

# Ambient Groundwater Quality of the Lower San Pedro Basin: A 1999-2000 Baseline Study

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**Report Cover:** At first glance, a well casing and turbine pump appear to be growing as part of a healthy riparian ecosystem, competing for sunlight with a grove of juvenile cottonwood trees. As indicated by the presence of Jason Ekstein of the Nature Conservancy (TNC) next to the casing, the turbine pump sits approximately 20 feet above land surface. The farmland surrounding this irrigation well was eroded away during 1993 flooding on the San Pedro River, a problem that has been ongoing since the 1890s<sup>39</sup>. This "well in the sky" is located at the TNC's San Pedro River Reserve near the community of Dudleyville.

## Other Publications of the ADEQ Ambient Groundwater Monitoring Program

- Ambient Groundwater Quality of the Lower San Pedro Basin: A 2000 Baseline Study. ADEQ Factsheet 02-09, August 2002, 4 p.
- Ambient Groundwater Quality of the Willcox Basin: A 1999 Baseline Study. ADEQ Open File Report 01-09, November 2001, 55 p.
- Ambient Groundwater Quality of the Willcox Basin: A 1999 Baseline Study. ADEQ Factsheet 01-13, October 2001, 4 p.
- Ambient Groundwater Quality of the Sacramento Valley Basin: A 1999 Baseline Study. ADEQ Factsheet 01-10, June 2001, 4 p.
- Ambient Groundwater Quality of the Sacramento Valley Basin: A 1999 Baseline Study. ADEQ Open File Report 01-04, June 2001, 77 p.
- Ambient Groundwater Quality of the Yuma Basin: A 1995 Baseline Study. ADEQ Factsheet 01-03, April 2001, 4 p.
- Ambient Groundwater Quality of the Virgin River Basin: A 1997 Baseline Study. ADEQ Factsheet 01-02, March 2001, 4 p.
- Ambient Groundwater Quality of the Prescott Active Management Area: A 1997-98 Baseline Study. ADEQ Factsheet 00-13, December 2000, 4 p.
- Ground-Water Quality in the Upper Santa Cruz Basin, Arizona, 1998. Joint Publication: USGS Water Resources Investigations Report 00-4117 ADEQ Open File Report 00-06, September 2000, 55 p.
- Ambient Groundwater Quality of the Douglas Basin: An ADEQ 1995-1996 Baseline Study. ADEQ Factsheet 00-08, September 2000, 4 p.
- Ambient Groundwater Quality of the Prescott Active Management Area: A 1997-98 Baseline Study. ADEQ Open File Report 00-01, May, 2000, 77 p.
- Ground-Water Quality in the Sierra Vista Sub-basin, Arizona, 1996-97. Joint Publication: USGS Water-Resources Investigations Report 99-4056 ADEQ Open File Report 99-12, July 1999, 50 p.
- Ambient Groundwater Quality of the Douglas Basin: A 1995-96 Baseline Study. ADEQ Open File Report 99-11, June 1999, 155 p.
- Ambient Groundwater Quality of the Virgin River Basin: A 1997 Baseline Study. ADEQ Open File Report 99-4, March 1999, 98 p.
- Ambient Groundwater Quality of the Yuma Basin: A 1995 Baseline Study. ADEQ Open File Report 98-7, September, 1998, 121 p.
- Collection and Analysis of Ground-Water Samples in the Sierra Vista Basin, Arizona, 1996. Joint Publication: USGS Factsheet FS-107-97 ADEQ Factsheet 97-8, August 1997, 4 p.
- 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.

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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

ASARCO American Smelting and Refining Company

BHP Broken Hill Properties bls below land surface

BLM U.S. Department of the Interior Bureau of Land Management

°C degrees Celsius

CI<sub>0.95</sub> 95 percent Confidence Interval

Cl chloride

EPA U.S. Environmental Protection Agency

F fluoride Fe iron

gpm gallons per minute

GWPL Groundwater Protection List pesticide

HCl hydrochloric acid
LLD Lower Limit of Detection

LSP Lower San Pedro groundwater basin

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 su standard pH units

SO4 Sulfate

TDS Total Dissolved Solids
TKN Total Kjeldahl Nitrogen
USGS U.S. Geological Survey
VOC Volatile Organic Compound



#### Ambient Groundwater Quality of the Lower San Pedro Basin: A 2000 Baseline Study

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**Abstract** - The Lower San Pedro Groundwater Basin (LSP) baseline groundwater quality study was conducted by the Arizona Department of Environmental Quality (ADEQ) in 2000. Located in southeastern Arizona, this semiarid basin is drained by the San Pedro and Gila Rivers. The LSP is a rural landscape with scattered towns and two extensive copper mining and processing operations. Groundwater from three aquifers (*floodplain*, *unconfined basin-fill*, and *confined basin-fill* or *artesian*) and fractured mountain hardrock is the principle source of water supply. For this study, 63 groundwater sites were sampled for inorganic constituents. In addition, fewer sites were also sampled for Volatile Organic Compounds (25), radiochemistry (19), radon (19), and pesticide (2) analyses.

