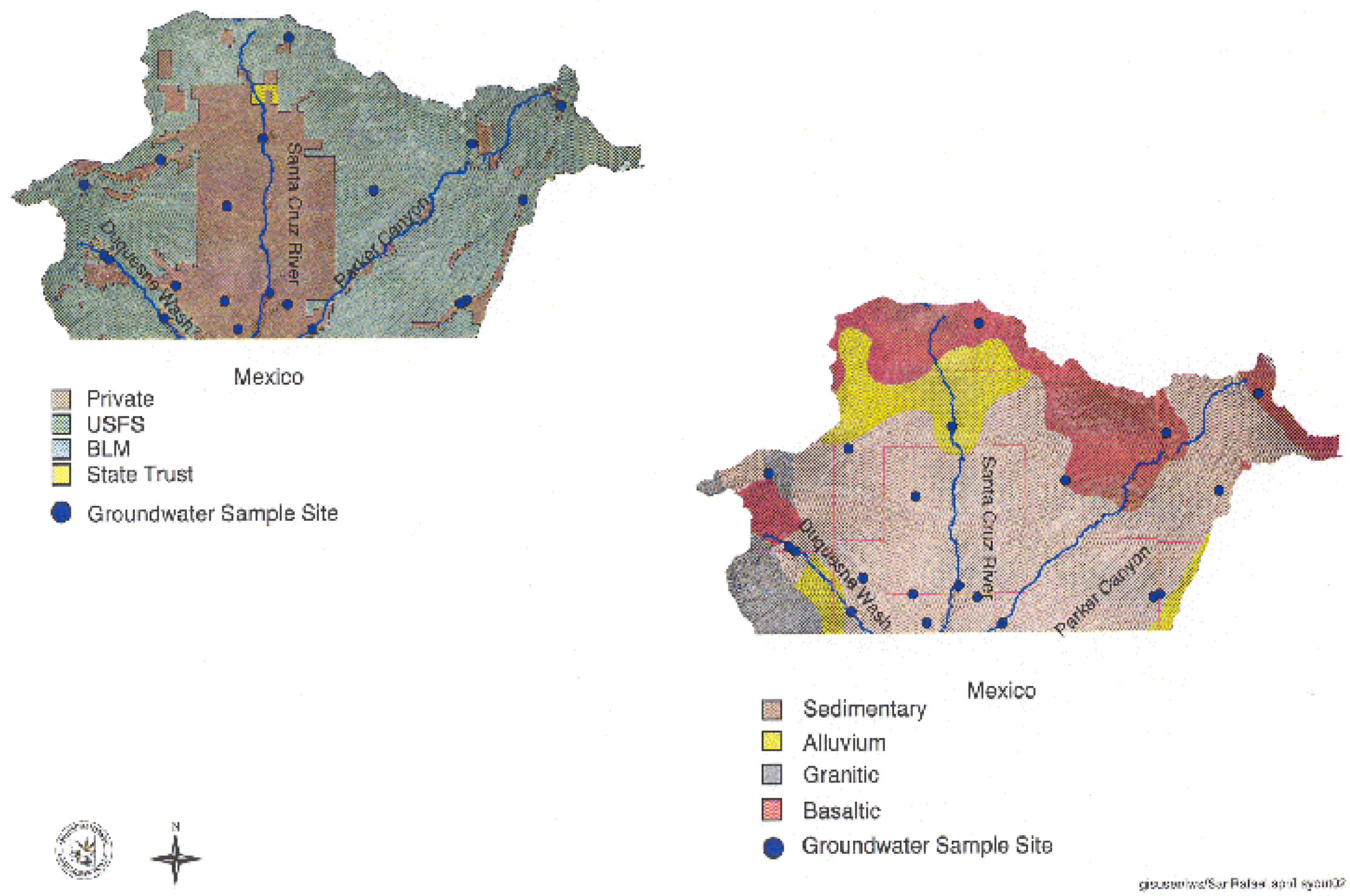
With access of the SRF limited to unpaved roads, the small communities within the basin have not become retirement centers or commuter "bedroom" communities for Tucson or Ambios Nogales. New subdivisions and low-density residential development have also been largely avoided because of the lack of convenient access.[25] The SRF landscape remains a beautiful Arizona anomaly that has avoided sprawl.

Figure 8. Contrary to the movie title, the classical musical *Oklahoma!* was actually filmed in the San Rafael Valley in a humorous example of Hollywood inaccuracy.[17] The SRF's stunning landscapes may have been the inspiration behind such famous songs as "Oh, What a Beautiful Mornin'"".

Ironically, the rolling grasslands and wide open spaces of the San Rafael Valley are probably best known to the general public as the backdrop for much of the 1955 Hollywood movie version of the Rogers and Hammerstein musical, *Oklahoma*! (**Figure 8**).[7]

The majority of the SRF is located in Santa Cruz County with only a small eastern portion within Cochise County. Land ownership in the SRF (**Figure 9**) is divided among the U.S. Forest Service (61 percent), private entities (37 percent), State trust (1 percent), and the Bureau of Land Management (1 percent).[5] Generally the lower-elevation grasslands are privately owned while higher elevations are publicly owned and managed by the Coronado National Forest.

Figure 9 - San Rafael Groundwater Basin Land Ownership & Rock Types



GEOHYDROLOGY

The SRF is considered part of the southern Basin and Range physiographic province. Much of the SRF consists of sedimentary rock with basaltic rock formations in the Patagonia Mountains and Canelo Hills and granitic rock outcrops in the Patagonia Mountains (**Figure 9**).[5]

Groundwater is found in two principal water-bearing units in the SRF:[6]

< **alluvial aquifer** -consists of three basic units including streambed alluvium, pediment gravels, and basin-fill alluvium.

< **hardrock** - consolidated bedrock found in the surrounding mountains.

The streambed alluvium is composed of well-sorted silt, sand, and gravel, that forms the narrow floodplain of the Santa Cruz River and major tributaries. Wells completed in streambed alluvium typically have yields of 115 to 350 gallons per minute (gpm).[6]

Pediment gravels form the terraces along the valley's eastern side while the basin-fill alluvium consisting of clay, silt, sand, and gravel deposits in the remainder of the valley. Wells completed in these units produce an average of 3 to 35 gpm.[6] There are at least two recognizable units of basin-fill: the lower unit consisting of the Nogales formation (previously mapped to the east in the Santa Cruz Active Management Area) and poorly to moderately well consolidated alluvium, the upper unit is composed of younger unconsolidated to poorly consolidated alluvium.[12] Wells in the basin draw water from the upper unit as only three mineral exploration wells drilled in the 1970s penetrated the lower unit.[12] The alluvial aquifer, which overlies bedrock, has an unknown thickness but deep exploration wells have penetrated almost 2000feet of alluvium.[6]

In hardrock areas in the surrounding mountains, only minor amounts of water found where the bedrock is sufficiently faulted and fractured.[6]

Groundwater Use - Groundwater is discharged from the SRF through both artificial means (groundwater pumping) and natural outflow southward to Mexico occurring with a combination of groundwater underflow as well as the base flow of the Santa Cruz River. Discharge also occurs through evapotranspiration by riparian vegetation in shallow groundwater areas in the vicinity of the Santa Cruz River.[6]

Groundwater pumpage is estimated to be less than 100 acre-feet per year and is used for domestic, stock, and irrigation purposes.[6] Irrigation is limited to 200 acres scattered in small plots next to the Santa Cruz River; and domestic use is limited to a few scattered ranches in the valley.[6]

The floodplain and basin-fill alluvium have the ability to transmit and supply large amounts of groundwater and combine as the *alluvial aquifer*, serving as the main water supply in the SRF. In contrast, surrounding mountain *hardrock* yields small amounts of water in areas sufficiently faulted and fractured.[6]

Groundwater Movement, Depth, and Recharge - Groundwater movement is from the surrounding mountains toward the Santa Cruz River and then south into Mexico, with the underflow roughly estimated to be about 2,000 acre-feet per year.[28]

Depth to water in the streambed alluvium ranges from 10 to 25 feet below land surface (bls).[28] Basin-fill water levels are usually over 100 feet bls with the deepest level approximately 350 feet bls.[6] A more recent study found the water table quite variable, but shallowest along the path of the Santa Cruz River.[12]

Groundwater recharge occurs in the SRF through mountain-front recharge and infiltration of runoff in stream channels.[6]

Small quantities of groundwater have historically been pumped, probably less than a 100 afpy, in the SRF and although few long-term water-level records are available, indications are that no significant changes have been observed.[28] This combined with limited groundwater use in the SRF suggests that a balance exists between groundwater discharge and recharge in the basin.

GROUNDWATER SAMPLING RESULTS

To characterize the regional groundwater quality of the SRF, ADEQ personnel sampled 20 groundwater sites (**Figure 10**) consisting of 15 wells and 5 springs (**Figure 11**). The 15 wells consisted of 12 domestic wells with submersible pumps (often with associated stock uses), 2 stock windmills (**Figure 12**), and 1 irrigation well with a turbine pump. Information on locations and characteristics of groundwater sample sites is provided in **Appendix A**. At the 20 sites, the following types of samples were collected:

- 20 inorganic samples;
- 20 hydrogen and oxygen isotope samples;
- 5 radon samples;
- 5 radiochemistry samples; and
- 2 VOC samples.

Water Quality Standards/Guidelines

As an environmental regulatory agency, the most important determination ADEQ makes concerning the collected samples is how the analytical results compare to various water quality standards. Three sets of drinking water standards which reflect the best current scientific and technical judgment available on the suitability of water for drinking purposes were used to evaluate the suitability of these groundwater sites for domestic purposes:

Figure 12. Saddle Mountain, a Meadow Valley windmill, and ADEQ Hydrologist Joe Harmon are pictured in this area swept by a wildfire in the spring of 2002.