Eighteen (18) percent of sample sites 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<sup>54</sup>. Constituents that exceeded these standards included antimony (2 sites), arsenic (1 site under current standards, 12 sites under standards effective in 2006), fluoride (8 sites), nitrate (1 site), and gross alpha (2 sites). In addition, 49 percent of sample sites 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<sup>54</sup>. Constituents that exceeded these guidelines included chloride (2 sites), fluoride (16 sites), iron (4 sites), manganese (9 sites), pH (4 sites), sulfate (11 sites), and total dissolved solids (24 sites). At one site, Volatile Organic Compounds that are common by-products of chlorination were detected. No pesticides or pesticide degradation by-products were detected.

Artesian conditions can exist when *confined basin-fill aquifers*, which are generally found along the central portion of the basin's axis, are intercepted<sup>35</sup>. Artesian water in the LSP is suitable for domestic and irrigation purposes at its southern boundary near Redington. Farther north, however the water quality deteriorates. Gypsum deposit dissolution and the associated cation exchange in the Mammoth-Dudleyville corridor creates groundwater with elevated sulfate and sodium concentrations. The *artesian aquifer* also has a *chemically closed hydrologic system* that favors alkaline pH values and depleted calcium concentrations, which also contribute to the elevated concentrations that can exceed water quality standards. The elevated sodium and other salt concentrations also make these *confined basin-fill aquifer* waters unsuitable for irrigation north of Redington.

The *floodplain aquifer* is the most productive in the basin and supplies water for most irrigation and municipal uses. This aquifer forms a long corridor following the major waterways and receives most of its recharge from surface water flows <sup>10</sup>. As such, this aquifer is considered to be a *chemically open hydrologic system*. However, leakage from the lower *confined basin-fill aquifer* upwards into the *floodplain aquifer* is thought to be largely responsible for the variable salinity and fluoride concentrations that are particularly elevated near Mammoth<sup>41</sup>. The elevated salinity, sodium, chloride, and potassium concentrations found in the most downgradient portions of the *floodplain aquifer* appear to be related to the high concentrations of these constituents in the Gila River. Elevated sulfate concentrations found along the *floodplain aquifer* between Mammoth and Winkelman may be from leakage from the *confined basin-fill aquifer* and the elevated concentrations carried north by the San Pedro River. The source of sulfates for both aquifers appears to be a combination of nearby gypsum deposits and mine tailing dumps, though the contribution of each would require an intensive targeted study to determine.

Groundwater collected from the *unconfined basin-fill aquifer* and from hardrock areas was the most dilute and had the fewest water quality standard exceedances. Unfortunately, these areas also have a somewhat limited groundwater production potential. Differences in water quality between these aquifers and the *floodplain aquifer* appear to be related to a more dilute recharge source (mountain precipitation and runoff) as well as minimal leakage from the *confined basin-fill aquifer*. Potential water quality problems appear largely confined to fault zones producing water from great depths and granitic rock areas which may have elevated radiochemistry concentrations<sup>28</sup>.

#### INTRODUCTION

The Lower San Pedro groundwater basin (LSP) is located in southeastern Arizona and characterized as a predominantly rural landscape with small scattered settlements. The San Pedro River, perennial in stretches, flows north through the center axis of the basin to the confluence with the Gila River. The Gila River, which enters the basin from San Carlos Reservoir in the east, is the main drainage north of Winkelman. Mining is the most important economic activity as several large copper mining and milling operations are located in the basin. Limited areas of irrigated farmland are scattered along stretches of floodplain. Upland areas have been utilized by ranches for livestock grazing. Recent population increases are largely the result of dispersed residential development by commuters and retirees drawn to the basin for its solitude and picturesque scenery, especially along the rare desert riparian habitat formed by perennial reaches of the San Pedro River (Figure 1).

Groundwater is the primary source for domestic, municipal, irrigation, livestock, and mining uses in the

LSP. As the population increases in the future, development will raise challenges of supplying groundwater that will meet U.S. **Environmental Protection Agency** (USEPA) Safe Drinking Water (SDW) Act water quality standards while under increased pressure from regional development.

To assess these hydrological issues, the Arizona Department of Environmental Quality (ADEQ) **Groundwater Monitoring Unit** conducted a study to characterize the current (2000) groundwater quality conditions in the LSP. 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<sup>5</sup> that authorizes:

"...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."

This ADEQ program examines regional groundwater quality in Arizona basins such as the LSP. Sample sites are chosen using a stratified random selection process. The analytical results of these samples are compared to water quality standards as well as statistically examined for significant patterns and relationships.

### Purpose and Scope

ADEQ sampled 63 sites for this groundwater quality assessment. Specific sample types and numbers collected and analyzed include inorganics (physical parameters, major ions, nutrient constituents, and trace elements) (63 sites), Volatile Organic Compounds (VOCs) (25 sites), radon gas (19 sites), radiochemistry (19 sites), and Groundwater Protection List (GWPL) pesticides (2 sites).

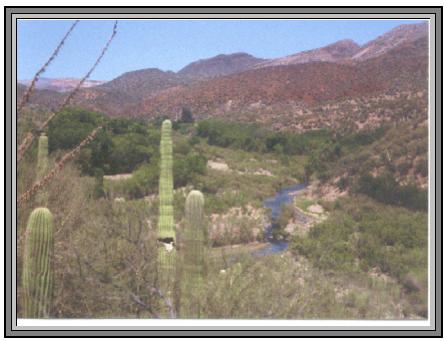


Figure 1. The San Pedro River and its cottonwood-willow-mesquite riparian area are shown here near the community of Dudleyville. This riparian ecosystem is used by a diversity of birds, mammals, and reptiles unequaled in the United States. The resource value of this watercourse is such that the Nature Conservancy has listed the San Pedro River as one of the Last Great Places in the western hemisphere<sup>40</sup>.

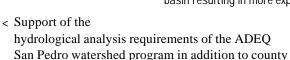
## Aspects of Study -Groundwater quality

concerns examined in this report include:

- < Current (2000) regional groundwater quality conditions;
- < Variation in groundwater quality using indices such as aquifers, geology, geographic location, and groundwater depth; and
- < Co-variation among concentrations of groundwater quality constituents.

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

and local governments.



- < To increase groundwater quality data available for the LSP due to the area's dependence on groundwater and the aquifer's vulnerability to contamination 34.
- < Greater access to investigate groundwater quality because of recent population growth and an associated increase in the number of wells.

**Benefits of Study** - This groundwater quality study was undertaken with the purpose of developing a reproducible scientific report utilizing statistical analysis to support conclusions concerning groundwater quality. It is anticipated this report will provide the following benefits:

#1 - Many residents in the LSP obtain domestic supplies from private wells that are seldom tested for a wide variety of possible pollutants. While Arizona statutes require well drilling contractors to disinfect for possible bacteria contamination new wells which



Figure 2. The varied landscape of the Lower San Pedro basin is captured in this panoramic view. Desert vegetation, a fallow agricultural field in the floodplain, the changing colors of the riparian forest, and the distant Gailuro Mountains are shown in this autumn pictorial. The steep gradient of the San Pedro River and its tributaries has resulted in a deeply dissected basin resulting in more exposed bedrock than in most alluvial areas in Arizona<sup>28</sup>.

- are to be used for human consumption, few wells are further tested for other groundwater quality concerns. Thus, contamination affecting groundwater pumped from private wells may go undetected for years and have the potential to contribute to adverse health effects for users of this resource. Testing all private wells for a wide variety of groundwater quality concerns would be prohibitively expensive. An affordable alternative is a statistically-based ambient study to characterize groundwater quality on a regional scale that identifies areas of impaired conditions.
- #2 A process to evaluate 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 evaluating the effectiveness of groundwater protection efforts such as aquifer protection permits and best management practices by tracking groundwater quality changes.
- #4 A process for identifying future locations of public supply wells and wellhead protection areas.

#### **Physical Setting**

The LSP is located in southeastern Arizona and lies entirely within the Basin and Range physiographic province. The basin consists of the northwesttrending San Pedro River alluvial fill and the surrounding elongated fault-block mountain ranges (Figure 3). Portions of Cochise, Graham, Pima, and Pinal Counties are within the basin. The LSP is about 65 miles long and varies from 10 to 25 miles wide, encompassing approximately 1,600 square miles 10.