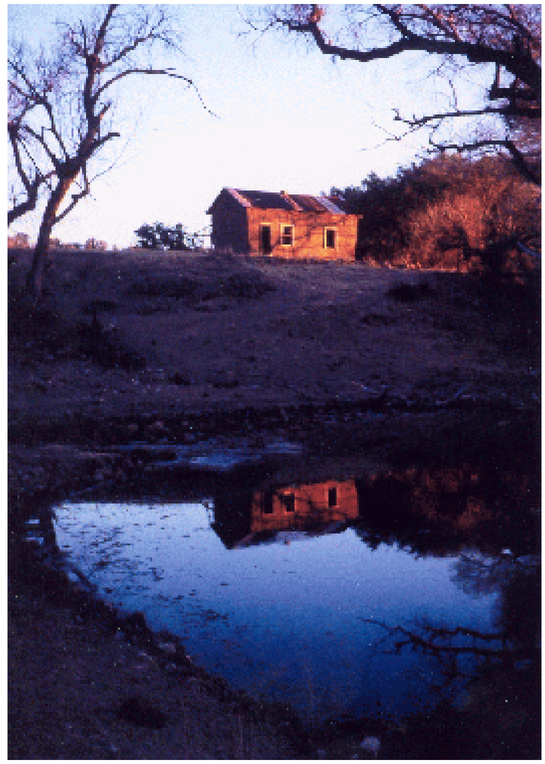


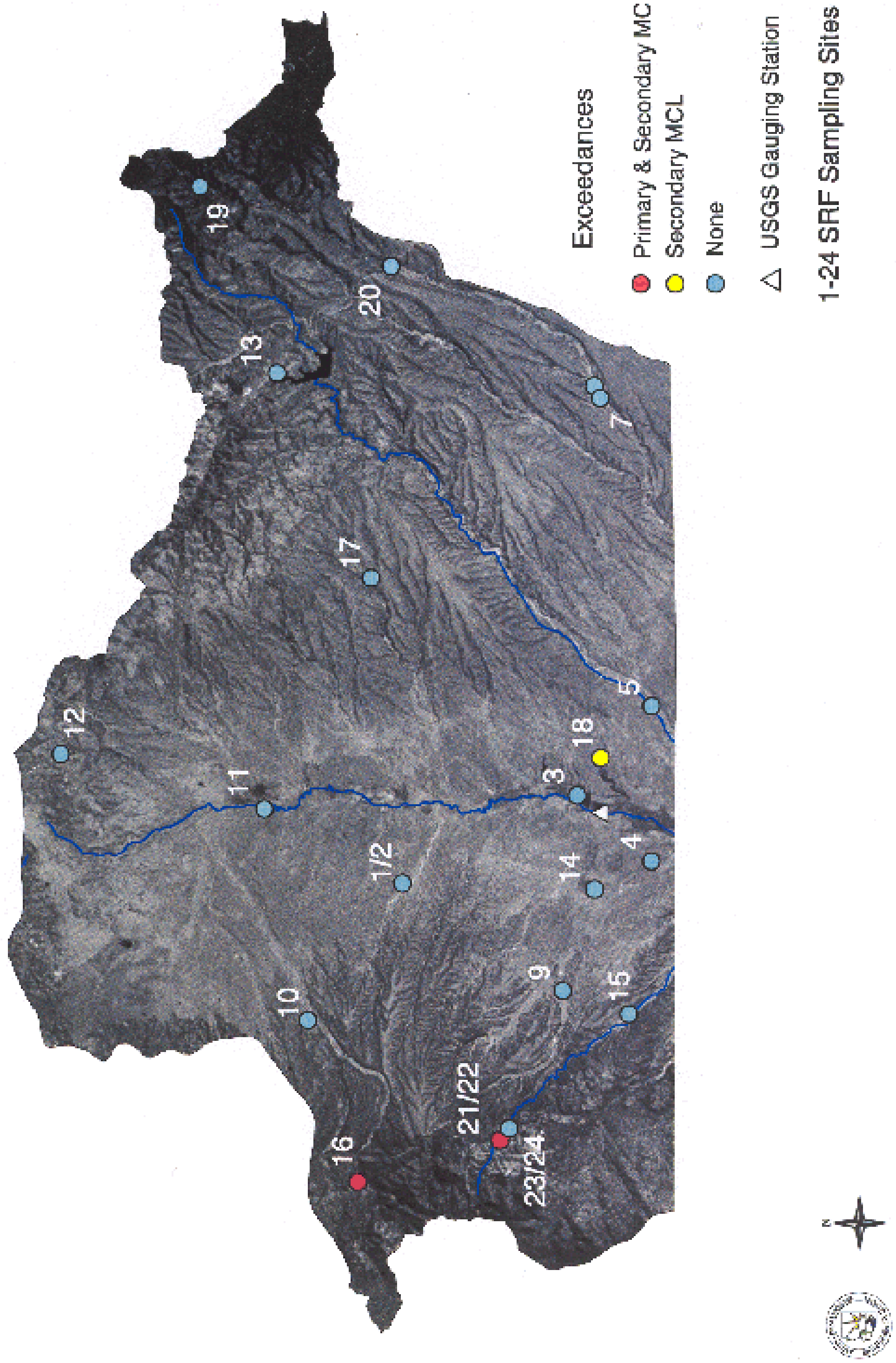
Figure 11. Overflow from Captain Spring quietly ponds forming a picturesque mirror image of a nearby abandoned homestead. Considered outcrops of groundwater, springs are often found near the base of a hill and are valuable sources are groundwater information in lightly-developed basins.

- 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.[34]

- State of Arizona **Aquifer Water-Quality Standards** apply to aquifers that are classified for drinking water protected use.[34] Currently all aquifers within Arizona are for drinking water use. These enforceable State standards are almost identical to the federal Primary MCLs.

- Federal SDW **Secondary MCLs**. These non-enforceable aesthetics-based guidelines define the maximum concentration of a constituent that can be present without imparting unpleasant taste, color, odor, or other aesthetic effect on the water.[34]

Figure 10 San Rafael Groundwater Basin Water Quality Exceedances and Sampling Sites



Water Quality Standard/Guideline Exceedances

Health-based Primary MCL water quality standards and State aquifer water quality standards were exceeded at 2 of 20 sites (10 percent) (**Figure 10**)(**Table 1**). Constituents above Primary MCLs include antimony (1 site), lead (1 site), gross alpha (1 site), and uranium (1 site). Potential health effects of these Primary MCL exceedances are also provided in **Table 1**.

Aesthetics-based Secondary MCL water quality guidelines were exceeded at 3 of 20 sites (15 percent) (**Table 2**)(**Figure 10**). Constituents above Secondary MCLs include: iron (1 site), manganese (2 sites), sulfate (2 sites), and TDS (2 sites).

Radon is a naturally occurring, intermediate breakdown product from the radioactive decay of uranium-238 to lead-206.[14] There are widely conflicting opinions on the risk assessment of radon in drinking water, with proposed drinking water standards varying from 300 piC/l to 4,000 piC/l.[14] Four of the five sites exceeded the 300 piC/l standard; none exceeded the 4,000 standard.

Figure 14. Groundwater in the SRB has both a low salinity and sodium hazard when used for irrigation. Farming is largely a subsidiary activity of livestock raising. This irrigation turnout and field is located in the floodplain of the Santa Cruz River. The river's terraces and the Huachuca Mountains are in the background.

Figure 13. The two sites having the vast majority of water quality standard exceedances are located in the Patagonia Mountains and may be effected by historic mining activities and the area's granitic geology.

Suitability for Irrigation

The suitability of groundwater at each sample site was assessed as to its suitability for irrigation use based on salinity and sodium hazards. With increasing salinity levels, leaching, salt tolerant plants, and adequate drainage are necessary. Excessive levels of sodium are known to cause physical deterioration of the soil.[35] Irrigation water may be classified using specific conductivity (SC) and the Sodium Adsorption Ratio (SAR) in conjunction with one another.[35] Groundwater sites in the SRF have both a low sodium hazard and a low salinity hazard when used for irrigation (**Figure 14**).

Analytical Results

Analytical inorganic and radiochemistry results of the 20 sample sites are summarized (**Table 3)** using the following indices: minimum reporting levels (MRLs), number of sample sites over the MRL, upper and lower 95 percent confidence intervals ($CI_{95\%}$), and the 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. Specific constituent information for each groundwater site is found in **Appendix B**.

Table 1. SRF Sites Exceeding Health-Based Water Quality Standards (Primary MCLs)

Constituent	Primary MCL	Sites Exceeding Primary MCLs	Concentration Range of Exceedances	Health Effects
Nutrients				
Nitrite (NO_2-N)	1.0	0	--	Methemoglobinemia
Nitrate (NO_3-N)	10.0	0	--	Methemoglobinemia
Trace Elements				
Antimony (Sb)	0.006	1	0.0145	Cancer
Arsenic (As)	0.05 0.01*	0 0	-- --	Dermal and nervous system toxicity
Barium (Ba)	2.0	0	--	Circulatory system damage
Beryllium (Be)	0.004	0	--	Bone and lung damage
Cadmium (Cd)	0.005	0	--	Kidney damage
Chromium (Cr)	0.1	0	--	Liver and kidney damage
Copper (Cu)	1.3	0		Liver & kidney damage
Fluoride (F)	4.0	0	--	Skeletal damage
Lead (Pb)	0.015	1	0.021	Development difficulties
Mercury (Hg)	0.002	0	--	Central nervous system disorders; kidney damage
Nickel (Ni)	0.1	0	--	Heart and liver damage
Selenium (Se)	0.05	0	--	Gastrointestinal damage
Thallium (Tl)	0.002	0	--	Gastrointestinal damage; liver, kidney, and nerve damage
Radiochemistry Constituents				
Gross Alpha	15 piC/l	1	21 piC/l	Cancer
Ra-226 + Ra-228	5 piC/l	0	--	Bone cancer
Uranium	30 Fg/l	1	30 Fg/l	Cancer & kidney toxicity

All units in mg/l except gross alpha, radium-226+228, and uranium.
* new arsenic primary MCL scheduled to be implemented in 2006
Source: [30 36]

Table 2. SRF Sites Exceeding Aesthetics-Based Water Quality Standards (Secondary MCLs)

Constituents	Secondary MCL	Sites Exceeding Secondary MCLs	Concentration Range of Exceedances	Aesthetic Effects
Physical Parameters				
pH - field	6.5 to 8.5	0	--	Corrosive water
General Mineral Characteristics				
TDS	500	2	795 - 1070 mg/l	Unpleasant taste
Major Ions				
Chloride (Cl)	250	0	--	Salty taste
Sulfate (SO_4)	250	2	295 - 490 mg/l	Rotten-egg odor, unpleasant taste, and laxative effect
Trace Elements				
Fluoride (F)	2.0	0	--	Mottling of teeth enamel
Iron (Fe)	0.3	1	0.75 mg/l	Rusty color, reddish stains, and metallic tastes
Manganese (Mn)	0.05	2	0.15 - 0.43 mg/l	Black oxide stains and bitter, metallic taste
Silver (Ag)	0.1	0	--	Skin discoloration and greying of white part of eye
Zinc (Zn)	5.0	0	--	Metallic taste

All units mg/l except pH is in standard units (su).
Source: [22 30 36]

Table 3. Summary Statistics for SRF Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Median	Mean	Upper 95% Confidence Interval	Mean of Santa Cruz River near Lochiel, Arizona
			Physical Parameters				
Temperature (ºC)	N/A	19	16.3	18.5	17.8	19.4	13.8
pH-field (su)	N/A	20	7.44	7.63	7.55	7.67	8.16
pH-lab (su)	0.01	20	7.24	7.30	7.34	7.44	8.26
Turbidity (ntu)	0.01	19	0.35	0.26	1.87	3.40	4.88
			General Mineral Characteristics				
Total Alkalinity	2.0	20	167	187	203	238	150
Phenol. Alkalinity	2.0	0		> 90% of data below MRL			
SC-field (FS/cm)	N/A	20	394	434	540	686	314
SC-lab (FS/cm)	N/A	20	407	440	540	673	315
Hardness-lab	10.0	20	170	180	247	323	147
Hardness-calculated	--	20	176	180	249	322	--
TDS	10.0	20	239	278	341	443	207
			Major Ions				
Calcium	5.0	20	58	60	79	99	47
Magnesium	1.0	20	7.3	8.5	13.2	19.1	7.1
Sodium	5.0	20	13	15	18	24	13
Potassium	0.5	20	1.3	1.5	1.6	1.9	2.6
Bicarbonate	2.0	20	204	230	247	290	172
Carbonate	2.0	0		> 90% of data below MRL			
Chloride	1.0	20	5.2	7.1	12.5	19.7	5.7
Sulfate	10.0	16	1	18	57	114	13.5
			Nutrients				
Nitrate (as N)	0.02	19	0.3	0.4	1.4	2.5	--
Nitrite (as N)	0.02	0		> 90% of data below MRL			--
Ammonia	0.02	1		> 90% of data below MRL			--
TKN	0.05	6	0.02	0.03	0.09	0.16	--
Total Phosphorus	0.02	7	0.013	0.010	0.028	0.043	--

All units mg/l except where noted with physical parameters   Source: [30]