The LSP consists of the drainage basin of the San Pedro River between *The Narrows* north of the town of Benson to the confluence with the Gila River near the town of Winkelman, exclusive of the drainage of Aravaipa Creek east of the mouth of Aravaipa Canyon. It also includes the drainage of the Gila River at the boundary with Dripping Springs Wash Basin to where the Gila River exits the LSP near the town of Kelvin and enters the Donnelly Wash basin. The western border of the LSP is the drainage divide between the San Pedro and Santa Cruz Rivers along the Rincon, Santa Catalina, Black, and Tortilla Mountains. The east border is the drainage divide formed by the Johnny Lyon Hills, Galiuro, (**Figure 3**) and Dripping Springs Mountains. These ranges average from 6,000 feet above mean sea level (amsl) to over 9,000 feet amsl in elevation. Elevations along the valley floor range from 3,400 feet amsl at *The Narrows* along the San Pedro River at the basin's southern end, to 1,700 feet amsl along the Gila River near Kelvin.

The basin's vegetation changes dramatically with elevation. From the cottonwood-willow-mesquite bosques found along portions of the San Pedro River, the vegetation transitions to a lower desert montage of mesquite, desert shrubs, grasses, and cacti. Oak/pine woodlands occur in mountain areas.

**Surface Water** - The LSP is drained by two major

waterways, the Gila River and the San Pedro River. The free-flowing San Pedro River enters from the south at the Narrows. an extensive hardrock formation located about 15 miles north of Benson. From the Narrows, the San Pedro flows north for 65 miles along the basin's central axis until debouching into the Gila River near Winkelman (Figure 4).

The San Pedro River's main tributary within this reach is Aravaipa Creek which enters the basin from the east about 12 miles south of Winkelman. Aravaipa Creek is perennial only in its upper reaches and is ephemeral at its confluence with the San Pedro River<sup>10</sup>. The flow

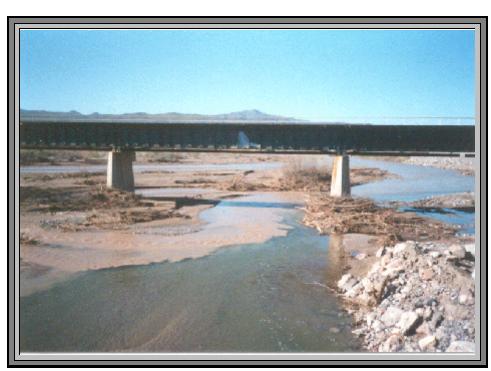
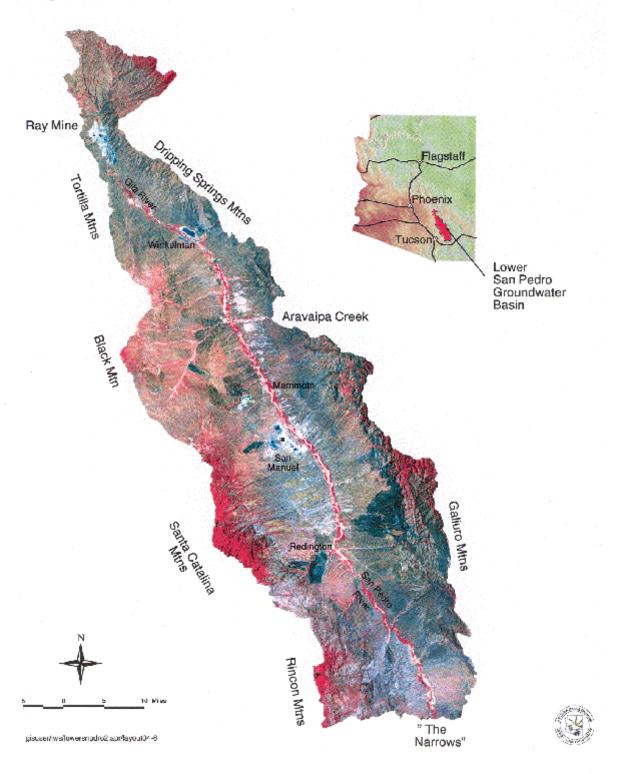


Figure 4. The co-mingling of waters from the San Pedro River and the Gila River during spring flow in 1995 is clearly seen here at the confluence near Winkelman. The San Pedro River, the largest freeflowing river in the Southwest, carries a thick, chocolate-colored silt load as the result of recent precipitation. In contrast, the Gila River, impounded approximately 25 miles upstream by Coolidge Dam, has had its silt-load drop out into San Carlos Reservoir and, thus is relatively clear.

Figure 3 Lower San Pedro Groundwater Basin



in the San Pedro River is perennial in places where the streambed intercepts hard rock or is fed by springs. Elsewhere, flow occurs only in direct response to precipitation<sup>47</sup>.

Streams having perennial stretches in the LSP include the Gila River, a 3 mile portion of the San Pedro River located 9 miles south of Redington, and parts of the tributaries of Hot Springs Canyon, Redfield Canyon, and Harden Cienega Creek<sup>10</sup>.



Figure 6. Ranches in this land of Western skies often advertise their presence using creative wrought iron gateways. Cattle grazing is the most extensive land use in this rugged, largely undeveloped basin. The Warbonnet Ranch sign is shown with the Winchester Mountains in the background, adding a threedimensional effect to the ranching scene.

The regulated Gila River, impounded upstream in the San Carlos Reservoir by Coolidge Dam, enters the northeast portion of the LSP a few miles east of Winkelman. The river flows north and west for approximately 15 miles before exiting the basin near Kelvin. The Gila River's main tributary in the northernmost section of the basin is Muddy Creek, which flows south from the Dripping Springs Mountains. Streams having perennial stretches in this watershed include Mineral Creek and Devils Canyon<sup>10</sup>.

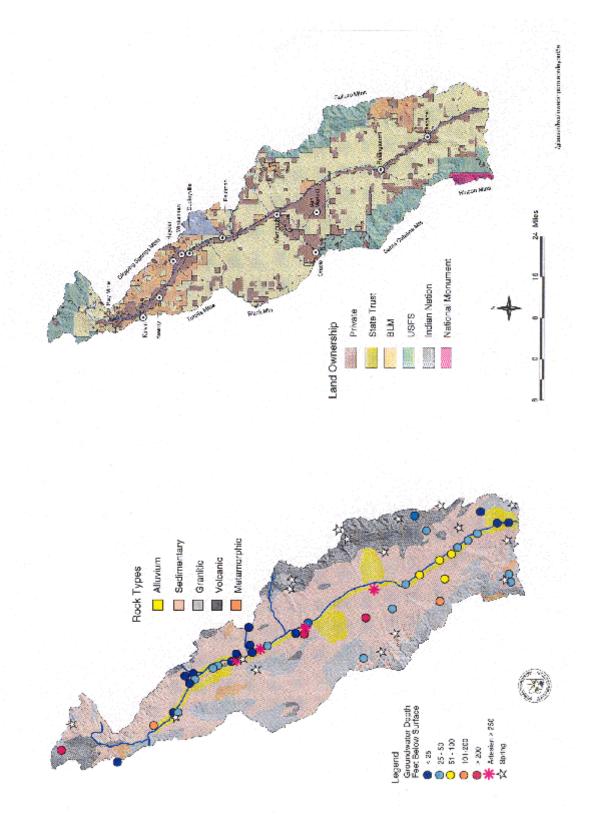
The LSP can be divided into four subwatersheds which are from south to north (Figure 3): Redington, Mammoth, Winkelman, and Kearny<sup>9</sup>. The Redington subwatershed extends from the Narrows northward to the U.S. Geological Survey (USGS) gaging station at Redington. The Mammoth subwatershed extends from Redington to the Mammoth gaging station located in Township 9 South, Range 16 East. The Winkelman subwatershed extends from the Mammoth gaging station northward to a gaging station near its confluence with the Gila River. The northern Kearny subwatershed contains all the lands north of the Winkelman gaging station.

Climate - The LSP's semiarid climate is characterized by hot summers and cool, moderate winters; climate becomes warmer and drier with decreasing elevation. Annual precipitation is extremely variable, averaging 10.5 inches at Redington, 19.5 inches at Oracle, and approximately 28 inches in the Santa Catalina Mountains<sup>28 47</sup>. Precipitation 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<sup>47</sup>. May is the driest month while July and August are the wettest months. Thunderstorm runoff tends to be short-lived and localized.

#### **Cultural Setting**

Land ownership in the LSP (**Figure 5**) consists of State Trust (64 percent), Bureau of Land Management (12 percent), private (11 percent), Forest Service (10 percent), San Carlos Indian Nation (2 percent), and the Saguaro National Monument (1 percent) (8). Much of the land along the San Pedro River and Gila River floodplains is privately owned.

Figure 5 Groundwater Depth and Land Ownership in The Lower San Pedro Groundwater Basin



Communities and their 2000 census data population figures (if large enough) within the basin, from south to north, are Cascabel, Redington, San Manuel (5,698), Oracle (2,065), Mammoth (2,065), Feldman, Dudleyville, Winkelman (440), Hayden (910), Kearny (2,545), and Kelvin<sup>3</sup>. Cascabel, Redington, Feldman, and Dudleyville are small agriculturally-oriented communities. Oracle, after a brief mining period, became a ranching and health-seekers tourism center<sup>39</sup>. The other communities are strongly linked to the mining industry.