Table 3. Summary Statistics for SRF Groundwater Quality Data--Continued

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Median	Mean	Upper 95% Confidence Interval	Mean of Santa Cruz River near Lochiel, Arizona
			Trace Elements				
Antimony	0.005	1		> 90% of data below MRL			--
Arsenic	0.01	1		> 90% of data below MRL			--
Barium	0.1	11	0.08	0.08	0.11	0.14	0.11
Beryllium	0.0005	0		> 90% of data below MRL			--
Boron	0.1	1		> 90% of data below MRL			--
Cadmium	0.001	0		> 90% of data below MRL			--
Chromium	0.01	0		> 90% of data below MRL			--
Copper	0.01	1		> 90% of data below MRL			--
Fluoride	0.20	14	0.17	0.23	0.22	0.28	0.27
Iron	0.1	2		> 90% of data below MRL			0.29
Lead	0.005	1		> 90% of data below MRL			--
Manganese	0.05	2		> 90% of data below MRL			0.06
Mercury	0.0005	0		> 90% of data below MRL			--
Nickel	0.1	0		> 90% of data below MRL			--
Selenium	0.005	0		> 90% of data below MRL			--
Silver	0.001	0		> 90% of data below MRL			--
Thallium	0.005	0		> 90% of data below MRL			--
Zinc	0.05	7	0.04	0.03	0.07	0.11	0.08
			Radiochemical Constituents				
Radon*	Varies	5	40	577	708	1376	--
Gross Alpha*	Varies	5	0.4	8.5	9.8	19.1	--
Gross Beta*	Varies	5	- 1.8	4.7	6.4	14.5	--
Ra-226*	Varies	3		> 90% of data below MRL			--
Uranium**	Varies	1		> 90% of data below MRL			--

All units mg/l except * = piC/l and ** = Fg/l

Santa Cruz River water quality data is a mean of 17 samples collected by ADEQ Surface Water Monitoring Unit between April 1990 and September 2001 at the U.S. Geological Survey gaging station (09480000) located 1.7 miles upstream from the international border. Source: [30]

VOC Results - Analytical results of the VOC samples collected at two sites revealed no detections at either site. None of the 35 VOC compounds on the EPA 601/602 VOC list, including the gasoline oxygenate, Methyl tertiary-Butyl Ether (MTBE), were detected at either site. Analytes on the EPA 601/602 VOC list is found in **Appendix C**.[6]

GROUNDWATER COMPOSITION

Groundwater in the SRF was characterized by qualitative classifications, chemistry, and cross-correlation of constituent concentrations.

General Summary - Groundwater in the SRF is generally *fresh*, *slightly alkaline*, and *hard* as indicated by TDS, pH, and hardness concentrations.

TDS concentrations (**Figure 15**) were considered *fresh* (below 1,000 mg/l) at 19 sites while 1 site was *slightly saline* (1,000 to 3,000 mg/l).[20] Levels of pH were *slightly alkaline* (above 7 SU) at 20 sites.[20] Hardness concentrations (**Figure 16**) were divided into *soft* (0 sites), *moderately hard* (4 sites), *hard* (11 sites), and *very hard* (5 sites).[15]

Nutrient concentrations were generally low with only nitrate (**Figure 16**), TKN, and total phosphorus detected at more than 10 percent of the sites. Nitrate (as nitrogen) concentrations were divided into *natural background* (8 sites at < 0.2 mg/l), *may or may not indicate human influence* (9 sites between 0.2 - 3.0 mg.l), *may result from human activities* (3 sites between 3.0 - 10 mg/l), and *probably result from human activities* (0 sites > 10 mg/l).[27]

Most trace elements such as antimony, arsenic, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium were rarely–if ever--detected. Only barium, fluoride, and zinc were detected at more than 10 percent of the sites.

Groundwater Chemistry - The chemical composition of sampled sites is illustrated using Piper trilinear diagrams (**Figure 17**):

- The cation triangle diagram (lower left in **Figure 17**) shows that the dominant (> 50 percent) cation is calcium at all 19 sites, sodium at 0 sites, magnesium at 0 sites, and is mixed at 1 site.

- The anion triangle diagram (lower right in **Figure 17**) shows that the dominant anion (> 50 percent) is bicarbonate at 18 sites, sulfate at 1 site, chloride at 0 sites, and is mixed at 1 site.

- The cation-anion diamond diagram (in center of **Figure 17**) shows that the groundwater chemistry is *calcium-bicarbonate* at 19 sites, *sodium-bicarbonate* at 0 sites, *calcium-sulfate* at 1 site, and *sodium-sulfate* at 0 sites.

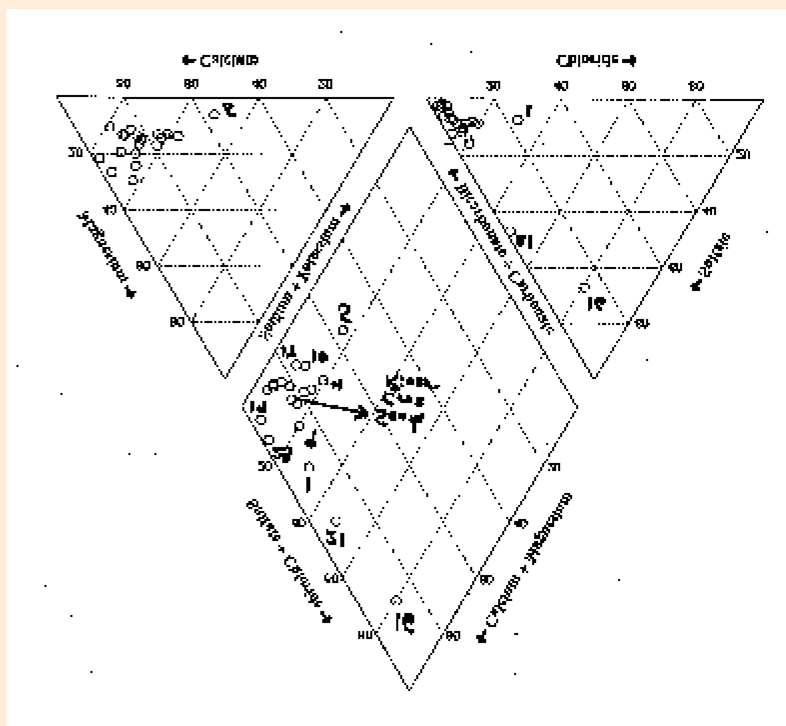


Figure 17. The majority of groundwater samples in the SRF–as well as the surface water sample from the Santa Cruz River--are of a calcium-bicarbonate water chemistry, which is typical of recharge areas in Arizona.[31] Only two samples (#16 and #21) collected in the Patagonia Mountains with elevated concentrations of sulfate, which may be impacted by historic mining operations, fall outside the cluster of calcium-bicarbonate samples.[23]

Figure 15 -TDS and Sulfate Levels In The San Rafael Groundwater Basin

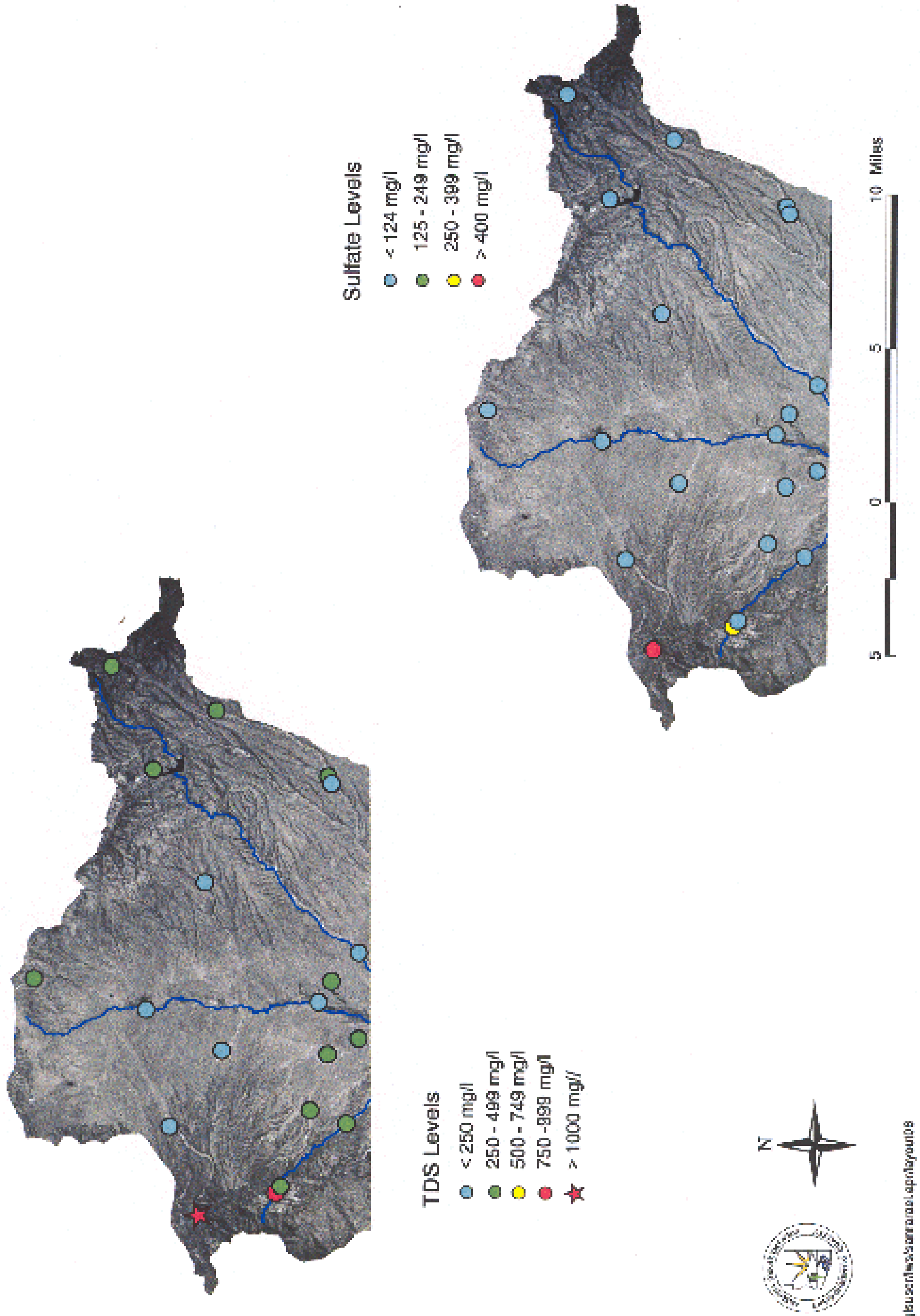
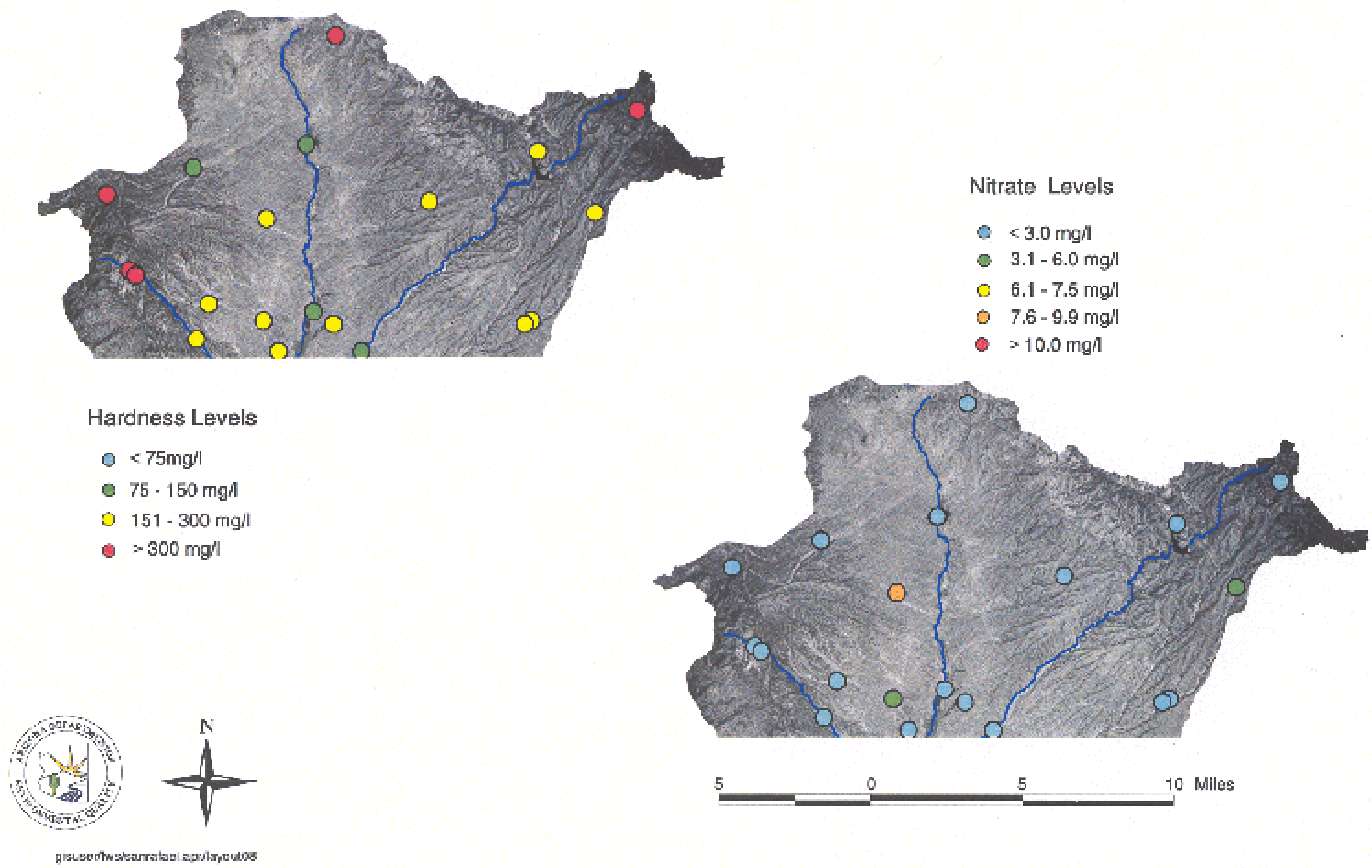