Mining is the principal economic activity within the LSP with major copper operations located in the San Manual/Mammoth area (Broken Hill Properties or BHP) and in the Hayden/Kearny/Winkelman area (American Smelting and Refining Company or ASARCO). These communities are attempting to diversify their economic base because of the cyclical nature of the mining industry. Agriculture has traditionally contributed to the basin's economy through cattle ranches (**Figure 6**) and farms located along river floodplains. In 1990, approximately 6,500 acres (**Figure 7**) were irrigated in the basin<sup>10</sup>. Tourist, retirement, and retail are growing sectors of the local economy. The lack of good transportation through

**Figure 7**. A field of barley in the floodplain of the San Pedro River near Dudleyville. Most crops grown in the LSP, including small grains, alfalfa, and pasture, are used for animal feed. Many farms in this area are owned by mining companies and crops are grown primarily to preserve water rights related to appropriable sub-flow. Cottonwoods along the San Pedro River, Malapais Hill, and the Dripping Springs Mountains can be seen in the background.

the LSP, especially the absence of a railroad south of Winkelman and the rough dirt roads found south of San Manuel have been suggested as reasons for the underdeveloped economy of the LSP<sup>39</sup>.

Historical Development - Prior to European settlement of the LSP, the area was inhabited by nomadic groups of Apache Indians<sup>39</sup>. Conflict between these groups led to the establishment of Camp Grant in 1860. Ranches and farms were established along the San Pedro River, until they were largely abandoned when the military closed Camp Grant in 1871<sup>39</sup>. Prospectors began exploring the area in the late 1870's. This led to the establishment of several mining districts: the Old Hat in the Santa Catalina Mountains, the Bunker Hill in the Galiuro Mountains, the Saddle Mountain in The Tablelands, and the San Pedro in the Tortilla Mountains<sup>39</sup>.

To supply food and feed to the mining operations, settlers once again began farming. During the 1890s, floods carried away many acres of farmland. These floods may have been due to heavy rains following long periods of drought and by the overgrazing of cattle<sup>39</sup>. By 1930, only a few farms remained as the

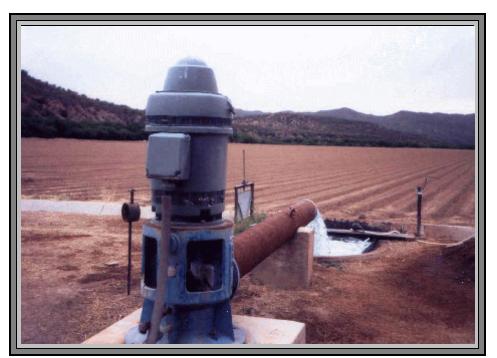
continued operation of diversion dams on the San Pedro River and their accompanying irrigation ditches proved too difficult. Mesquite brush subsequently invaded the many abandoned farm fields.

The San Manual/Mammoth area was originally mined for gold, silver, and minor amounts of copper until molybdenum extraction began in 1936<sup>39</sup>. In the 1950s, large scale copper mining began at San Manuel. Both underground and open pit mines, a concentrator, smelter, refinery, and rod manufacturing plant were located in this town. In 1996, the operation was acquired by BHP from Magma Copper Company (**Figure 8**). This operation, which included the largest underground metal mine in North America, ceased production in June 1999<sup>23</sup>.

The Ray/Kearny/Winkelman area is also a major copper producer. A copper smelter was built at the town of Hayden in 1912 to process ores from the nearby Ray Mine. Another smelter was built at the Ray Mine and processed the mine concentrates from 1958 until 1983 when once again the ore was shipped to the Hayden smelter<sup>1</sup>. Currently the mining operation consists of an open-pit mine and a solvent extraction and electrowinning plant at the Ray Mine and a smelter in Hayden. Kearny, a company town founded in 1958, and Winkelman are primarily residential communities for mining employees.



**Figure 8**. The San Manuel copper mining complex, including the smelter smokestack and tailings piles are shown in this photo. Groundwater from the underground mining operations had been pumped at a rate of 4,000 gpm and applied to the tailings piles for dust control. This practice ended in January 2002 when a four inch cover of rock material capped the more than 3,000 acres of tailings dumps<sup>23</sup>.



**Figure 9**. Powered by a turbine pump, a well draws groundwater from the floodplain aquifer for delivery to a field planted with cotton seed. Furrow irrigation systems are used to distribute water to scattered fields of cotton grown between the towns of Mammoth and Kearny. Recently, some fields are being replanted to riparian vegetation in an attempt to replace willow flycatcher habitat lost during the recent expansion of Roosevelt Dam and Lake. The pictured field is located near the confluence of the San Pedro River and Aravaipa Creek.

#### GEOHYDROLOGY

#### Geology

The San Pedro River occupies a north-south trending structural trough bounded on the east and west by mountain ranges. These surrounding mountains (Figure 5) are composed of granitic, volcanic, sedimentary, and metamorphic rocks<sup>35</sup>. This trough has filled with sediments deposited from the adjacent mountain ranges<sup>35</sup>. The relatively steep gradient of the

San Pedro River, up to 30 feet per mile, has deeply dissected the LSP more so than other desert basins<sup>28</sup>. Tributary stream gradients are also correspondingly higher, and consequently the basin has more exposed bedrock than other basins. Of particular interest to groundwater quality are the sandstone beds that grade into gypsiferous silt containing economicallyviable gypsum beds in the central part of the valley in the Mammoth-Winkelman area<sup>47</sup>.

#### Aquifers

Groundwater in the LSP is found in four principal water-bearing units: the floodplain aquifer, the unconfined and confined basin-fill aquifers, and in the consolidated hardrock mountain areas (Figure **13**). The *floodplain* and both *basin-fill aquifers* have the ability to transmit and supply large amounts of groundwater; the hardrock yields limited groundwater from areas sufficiently faulted and fractured<sup>10</sup>. The streambed alluvium forming the floodplain aquifer is more permeable than the alluvial basin-fill sediments that fill the valley; however, the narrow *floodplain aquifer* has a very limited extent along the LSP's central valley.

The *floodplain aquifer* is found in close proximity to the San Pedro River, the Gila River, and their major tributaries (**Figure 9**). The aquifer is 40 to 150 feet thick and consists of gravel, sand, silt, and clay<sup>35</sup>. The floodplain width averages about half a mile, though large tributaries such as Aravaipa and Hot Springs Creeks have flood plains as much as a mile wide at their mouths<sup>28</sup>. This very permeable aquifer has well yields averaging from 250 to 2,700 gallons per minute (gpm)<sup>10</sup>. Groundwater in this aquifer is unconfined, and water levels are usually less than 60 feet below land surface (bls)<sup>35</sup>. The *floodplain* aquifer is recharged primarily by surface water flows of the San Pedro and Gila Rivers; this results in seasonal water level fluctuations in response to surface water flows in the riverbed<sup>41</sup>. Groundwater levels typically rise slightly in the spring and early summer and decline in the fall and winter<sup>41</sup>.

The unconfined basin-fill aquifer is composed of vounger basin-fill, older basin-fill, and basal conglomerate, which makes for highly variable hydrologic characteristics depending upon the amount of compaction and the presence of finegrained layers in the basin-fill<sup>10</sup>. The younger and

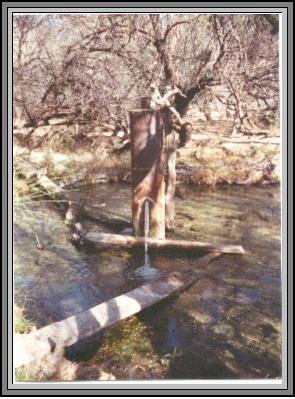


Figure 10. An artesian well creates a riparian area amidst a mesquite bosque near the San Pedro River just south of the town of Mammoth. Tapping the confined basin-fill aquifer, this 1485 foot deep well drilled in 1934 spills water out of the casing at a hot 38.6 degrees Celsius. Groundwater chemistry-very soft with elevated levels of pH and fluoride-is suggestive of a chemically-closed system.

older basin-fill units generally provide the bulk of water pumped from the regional aquifer, with reported well yields of 70 to 1,900 gpm<sup>41</sup>. In contrast, well yields from tightly cemented basal conglomerate are only several hundred gpm and found only in areas that are weakly cemented or fractured by faults 41.

The *confined basin-fill aquifer* is encountered in most wells drilled deeper than 500 feet (Figure 10). These deep wells located in or near the river's floodplain encounter fine-grained layers that restrict vertical groundwater movement, creating artesian conditions<sup>28</sup>. Two main zones of artesian activity are associated with sand and gravel layers from 600 to 800 feet and from 1,200 to 1,300 feet in depth<sup>41</sup>. Discharge from artesian conditions span the San Pedro River's floodplain from about 5 miles north to 10 miles south of Mammoth<sup>10</sup>. The discovery of the

confined aquifer may be traced to the oil rush of 1904 after it was observed that water coming from wells around Mammoth contained colored spots that looked very much like drops of oil on water<sup>39</sup>. Oil speculators quickly purchased all the land around the town. The oil rush ended quickly when well drillers encountered artesian water<sup>39</sup>.