Figure 16 -Hardness and Nitrate Levels in the San Rafael Groundwater Basin



Constituent Covariation - The covariation of constituent concentrations from random sites were determined to scrutinize the strength of the association. 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. A ***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 an inverse relationship.

Many significant correlations occurred among the 20 SRF sites. Generally, major ions (calcium (**Figure 18**), magnesium, sodium, chloride, and sulfate) as well as TDS (**Figure 19**), SC, hardness, and turbidity were positively correlated. Four unique patterns emerged, many involving constituents with Primary MCL exceedances (Pearson Correlation Coefficient test, p# 0.05):

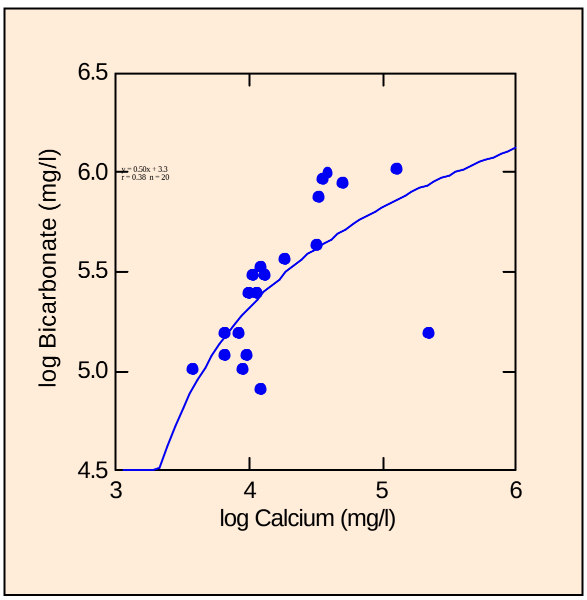


Figure 18, Calcium and bicarbonate, the predominant cation and anion in SRF groundwater have a positive biphasic relationship. The only site that isn't along the regression curve is strongly influenced by elevated sulfate concentrations probably resulting from nearby historic mines.

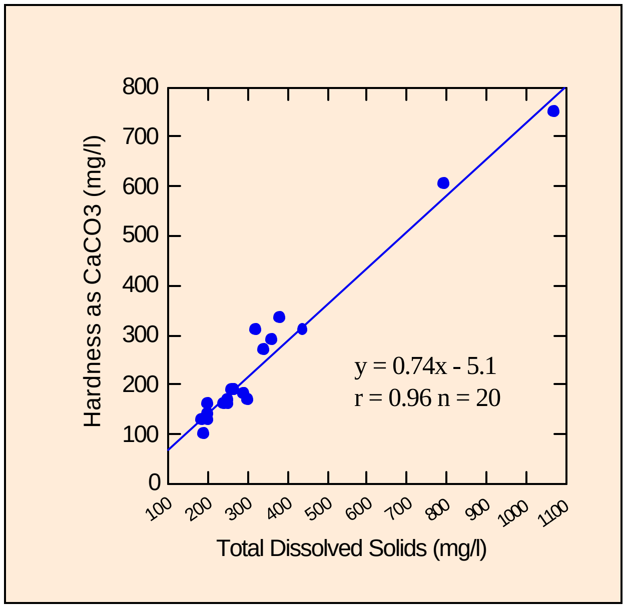


Figure 19. Total dissolved solids or TDS and hardness have a strong positive correlation (Pearson Correlation Coefficient, p # 0.01). This relationship indicates that sodium is a relatively minor cation in SRF groundwater.

- Barium was positively correlated with bicarbonate and total alkalinity.
- Zinc was positively correlated with turbidity and negatively correlated with bicarbonate and total alkalinity.
- Fluoride was positively correlated with both TKN and oxygen^{18} and negatively correlated with temperature.
- Temperature was negatively correlated with fluoride, TKN, total phosphorus, deuterium, and oxygen^{18} .
- pH-field was negatively correlated with bicarbonate and total alkalinity.
- Bicarbonate and total alkalinity were positively correlated with calcium, hardness, TKN, and barium, and negatively correlated with pH-field and zinc.

GROUNDWATER QUALITY PATTERNS

Groundwater in the SRF was characterized by assessing the spatial variation of groundwater quality among aquifers, watersheds, and rock types.

Aquifer Comparison - The SRF may be thought of as composed of two water-bearing units: an *alluvial aquifer* composed of undifferentiated alluvium consisting of gravel, sand, silt, and clay of the San Rafael Valley and, where sufficiently fractured or faulted, mountain *hardrock* composed of volcanic, granitic, metamorphic, or sedimentary rock with very limited water production potential.[5, 28]

Analytical results were compared between these two water-bearing units to examine for significant differences in concentrations of groundwater quality constituents. No significant differences were found (Kruskal-Wallis test, p # 0.05).

Watershed Comparison - The SRF is composed of three major drainages: the Santa Cruz River in the central basin, Parker Canyon to the east, and Duquesne Wash to the west.

Analytical results were compared between these three watersheds to examine for significant differences in concentrations of groundwater quality constituents. Only sodium (**Figure 20**) had a significant watershed relationship with higher concentrations found in Parker Canyon than the Santa Cruz River (Kruskal-Wallis test in conjunction with the Tukey test, p # 0.05).

Geological Comparison - The SRF can be divided into four geologic classifications (**Figure 9**):[5, 28]

< **Sedimentary Rock** - composes the majority of the SRF.

< **Volcanic Rock** - includes portions of the Canelo Hills, Saddle Mountain, Huachuca Mountains, and the Patagonia Mountains.

< **Granitic Rock** - includes portions of the Patagonia Mountains.

< **Alluvium** - includes an area downgradient of Saddle Mountain and another downgradient of the town of Duquesne.

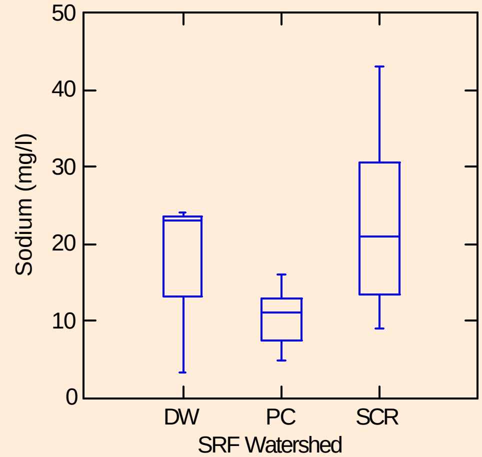


Figure 20. Sodium concentrations are significantly higher at sites in the Santa Cruz River watershed than at sites in Parker Canyon (Kruskal-Wallis test in conjunction with the Tukey test, p # 0.05). The greater recharge occurring in the higher elevations of the Huachuca Mountains probably contributes to this relationship.

Analytical results were again examined for differences in concentrations of groundwater quality constituents among the four geologic classifications. No significant patterns were revealed with this geological comparison (Kruskal-Wallis test, p# 0.05).

Isotope Comparison - Groundwater characterizations 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.[13]

These characterizations are done by comparing oxygen-18(d^{18}O) and deuterium (dD) data to the Global Meteoric Water Line. The Global Meteoric Water Line (GMWL) is described by the linear equation: dD = 8d^{18}O - 10 where dD is deuterium in parts per thousand per mil ($^{0}/_{00}$), 8 is the slope of the line, d^{18}O is oxygen-18 $^{0}/_{00}$, and 10 is the y-intercept.[13] The GMWL is the standard by which water samples are compared and represents the best fit isotopic analysis of thousands of water samples from around the world.

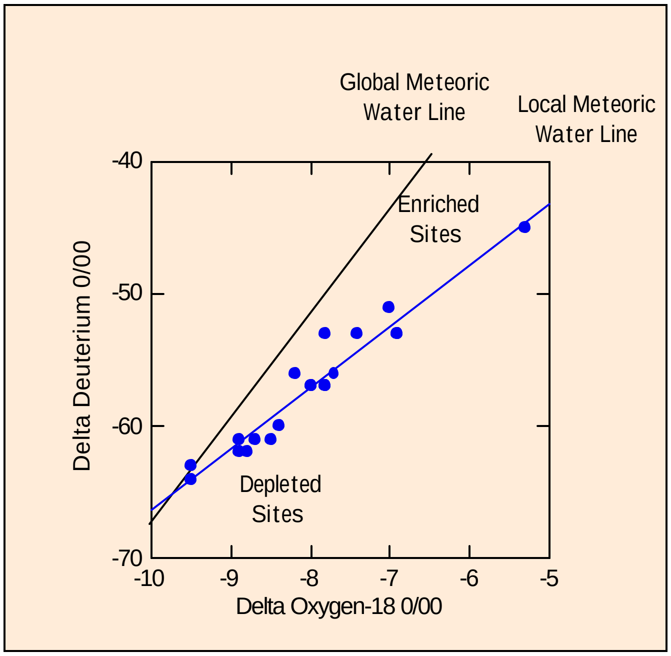


Figure 21. Stable isotopes of oxygen and hydrogen (deuterium) form a Local Meteoric Water Line (*D = 4.6 *^{18}O - 19.9). The most depleted, or isotopically lighter, sites tend to be at sites in the Huachuca and Patagonia Mountains; whereas, the most enriched, or isotopically heaviest, sites tend to be at lower elevations.

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 of the local water.[13]

The LMWL created by d^{18}O and dD values for samples collected at sites in the SRF, were compared to the GMWL. Most of the dD and d^{18}O data lie to the right of the GMWL (**Figure 21**). Meteoric waters exposed to evaporation 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.[13] Groundwater from arid environments is typically subject to evaporation which enriches dD and d^{18}O resulting in a lower slope value (usually between 3 and 6) as compared to the slope of 8 associated with the GMWL.[13] The data for the arid SVGB conform to this theory, having a slope of 4.6, with the LMWL described by the linear equation: dD = 4.6^{18}O - 19.9. The intersection of the LMWL with the GMWL is thought to indicate the location of the original un-evaporated composition of the water.

The most *depleted*, or isotopically lighter sites were at high elevations in the Huachuca Mountains. These *depleted* sites are both above the GMWL that is the start of the evaporation trajectory. These sites (a spring and a windmill) may be from recent local precipitation and are less subject to evaporation than other sites in the basin. The Huachuca Mountains are the highest in the SRF and have the greatest precipitation and logically, the most recharge to the basin. Other *depleted* sites were at lower sites receiving Huachuca Mountain recharge or at locations in the Patagonia Mountains. The two sites that did not follow this pattern were Collins Spring (SRF-13) in the Huachuca Mountains and a deep well (SRF-23/24) in the Patagonia Mountains that were more enriched than would be expected from the other SRF data. These sites may produce water from deeper sources and may be little effected by recent local precipitation.

In contrast, the most *enriched*, or isotopically heaviest, site (SRF–18) was a spring along the Santa Cruz River near Mexico. Generally, most samples within the central portion of the SRF, including the sample from the Santa Cruz River itself (SRF-25 at the USGS Gaging Station), were also *enriched*. *Enriched* and *depleted* d^{18}O and dD values were compared to examine for significant differences. Using a Kruskal-Wallis test combined with a Tukey test, significant (p#0.01) spatial differences were found in the d^{18}O and dD values.

CONCLUSIONS

Groundwater Suitability for Domestic Use

Two sites (or 10 percent of sites) had at least one constituent exceeding a health-based, Primary MCL standard. Primary MCL exceedances involving gross alpha, uranium, antimony, and lead were all at sites located in the Patagonia Mountains. Similarly, three sites (or 15 percent of sites) had at least one constituent exceeding an aesthetics-based, SDW Secondary MCL guideline. Two of these were also the same sites that had Primary MCL exceedances. TDS and sulfate exceeded Secondary MCL in the sites located in the Patagonia Mountains with iron and manganese also exceeding aesthetic standards in one well. A spring near the Santa Cruz River also had manganese concentrations exceeding Secondary MCLs.

Based upon comparing the results of this regional study with water quality standards/guidelines, groundwater in the SRF appears to be largely suitable for domestic purposes. Only sites in the Patagonia Mountains, a highly mineralized and subsequently mined range, had samples that did not meet water quality standards.

The elevated radiochemical constituents may be impacted by the granitic geology in the area with one site having gross alpha and uranium concentrations over health-based water quality standards.[23 26] These constituents may be further elevated by the extensive hardrock mining in the area that has increased rock surface exposure.

The antimony and lead exceedances are more problematic since, in particular, the natural occurrence of lead in groundwater is very rare.[22] These trace elements were confirmed by a split sample conducted at the site with both the ADHS and Del Mar laboratories detecting the constituents at similar concentrations. Lead contamination in drinking water is usually attributable to plumbing corrosion.[22] The elevated alkalinity at this site (the highest of any SRF groundwater site) is indicative of high concentrations of carbon dioxide gases which can promote corrosion of plumbing and the occurrence of lead.[22] A more likely explanation is the weathering of ore deposits which often proudces increased metal concentrations in groundwater.[23] Lead, along with silver, zinc, copper, manganese, and lead were the metals chiefly mined in the SRF.[19]

The quality of groundwater pumped at SRF-1/2, a shallow (100 feet in depth) windmill with groundwater about 60 feet bls, may be impacted by either animal waste from an adjoining corral or septage from a nearby house. The nitrate concentration of two split samples from this well were both just below the health-based water quality standard of 10 mg/l. Nitrate and chloride concentrations each exceeded the 95 percent confidence intervals established for the SRF. These constituents, both indicators of wastewater impacts, support this conclusion.[9 27] The site is situated in the *White House* soil series that has *severe* limitations for use in septic tank adsorption fields also supports this conclusion.[29]

Groundwater Basin Overview

Overall, groundwater in the SRF is remarkably uniform as evidenced by the narrow 95 percent confidence intervals for most constituents with the exception of sulfate. Groundwater may be considered generally *fresh*, *slightly alkaline*, and *hard* based on TDS, pH, and hardness concentrations.[15 20] The basin's predominant *calcium-bicarbonate* groundwater chemistry is common in Arizona and typical of recharge areas.[31] The two *calcium-sulfat*e sites were both located in the Patagonia Mountains and are probably influenced by nearby historic mining activity which often elevates concentrations of sulfate in the groundwater.[23]

The SRF appears to be an *open hydrologic system* or one in which groundwater chemistry is in part controlled or influenced by atmospheric gases or liquids that enter the system along flow paths subsequent to initial recharge.[31] This statement is supported by the predominant *calcium-bicarbonate* chemistry, the shallow depths to groundwater, and permeable alluvial deposits found in the SRF. These factors suggest that recharge occurs not only along mountain fronts in the basin but also along the Santa Cruz River and its major tributaries.

Constituent concentrations in the surface flow of the Santa Cruz River (a mean of 17 samples) tend to be below the lower 95 percent confidence interval established from the 20 groundwater sites. This pattern is especially applicable with general mineral characteristics, major ions, and nutrients. This relationship may be explained as the dilution of the stream's base flow by direct runoff from precipitation events.[22] The Santa Cruz River's base flow consists of groundwater infiltrating into the channel and they should both have a similar chemical composition. Direct runoff should have a lower TDS concentration than the base flow and with very high precipitation and stream flow rates, the surface water may be nearly as dilute as rainwater.[22]

Trace elements above ADHS laboratory MRLs were seldom encountered in SRF groundwater samples. Barium, fluoride, and zinc were the most common trace elements and these were always below water quality standards. This supports the findings of a previous 1984 report in which concentrations of fluoride were also below water quality standards.[28]

Of particular interest was the laboratory analyses for the trace element, mercury which has been found in the tissue of warm-water species of fish in Parker Canyon Lake.[32] Mercury was not detected above the ADHS laboratory MRL of 0.0005 in any of the 20 groundwater samples, including the sample from Collins Spring located just upgradient of the Parker Canyon Lake.

Study Design and Data Evaluation

The 20 groundwater sample sites were selected using a systematic, grid-based, random site-selection approach. The sample collection methods for this study conformed to the *Quality Assurance Project Plan*[2] and the *Field Manual for Water Quality Sampling*.[8]

Quality assurance procedures were followed and quality control samples were collected to ensure the validity of the groundwater quality data. Analysis of equipment blank samples indicated systematic contamination of SC-lab and turbidity; however, the extent of the contamination by these parameters was not considered significant. Analysis of duplicate samples revealed excellent correlations of less than 5 percent with only turbidity analyses having a wide median difference of 29 percent. Similarly, analysis of split samples showed the maximum difference between split constituents rarely exceeded 20 percent. Data validation was also examined in five QA/QC correlations that affirmed the acceptability of the groundwater quality data for further analysis. Overall, the effects of sampling procedures and laboratory methods on the data were not considered significant.

Data analysis for this study was conducted using Systat software.[37] The non-normality of both non-transformed data and log-transformed data was determined by using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.[11] Spatial variations in constituent concentrations were investigated using the non-parametric Kruskal-Wallis test in conjunction with the Tukey test.[21] Correlations among constituent concentrations were analyzed using the Pearson Correlation Coefficient test.[21]

RECOMMENDATIONS

Recommendations for domestic well owners are provided in this section. These are based on interpretations of the analytical results from groundwater samples collected for this study.

The following recommendations are provided for domestic well owners in the SRF.

< ADEQ encourages well owners concerned about their water supply to periodically collect samples, with the assistance of certified laboratories, for analysis of the full range of groundwater quality constituents. The ADHS, Environmental Laboratory Licensure and Certification Section at (602) 255-3454 provides a list of certified labs.

< Well owners in the vicinity of the Patagonia Mountains should be particularly vigilante in determining if their supply meets water quality standards. Health-based water quality exceedances may exist in other areas of the SRF; however, based upon the results of this regional groundwater quality report, their occurrence should not be widespread in nature. Again, it should be noted for full assurance that groundwater pumped by a private well meets all water quality standards for domestic use, tests should be conducted on a wide range of groundwater quality constituents.

< ADEQ encourages well owners to inspect and, if necessary, repair faulty surface seals, degraded casing, or other factors that may affect well integrity. Septic systems should also be inspected periodically to assure safety and compliance with ADEQ's *Engineering Bulletin #12*.[1]

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Appendix A. Data for Sample Sites, San Rafael Basin, 2002

Site #	Cadastral	Latitude - Longitude	ADWR #	ADEQ #	Samples Collected	Well Depth	Water Depth	Geology / Watershed
				1st Field Trip, February 26 - 28, 2002 - Towne & Boettcher (Equipment Blank, SRF-8)				
SRF-1/2	(D-23-17)27bbc	31°24'17.824" 110°36'40.079"	602669	43833	Inorganic O, H isotopes	100'	63'	Sedimentary Santa Cruz River
SRF-3	(D-24-17)11dbb	31°21'32.552" 110°35'03.671"	602650	59765	Inorganic O, H isotopes	240'	8'	Sedimentary Santa Cruz River
SRF-4	(D-24-17)15cdc	31°20'22.990" 110°36'16.501"	602274	44250	Inorganic, Radon, VOC, O, H isotopes	37'	29'	Sedimentary Santa Cruz River
SRF-5	(D-24-18)18abd	31°20'22.059" 110°33'25.311"	601963	59532	Inorganic, Radon O, H isotopes	70'	40'	Sedimentary Parker Canyon
SRF-6	(D-24-19)07ccb	31°21'14.617" 110°27'31.920"	635371	59533	Inorganic, Radon O, H isotopes	25'	16'	Sedimentary Parker Canyon
SRF-7	(D-24-18)13aba	31°21'09.160" 110°27'45.668"	--	59534	Inorganic O, H isotopes	Captain Spring	Captain Spring	Sedimentary Parker Canyon
SRF-9	(D-24-17)08bcb	31°21'47.174" 110°38'39.570"	608254	59536	Inorganic O, H isotopes	1572'	145'	Sedimentary Santa Cruz River
SRF-10	(D-23-17)18dbc	31°25'48.044" 110°39'11.171"	804662	59535	Inorganic, Radon O, H isotopes	450'	--	Sedimentary Santa Cruz River
SRF-11	(D-23-17)11cdd	31°26'28.180" 110°35'17.042"	624903	59766	Inorganic	137'	--	Alluvium Santa Cruz River
SRF-12	(D-22-17)25bda	31°29'40.725" 110°34'15.003"	630082	43345	Inorganic, Radiochem O, H isotopes	--	--	Volcanic Santa Cruz River
SRF-13	(D-23-19)18bab	31°26'13.991" 110°27'15.835"	--	59503	Inorganic O, H Isotopes	Collins Spring	Collins Spring	Volcanic Parker Canyon
SRF-14	(D-24-17)09ddd	31°21'16.753" 110°36'47.317"	602655	44238	Inorganic VOC	34'	17'	Sedimentary Santa Cruz River
SRF-15	(D-24-17)18acc	31°20'44.831" 110°39'05.735"	608265	59501	Inorganic	600'	200'	Sedimentary Duquesne Wash
SRF-16	(D-23-16)22bbb	31°25'01.776" 110°42'09.456"	641621	59502	Inorganic, Radiochem O, H isotopes	--	--	Granitic Santa Cruz River
				2nd Field Trip, March 12-14, 2002 - Towne & Rodin				
SRF-17	(D-23-18)21dcd	31°24'46.056" 110°31'02.803"	--	59531	Inorganic O, H isotopes	Palmoa Spring	Paloma Spring	Volcanic Santa Cruz River
SRF-18	(D-24-17)14aaa	31°21'10.298" 110°34'22.261"	--	59537	Inorganic O, H isotopes	Sharps Spring	Sharps Spring	Sedimentary Santa Cruz River
SRF-19	(D-23-19)03dbd	31°27'25.707" 110°23'49.282"	--	43848	Inorganic, Radiochem O, H isotopes	Peterson Spring	Peterson Spring	Volcanic Parker Canyon
SRF-20	(D-23-19)28bbd	31°24'25.524" 110°25'18.773"	612480	43856	Inorganic O, H isotopes	120'	--	Sedimentary Parker Canyon
				3rd Field Trip, May 9, 2002 - Towne &Harmon (Equipment Blank, SS-14)				
SRF-21/22	(D-24-16)02cab	31°22'46.999" 110°41'24.285"	581092	59764	Inorganic, Radiochem Radon, O, H isotopes	110'	80'	Sedimentary Duquesne Wash

Appendix A. Data for Sample Sites, San Rafael Basin, 2002–Continued

Site #	Cadastral	Latitude - Longitude	ADWR #	ADEQ #	Samples Collected	Well Depth	Water Depth	Geology / Watershed
				4th Field Trip, May 31, 2002 - Towne &Harmon (Equipment Blank, SS-42)				
SRF-23/24	(D-24-16)02bac	31°22'38.413" 110°41'11.355"	574831	59791	Inorganic, Radiochem O, H isotopes	440'	420'	Sedimentary Duquesne Wash

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002

Site #	MCL Exceedances	Temp (°C)	pH-field (su)	pH-lab (SU)	SC-field (FS/cm)	SC-lab (FS/cm)	TDS (mg/l)	Hardness (mg/l)	Total Alk (mg/l)	Turbidity (ntu)
SRF-1/2	--	19.21	7.86	*7.3*	433	420	265	190	120	*0.90*
SRF-3	--	19.55	7.29	*6.9*	327	330	185	130	150	*0.28*
SRF-4	--	19.45	7.17	*7.5*	497	500	290	180	202	*4.8*
SRF-5	--	21.12	7.74	*7.3*	328	330	200	140	*130*	*0.17*
SRF-6	--	-	7.44	*7.2*	424	440	260	190	210	*0.18*
SRF-7	--	14.17	7.65	*7.3*	350	350	200	160	180	*0.14*
SRF-9	--	21.01	7.74	*7.7*	367	370	250	160	150	*3.7*
SRF-10	--	22.45	7.89	*7.4*	293	290	190	100	120	*3.7*
SRF-11	--	18.42	7.77	*7.6*	323	330	200	130	130	*0.10*
SRF-12	--	18.53	7.09	*7.5*	720	730	440	310	320	*1.1*
SRF-13	--	13.70	7.44	*7.6*	403	410	250	170	193	*0.23*
SRF-14	--	15.00	7.60	*7.5*	457	470	290	180	180	*0.17*
SRF-15	--	18.73	7.78	*7.5*	434	440	300	170	120	*4.0*
SRF-16	TDS, SO_4, Fe, Mn, gross a, uranium	16.73	7.50	*7.2*	1637	1450	**1070**	750	150	*14*
SRF-17	---	15.76	7.75	*7.0*	409	410	240	160	200	0.16
SRF-18	Mn	9.13	7.70	*7.4*	596	600	360	290	330	2.0
SRF-19	--	18.25	7.57	*7.2*	572	590	320	310	290	1.6
SRF-20	--	17.9	7.65	*7.3*	573	590	340	270	230	0.16
SRF-21/22	TDS, SO_4, Sb, Pb	18.9	7.17	7.15	1042	1100	**795**	605	340	ND
SRF-23/24	--	20.8	7.22	7.25	619	655	380	335	310	0.035

bold = constituent level exceeds Primary or Secondary MCL
italics = constituent exceeded holding time
* = concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002--Continued

Site #	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	SAR (value)	Potassium (mg/l)	Bicarbonate (mg/l)	Carbonate (mg/l)	Chloride (mg/l)	Sulfate (mg/l)
SRF-1/2	60	9.9	9.1	0.27	1.9	135	ND	26.5	11.5
SRF-3	46	6.1	14	0.51	2.2	180	ND	4.3	11
SRF-4	60	8.7	35	1.12	1.0	250	ND	20	21
SRF-5	54	3.8	7.6	0.27	1.9	160	ND	5.1	18
SRF-6	72	5.8	11	0.34	0.83	260	ND	3.4	ND
SRF-7	55	6	11	0.38	0.55	220	ND	4	ND
SRF-9	51	9.2	12	0.41	1.5	180	ND	6.3	28
SRF-10	36	4.7	18	0.75	1.3	150	ND	4.2	10
SRF-11	46	5.4	13	0.48	1.5	160	ND	8.3	13
SRF-12	96	16	38	0.95	2.5	390	ND	15	38
SRF-13	62	6	16	0.52	1.4	240	ND	7.3	ND
SRF-14	58	8.2	26	0.85	1.5	220	ND	15	17
SRF-15	52	8.3	23	0.78	1.7	150	ND	8.2	73
SRF-16	210	48	43	0.70	1.8	180	ND	72	**490**
SRF-17	56	7	24	0.80	2.4	240	ND	6.3	9.5
SRF-18	99	11	21	0.53	2.3	400	ND	9.2	ND
SRF-19	92	21	4.8	0.12	0.65	354	ND	3.7	19
SRF-20	91	12	13	0.34	2.6	280	ND	20	29
SRF-21/22	165	47	24	0.43	1.35	410	ND	6.9	**295**
SRF-23/24	110	19	3.3	0.08	0.88	380	ND	3.7	43

bold = constituent level exceeds Primary or Secondary MCL

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002--Continued

Site #	Nitrate-Nitrite-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Total Phosphorus (mg/l)
SRF-1/2	9.5	9.5	*ND*	ND	ND	ND
SRF-3	0.28	0.28	*ND*	ND	ND	0.068
SRF-4	0.056	0.056	*ND*	ND	ND	ND
SRF-5	2.6	2.6	*ND*	ND	ND	ND
SRF-6	0.44	0.44	*ND*	ND	ND	ND
SRF-7	0.16	0.16	*ND*	0.052	ND	ND
SRF-9	0.39	0.39	*ND*	ND	ND	ND
SRF-10	0.18	0.18	*ND*	ND	ND	ND
SRF-11	1.8	1.8	*ND*	ND	ND	ND
SRF-12	0.95	0.95	*ND*	ND	ND	0.030
SRF-13	0.13	0.13	*ND*	ND	ND	0.028
SRF-14	3.2	3.2	*ND*	ND	ND	ND
SRF-15	0.53	0.53	*ND*	ND	ND	ND
SRF-16	1.7	1.7	*ND*	0.11	ND	ND
SRF-17	0.094	0.094	*ND*	ND	ND	0.037
SRF-18	0.024	0.024	*ND*	0.52	ND	0.12
SRF-19	0.38	0.38	*ND*	0.23	ND	0.055
SRF-20	5.0	5.0	*ND*	0.054	ND	0.090
SRF-21/22	ND	ND	*ND*	0.49	0.26	ND
SRF-23/24	0.18	0.18	*ND*	ND	ND	ND

bold = constituent level exceeds Primary or Secondary MCL
italics = constituent exceeded holding time

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002--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)
SRF-1/2	ND	ND	0.175	ND	ND	ND	ND	ND	0.265
SRF-3	ND	ND	ND	ND	ND	ND	ND	ND	0.27
SRF-4	ND	ND	0.16	ND	ND	ND	ND	ND	0.25
SRF-5	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-6	ND	ND	0.12	ND	ND	ND	ND	ND	0.21
SRF-7	ND	ND	0.10	ND	ND	ND	ND	ND	0.23
SRF-9	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-10	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-11	ND	ND	0.14	ND	ND	ND	ND	ND	0.23
SRF-12	ND	ND	0.25	ND	ND	ND	ND	ND	0.26
SRF-13	ND	ND	ND	ND	ND	ND	ND	ND	0.33
SRF-14	ND	ND	ND	ND	ND	ND	ND	ND	0.27
SRF-15	ND	ND	ND	ND	ND	ND	ND	ND	0.21
SRF-16	ND	ND	ND	ND	ND	ND	ND	ND	0.31
SRF-17	ND	ND	0.084	ND	ND	ND	ND	ND	ND
SRF-18	ND	ND	0.18	ND	ND	ND	ND	ND	0.52
SRF-19	ND	ND	0.28	ND	ND	ND	ND	ND	ND
SRF-20	ND	ND	0.18	ND	ND	ND	ND	ND	ND
SRF-21/22	**0.0145**	0.0052	0.080	ND	0.21	ND	ND	0.011	0.36
SRF-23/24	ND	ND	ND	ND	ND	ND	ND	ND	0.14

bold = constituent level exceeds Primary or Secondary MCL
***** = concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002--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)
SRF-1/2	ND	ND	ND	ND	ND	ND	ND	ND	0.16
SRF-3	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-4	0.19	ND	ND	ND	ND	ND	ND	ND	0.16
SRF-5	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-6	ND	ND	ND	ND	ND	ND	ND	ND	0.18
SRF-7	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-9	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-10	ND	ND	ND	ND	ND	ND	ND	ND	0.22
SRF-11	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-12	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-13	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-14	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-15	ND	ND	ND	ND	ND	ND	ND	ND	0.21
SRF-16	**0.75**	ND	**0.15**	ND	ND	ND	ND	ND	0.15
SRF-17	ND	ND	ND	ND	ND	ND	ND	ND	0.061
SRF-18	ND	ND	**0.43**	ND	ND	ND	ND	ND	ND
SRF-19	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-20	ND	ND	ND	ND	ND	ND	ND	ND	ND
SRF-21/22	ND	**0.021**	ND	ND	ND	ND	ND	ND	ND
SRF-23/24	ND	ND	ND	ND	ND	ND	ND	ND	ND

bold = constituent level exceeds Primary or Secondary MCL

Appendix B. Groundwater Quality Data, San Rafael Basin, 2002–Continued

Sample #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	Ra-226 (pCi/L)	Uranium (µg/l)	VOCs (µg/l)	d[18] O ($^{0}/_{00}$)	d D ($^{0}/_{00}$)	Type of Chemistry
SRF-1/2	--	--	--	--	--	--	- 8.2	- 56	calcium-bicarbonate
SRF-3	--	--	--	--	--	--	- 7.8	- 57	calcium-bicarbonate
SRF-4	577+/-59	--	--	--	--	ND	- 7.8	- 57	calcium-bicarbonate
SRF-5	448+/-47	--	--	--	--	--	- 7.4	- 53	calcium-bicarbonate
SRF-6	190+/-21	--	--	--	--	--	- 8.7	- 61	calcium-bicarbonate
SRF-7	--	--	--	--	--	--	- 8.4	- 60	calcium-bicarbonate
SRF-9	--	--	--	--	--	--	- 8.8	- 62	calcium-bicarbonate
SRF-10	718+/-73	--	--	--	--	--	- 8.9	- 62	calcium-bicarbonate
SRF-11	--	--	--	--	--	--	- 8.0	- 57	calcium-bicarbonate
SRF-12	--	8.5 +/- 1.4	4.7 +/- 0.9	048 +/- .12	--	--	- 6.9	- 53	calcium-bicarbonate
SRF-13	--	--	--	--	--	--	- 7.7	- 56	calcium-bicarbonate
SRF-14	--	--	--	--	--	ND	--	--	calcium-bicarbonate
SRF-15	--	--	--	--	--	--	- 8.0	- 57	calcium-bicarbonate
SRF-16	--	**21 +/- 1.3**	17 +/- 1.2	1.3 +/- .16	**30 +/- 2.4**	--	- 8.5	- 61	calcium-sulfate
SRF-17	--	--	--	--	--	--	- 7.0	- 51	calcium-bicarbonate
SRF-18	--	--	--	--	--	--	- 5.3	- 45	calcium-bicarbonate
SRF-19	--	2.8 +/- 0.9	< 1.3	--	--	--	- 9.5	- 63	calcium-bicarbonate
SRF-20	--	--	--	--	--	--	- 9.5	- 64	calcium-bicarbonate
SRF-21/22	1605 +/- 162	13 +/- 0.84	7.8 +/- 0.98	0.77 +/- 0.14	--	--	- 8.9	- 61	calcium-mixed
SRF-23/24	--	3.5 +/- 1.1	1.7 +/- 0.84	--	--	--	- 7.8	- 53	calcium-bicarbonate
SRF-25	--	--	--	--	--	--	- 6.9	- 53	calcium-bicarbonate

bold = Primary MCL Exceedance
LLD = Lower Limit of Detection
italics = constituent exceeded holding time

Appendix C. 601/602 Volatile Organic Compounds (VOCs) Analyte List

Benzene	cis-1,2-Dichloroethene *
Bromodichloromethane	trans-1,2-Dichlorothene
Bromoform	1,2-Dichloropropane
Bromomethane	cis-1,3-Dichloropropene
Carbon Tetrachloride	trans-1,3-Dichloropropene
Chlorobenzene	Ethylbenzene
Chloroethane	Methylene Chloride
Chloroform	Methyl-t-butyl ether (MTBE) *
Chloromethane	1,1,2,2-Tetrachloroethane
Dibromochloromethane	Tetrachloroethene
1,2-Dichlorobenzene	Toluene
1,3-Dichlorobenzene	1,1,1-Trichloroethane
1,4-Dichlorobenzene	1,1,2-Trichloroethane
Dichlorodifluormethane	Trichloroethene
1,1-Dichloroethane	Trichlorofluormethane
1,2-Dichloroethene	Vinyl Chloride
1,1-Dichloroethene	Total Xylenes *

* = Not a target compound listed by either method 601 or 602 but included as an analyte of interest.
All VOCs have a Minimum Reporting Level (MRL) of 1 Fg/l.
Source [30]

APPENDIX D. INVESTIGATION METHODS

Various groundwater sites were sampled by the ADEQ Groundwater Monitoring Program to characterize regional groundwater quality in the SRF. Samples were collected at all sites for inorganic (physical parameters, major ions, nutrients, and trace elements) as well as hydrogen and oxygen isotope analyses. At selected sites radiochemistry, radon, and VOC samples were collected for analysis. No bacteria sampling was conducted since microbiological contamination in groundwater are often transient and subject to a variety of changing environmental conditions including soil moisture content and temperature.[18]

Sampling Strategy

This study focused on groundwater quality conditions that are large in scale and persistent in time. This research is designed to identify regional degradation of groundwater quality such as occurs from non-point sources of pollution or a high density of point sources. The quantitative estimation of regional groundwater quality conditions requires the selection of sampling locations that follow scientific principles for probability sampling.[21]

Sampling in the SRF conducted by ADEQ followed a systematic stratified random site-selection approach. This is an efficient method because it requires sampling relatively few sites to make valid statistical statements about the conditions of large areas. This systematic element requires that the selected wells be spatially distributed while the random element ensures that every well within an aquifer has an equal chance of being sampled. This strategy also reduces the possibility of biased well selection and assures adequate spatial coverage throughout the study area.[21] The main benefit of a statistically-designed sampling plan is that it allows much greater groundwater quality assumptions than would be allowable with a non-statistical approach.

Wells pumping groundwater for a variety of purposes - domestic, stock, and irrigation - were sampled for this study, provided each individual well met ADEQ requirements. A well was considered suitable for sampling if the well owner gave permission to sample, if a sampling point existed near the wellhead, and if the well casing and surface seal appeared to be intact and undamaged. Other factors such as casing access to determine groundwater depth and construction information were preferred but not essential.

If no registered wells were available, springs or unregistered wells were randomly selected for sampling. Springs were considered adequate for sampling if they had a constant flow through a clearly-defined point of egress, and if the sample point had minimal surface impacts. Well information compiled from the ADWR well registry and spring characteristics are found in **Appendix A**.

Several factors were considered to determine sample size for this study. Aside from administrative limitations on funding and personnel, this decision was based on three factors related to the conditions in the area:[21]

- Amount of groundwater quality data already available;
- Extent to which impacted groundwater is known or believed likely to occur; and
- Hydrologic complexity and variability of the area.

Sample Collection

The personnel who designed the SRF study were also responsible for the collection and interpretation of the data.[21] This protocol helps ensure that consistently high quality data are collected, from which are drawn relevant and meaningful interpretations. The sample collection methods for this study conformed to the *Quality Assurance Project Plan* (*QAPP*)[2] and the *Field Manual For Water Quality Sampling*.[8] While these sources should be consulted as references to specific sampling questions, a brief synopsis of groundwater sampling procedures is provided.

After obtaining permission from the owner to sample the well, the water level was measured with a sounder if the casing had access for a probe. The volume of water needed to purge the well three bore hole volumes was calculated from well log and on-site information. Physical parameters - temperature, pH, and specific conductivity - were monitored at least every five minutes using a YSI multi-parameter instrument. Typically, after three bore volumes had been pumped and the physical parameters were 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:

1. Radon
2. VOC
3. Inorganic
4. Radiochemistry
5. Isotope

Radon samples were collected in 2, unpreserved, 40-ml clear glass vials. Radon samples were filled so as little off-gassing occurred as possible and there was no air trapped within the bottles.[16]

VOC samples were collected in 2, 40-ml amber glass vials which contained 10 drops 1:1 hydrochloric (HCl) acid preservative prepared by the laboratory. Before sealing the vials with Teflon caps, litmus paper was used to make certain the pH of the sample was below 2 su; additional HCl was added if necessary. VOC samples were also checked to make sure there was no headspace.[30]

The inorganic constituents were collected in 3, 1-liter polyethylene bottles:[30]

< Samples to be analyzed for dissolved metals were filtered into bottles preserved with 5 mL nitric acid (70 percent). An on-site positive pressure filtering apparatus with a 0.45 micron (µM) pore size groundwater capsule filter was used.

< Samples to be analyzed for nutrients were collected in bottles preserved with 2 ml sulfuric acid (95.5 percent).

< Samples to be analyzed for other parameters were collected in unpreserved bottles.

Radiochemistry samples were collected in 2, collapsible 1-liter plastic containers and preserved with 5 ml nitric acid to reduce the pH below 2.5 su.[4]

Hydrogen and oxygen isotope samples were both collected in a single 500 ml unpreserved plastic bottle.

All samples were kept at 4^0C using ice in an insulated cooler, with the exception of the isotope and radiochemistry samples. Chain of custody procedures were followed in sample handling. Samples for this study were collected between February and May 2002.

Laboratory Methods

The inorganic and VOC analyses for this study were conducted by the ADHS Laboratory in Phoenix, AZ, the only exception being inorganic splits analyzed by Del Mar Laboratory in Phoenix. A complete listing of inorganic parameters, including laboratory method, EPA water method, and Minimum Reporting Level (MRL) for both laboratories is provided in **Table 4**.

Radiochemistry samples were analyzed by the Arizona Radiation Regulatory Agency (ARRA) laboratory in Phoenix, AZ. The analysis of radiochemistry samples was treated according to the following SDW protocols.[4] Gross alpha and gross beta were analyzed, and if the gross alpha levels exceeded 5 pCi/L, then radium-226 was measured. When radium-226 exceeded 3 pCi/L, radium-228 was measured. If gross alpha levels exceeded 15 pCi/L, then radium-226/228 and mass uranium were measured.

Radon samples were analyzed by Lucas Laboratories in Sedona, AZ. Hydrogen and oxygen isotope samples were analyzed by the University of Arizona Laboratory of Isotope Geochemistry in Tucson, AZ.

Sample Numbers

Twenty (20) sites (plus one surface water site where only an isotope sample was collected) were sampled for the study. Various numbers and types of samples were collected and analyzed:

< 20 - inorganic
< 21 - hydrogen and oxygen isotopes
< 5 - radon
< 5 - radiochemistry
< 2 - VOCs

Table 4. ADHS/Del Mar Laboratory Methods Used for the SRF Study

Constituent	Instrumentation	ADHS / Del Mar Water Method	ADHS / Del Mar Minimum Reporting Level
Physical Parameters and General Mineral Characteristics			
Alkalinity	Electrometric Titration	SM232OB	2 / 5
SC (FS/cm)	Electrometric	EPA 120.1/ SM2510B	1 / 2
Hardness	Titrimetric, EDTA	EPA 130.2 / SM2340B	10 / 1
Hardness - Calc.	Calculation	--	--
pH (SU)	Electrometric	EPA 150.1	0.1
TDS	Gravimetric	EPA 160.1 / SM2540C	10 / 20
Turbidity (NTU)	Nephelometric	EPA 180.1	0.01 / 1
Major Ions			
Calcium	ICP-AES	EPA 200.7	5 / 2
Magnesium	ICP-AES	EPA 200.7	1 / 0.5
Sodium	ICP-AES	EPA 200.7 / EPA 273.1	5
Potassium	Flame AA	EPA 258.1	0.5 / 1
Bicarbonate	Calculation	--	2
Carbonate	Calculation	--	2
Chloride	Potentiometric Titration	SM 4500 CLD / EPA 300.0	1 / 5
Sulfate	Colorimetric	EPA 375.2 / EPA 300.0	10 / 5
Nutrients			
Nitrate as N	Colorimetric	EPA 353.2	0.02 / 0.50
Nitrite as N	Colorimetric	EPA 353.2	0.02
Ammonia	Colorimetric	EPA 350.1/ EPA 350.3	0.02 / 0.5
TKN	Colorimetric	EPA 351.2 / SM4500	0.05 / 0.5
Total Phosphorus	Colorimetric	EPA 365.4 / EPA 365.3	0.02 / 0.05

All units are mg/l except as noted
Source [16,30]

Table 4. ADHS/Del Mar Laboratory Methods Used for the SRF Study--Continued

Constituent	Instrumentation	ADHS / Del Mar Water Method	ADHS / Del Mar Minimum Reporting Level
Trace Elements			
Antimony	Graphite Furnace AA	EPA 200.9	0.005 / 0.004
Arsenic	Graphite Furnace AA	EPA 200.9	0.01 / 0.003
Barium	ICP-AES	EPA 200.7	0.1 / 0.01
Beryllium	Graphite Furnace AA	EPA 200.9	0.0005
Boron	ICP-AES	EPA 200.7	0.1 / 0.5
Cadmium	Graphite Furnace AA	EPA 200.9	0.001 / 0.0005
Chromium	Graphite Furnace AA	EPA 200.9	0.01 / 0.004
Copper	Graphite Furnace AA	EPA 200.9	0.01 / 0.004
Fluoride	Ion Selective Electrode	SM 4500 F-C	0.2 / 0.1
Iron	ICP-AES	EPA 200.7	0.1
Lead	Graphite Furnace AA	EPA 200.9	0.005 / 0.002
Manganese	ICP-AES	EPA 200.7	0.05 / 0.02
Mercury	Cold Vapor AA	SM 3112 B / EPA 245.1	0.0005 / 0.0002
Nickel	ICP-AES	EPA 200.7	0.1 / 0.05
Selenium	Graphite Furnace AA	EPA 200.9	0.005 / 0.004
Silver	Graphite Furnace AA	EPA 200.9 / EPA 273.1	0.001 / 0.005
Thallium	Graphite Furnace AA	EPA 200.9	0.002
Zinc	ICP-AES	EPA 200.7	0.05

All units are mg/l
Source [16 30]

APPENDIX E. 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 SRF study. The design of the QA/QC plan was based on recommendations included in the *Quality Assurance Project Plan (QAPP)*[2] and the *Field Manual For Water Quality Sampling*.[8] The types and numbers of QC samples collected for this study are as follows:

Inorganic:	(1 duplicate, 2 splits, 3 blanks).
Isotope:	(1 duplicates, 0 splits, 0 blanks).
Radiochemical:	(0 duplicates, 0 splits, 0 blanks).
Radon:	(0 duplicates, 0 splits, 0 blanks).
VOC:	(0 duplicates, 0 splits, 1 blank).

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

Blanks - Equipment blanks for inorganic analyses were collected to ensure adequate decontamination of sampling equipment, and that the filter apparatus and/or deionized water were not impacting the groundwater quality sampling.[8] Equipment blank samples for major ion and nutrient analyses were collected by filling unpreserved and sulfuric acid preserved bottles with deionized water. Equipment blank samples for trace element analyses were collected with deionized 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.[21] As such, SC-lab and turbidity were considered to be affected by systematic contamination; however, the extent of contamination was not considered significant. Both SC and turbidity were detected in all three equipment blanks. SC had a mean level of 1.9 FS/cm which was less than 1 percent of the SC mean level for the study. The SC detections may be explained in two ways: water passed through a deionizing exchange unit will normally have an SC value of at least 1 FS/cm while carbon dioxide from the air can dissolve in deionized water with the resulting bicarbonate and hydrogen ions imparting the observed conductivity.[30] Similarly, turbidity had a mean level of 0.024 ntu, less than 1 percent of the turbidity median 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.[30] The only other constituent detections were chloride (5.0 mg/l), copper (0.011 mg/l), and total phosphorus (0.032 mg/l).

There were no detections of any organic compounds in the VOC travel blank.

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.[8] Duplicate samples were collected from sampling sites that were believed to have elevated constituent concentrations as judged by field SC values. Variability in constituent concentrations between each pair of duplicate samples is provided both in terms of absolute levels and as the percent difference. Percent difference is defined as the absolute difference between levels in the duplicate samples divided by the average level for the duplicate samples, multiplied by 100. Only parameters having levels exceeding the Minimum Reporting Level (MRL) were used in this analysis.

Analytical results indicate that of the 41 constituents examined, only 7 had any quantitative difference. The maximum difference between duplicate constituents never exceeded 5 percent with the exception of turbidity (29 percent). Turbidity values can be impacted by the exceedance of this parameter's holding time[30]; this occurred frequently during the study due to turbidity's short holding time. The absolute and percentage differences for the seven parameters with differences are as follows: pH (0.1 su - 1 percent), SC(10 FS/cm - 2 percent), turbidity (0.01 ntu - 29 percent), hardness (10 mg/l - 3 percent), potassium (0.02 mg/l - 2 percent), chloride (0.2 mg/l - 5 percent), and nitrate (0.01 mg/l - 5 percent).

Based on these results, the differences in constituent concentrations of duplicate samples were not considered to significantly impact the groundwater quality data.

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.[8] Seven inorganic split samples were collected. Analytical results from the split samples 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 37 constituents examined, only 17 had any absolute differences between laboratories. The maximum difference between split constituents rarely exceeded 20 percent (**Table 5**). Split samples were also evaluated using the non-parametric Sign test to determine if there were any significant (p # 0.05) differences between ADHS laboratory and Del Mar Laboratory analytical results.[21] Results of the Sign test showed that none of the 17 constituents examined had significantly different concentrations between the laboratories.

Based on these results, the differences in parameter levels of split samples were not considered to significantly impact the groundwater quality data.

Data Validation

The analytical work for this study was subjected to the following six QA/QC correlations.

Cation/Anion Balances - In theory, water samples exhibit electrical neutrality. Therefore, the sum of milliequivalents per liter (meq/L) of the cations must equal the sum of the anions. However, this neutrality is rarely seen in practice due to unavoidable variation present in all water quality analyses. Still, cation/anion balance is an analysis such that, if found to be within acceptable limits, it can be assumed there are no gross errors in concentrations reported for major ions.[22]

Overall, cation/anion balances of SRF samples were significantly correlated (regression analysis, p # 0.01) and within acceptable limits (90 - 110 percent).

SC/TDS - The SC and TDS concentrations measured by contract laboratories were significantly correlated as were field-SC and TDS concentrations (regression analysis, p # 0.01). Typically, the TDS concentration in mg/l should be from 0.55 to 0.75 times the SC in FS/cm for groundwater up to several thousand mg/l.[22] Groundwater in which the ions are mostly bicarbonate and chloride will have a factor near the lower end of this range and groundwater high in sulfate may reach or even exceed the upper end. The relationship of TDS to SC becomes indefinite for groundwater both with very high and low concentrations of dissolved solids.[22]

Hardness - Concentrations of laboratory-measured and calculated values were significantly correlated (regression analysis, p # 0.01). Hardness concentrations were calculated using the following formula: [(Ca x 2.497) + (Mg x 4.118)].

SC - The SC measured in the field using a YSI meter at the time of sampling was significantly correlated with the SC measured by contract laboratories (regression analysis, p # 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.[22] Thus, 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, p # 0.05).

Groundwater Temperature/Groundwater Depth - Groundwater temperature measured in the field was compared to groundwater depth to examine the relationship that exists between temperature and depth. Groundwater temperature should increase with depth, approximately 3 degrees Celsius with every 100 meters or 328 feet.[10] Groundwater temperature and well depth were not significantly correlated (regression analysis, p # 0.05). The many springs and shallow wells sampled as part of the SRF study probably contributed to the non-significance of this relationship.

The analytical work conducted for this study was considered valid based on the quality control samples and the QA/QC correlations.

Table 5. Summary Results of SRF Split Samples From ADHS/Del Mar Labs

Constituents	Number	Difference in Percent		Difference in Levels		Significance
		Minimum	Maximum	Minimum	Maximum	
Physical Parameters and General Mineral Characteristics						
Alkalinity, total	2	0%	0%	0	0	ns
SC (FS/cm)	2	0%	10%	0	40	ns
Hardness	2	0%	8%	0	50	ns
pH (su)	2	1%	7%	0.08	0.54	ns
TDS	2	1%	11%	10	30	ns
Turbidity (ntu)	2	0%	22%	0	0.2	ns
Major Ions						
Calcium	2	0%	6%	0	10	ns
Magnesium	2	2%	4%	0.2	.2	ns
Sodium	2	0%	14%	0	1.3	ns
Potassium	2	11%	22%	0.2	0.3	ns
Chloride	2	4%	32%	1	2.2	ns
Sulfate	2	9%	10%	1	30	ns
Nutrients						
Nitrate as N	2	0%	6%	0	0.6	ns
TKN	2	0%	148%	0	0.71	ns
Trace Elements						
Barium	2	0%	6%	0	0.01	ns
Fluoride	2	4%	28%	0.01	0.10	ns
Lead	2	0%	10%	0	0.02	ns

All units are mg/l except as noted with certain physical parameters
ns = No significant (p # 0.05) difference between labs

Statistical Considerations

Various methods were used to complete the statistical analyses for the groundwater quality data of this study. All statistical tests were conducted on a personal computer using SYSTAT software.

Data Normality: Initially, data associated with 22 constituents were tested for both non-transformed and log-transformed normality using the Kolmogorov-Smirnov one-sample test with the Lilliefors option.[11]

Results of this test using non-transformed data revealed that ten constituents (temperature, pH-field, pH-lab, total alkalinity, sodium, potassium, bicarbonate, fluoride, deuterium, and oxygen-18) were normally distributed. The distribution of many groundwater quality parameters is often not Gaussian or normal, but skewed to the right.[21]

The results of the log-transformed test revealed that 16of the 22 log-transformed constituents were normally-distributed with only temperature, hardness, calculated hardness, calcium, fluoride, and barium not normally distributed.

In summary, non-transformed data are overwhelmingly not normally-distributed while roughly one-third of the log-transformed constituents are normally-distributed.

The most recent and comprehensive statistical references specifically recommend the use of non-parametric tests when the non-normality assumption is violated.[21]

Various aspects of SRF groundwater quality were analyzed using the following statistical methods:

Spatial Relationships: The non-parametric Kruskal-Wallis test was applied to investigate the hypothesis that constituent concentrations from groundwater sites in different aquifers, rock types, and/or watersheds of the SRF were the same. The Kruskal-Wallis test uses the differences, but also incorporates information about the magnitude of each difference.[21] The null hypothesis of identical median values for all data sets within each test was rejected if the probability of obtaining identical medians by chance was less than or equal to 0.05. Comparisons conducted using the Kruskal-Wallis test include basin aquifers (alluvial and hardrock), watersheds (Duquesne Wash, Parker Canyon, and Santa Cruz River), and rock types (alluvium, granitic rock, metamorphic rock, volcanic rock, and sedimentary rock).[5]

If the null hypothesis was rejected for any of the tests conducted, the Tukey method of multiple comparisons on the ranks of the data was applied. The Tukey test identified significant differences between constituent concentrations when compared to each possibility within each of the four tests.[21]

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.[21] Consequently, the Kruskal-Wallis test was not calculated for trace parameters such as antimony, arsenic, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc as well as phenolphthalein alkalinity, carbonate, nitrite, ammonia, TKN, and total phosphorus. Highlights of these statistical tests are summarized in the groundwater quality section.

Correlation Between Constituent Concentrations: In order to assess the strength of association between constituents, their various 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.[37]

The Pearson test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL.[21] Consequently, Pearson Correlation Coefficients were not calculated for trace parameters such as antimony, arsenic, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc as well as phenolphthalein alkalinity, carbonate, nitrite, ammonia, TKN, and total phosphorus. Significant highlights from this statistical test are summarized in the groundwater quality section.