Groundwater is extracted from the consolidated *hardrock* of the mountains surrounding the basin where the bedrock is sufficiently fractured or faulted10. Fault zones create small, localized aguifers that are tapped by windmills (Figure 11) and other low-capacity wells for stock and domestic use. Springs issue water from bedrock, typically with low flows, although Leroy

Spring, located 6 miles upstream from Winkelman along the San Pedro River has an average flow of 1,032 gpm<sup>47</sup>.

#### **Groundwater Characteristics**

Groundwater movement in the basin is from the higher mountain elevations toward the valley; however little if any moves northwest along the riverbed<sup>39</sup>. Groundwater moves readily between the floodplain aquifer and unconfined basin-fill aquifer10. The unconfined basin-fill aquifer, and especially the *floodplain aquifer*, may also receive water leaking upwards from the artesian confined aguifer in the Mammoth area<sup>41</sup>. The LSP contains an estimated 25.6 million acre-feet in storage<sup>10</sup>.

Groundwater levels are generally stable in the basin except in the area around San Manuel and Mammoth where large groundwater pumpage rates are causing water-level declines<sup>9</sup>. Depth to water in unconfined areas of the basin-fill in 1978 ranged from 50 to 253 feet bls 35.



Figure 11. Successful field work sometimes requires hydrologists to think-and resemble-the wells they sample. ADEQ's Elizabeth Boettcher (above) accurately parrots this derelict windmill's form while examining its missing blades. This cultural icon of the West is fast becoming a museum piece because of expensive and time-consuming maintenance costs. Windmills are increasingly non-operable and the water tanks formerly supplied using wind power are now filled by ranchers using submersible pumps powered by portable generators or solar energy. Abandoned windmills are left to slowly deteriorate but serve as excellent observation posts for vertigo-free souls.

**Groundwater Recharge** - Recharge occurs in the LSP through four routes 10:

- Mountain-front recharge;
- Sreambed infiltration;
- Underflow from Aravaipa Canyon basin; and
- Underflow from the Upper San Pedro basin.

Mountain-front recharge occurs through surface runoff flowing off mountain bedrock and infiltrating the permeable sediments on surrounding alluvial fans. This is the main source of replenishment to the basin-fill aquifers <sup>10</sup>. Streambed infiltration is the main recharge source for the *floodplain aquifer* as well as providing some recharge to the basin-fill aquifers. Streambed infiltration occurs when surface water flows in the Gila and San Pedro Rivers and their tributaries infiltrate through coarse riverbeds<sup>10</sup>.

In the LSP, total recharge is estimated at 25,000 acrefeet per year (af/yr). Mountain front recharge and streambed infiltration contribute 24,000 af/yr, while underflow from Aravaipa Canyon basin is 800 af/yr and 120 af/yr from the Upper San Pedro basin<sup>9</sup>.

#### Groundwater Discharge -

Groundwater discharge from the LSP occurs through five processes: pumpage from wells; evapotranspiration from phreatophytes and crops: evaporation from surface water in riverbeds; by discharge from springs and seeps; and through underflow to the Donnelly Wash Basin<sup>9</sup>. Pumpage from wells is considered the largest source of discharge and, in the late 1980s, was estimated to total approximately 36,000 af 9. Of this total well discharge, 59 percent was for mining use (**Figure 12**), 37 percent for irrigation use, 4 percent for public supply and/or domestic use<sup>10</sup>.



Figure 12. Groundwater quality assessments are much easier and complete when local sources of hydrologic knowledge are utilized. ASARCO's Kip Gambee (pictured in hard hat with Maureen Freark of ADEQ) is one such fount. These hydrologists are posing next to one of the high-capacity mining wells located in the ASARCO wellfield near the confluence of the Gila and San Pedro Rivers. Mining is the single largest water use in the Lower San Pedro basin.

#### **GROUNDWATER** SAMPLING RESULTS

To characterize the regional groundwater quality of the LSP, ADEQ personnel sampled 63 groundwater sites (**Figure 13**) consisting of 46 wells (**Figure 5**) and 17 springs (Figure 14). The 46 wells consisted of 4 artestian, 23 domestic with submersible pumps, 9 irrigation with turbine pumps, 2 mining with turbine pumps, 4 public water-supply with submersible pumps, and 4 stock windmills. Information on locations and characteristics of groundwater sample sites is provided in **Appendix A**. At the 63 sites, the following types of samples were collected:

- < 63 inorganic samples;
- < 25 VOC samples;
- < 19 radon samples;
- < 19 radiochemistry samples; and
- < 2 pesticide samples.

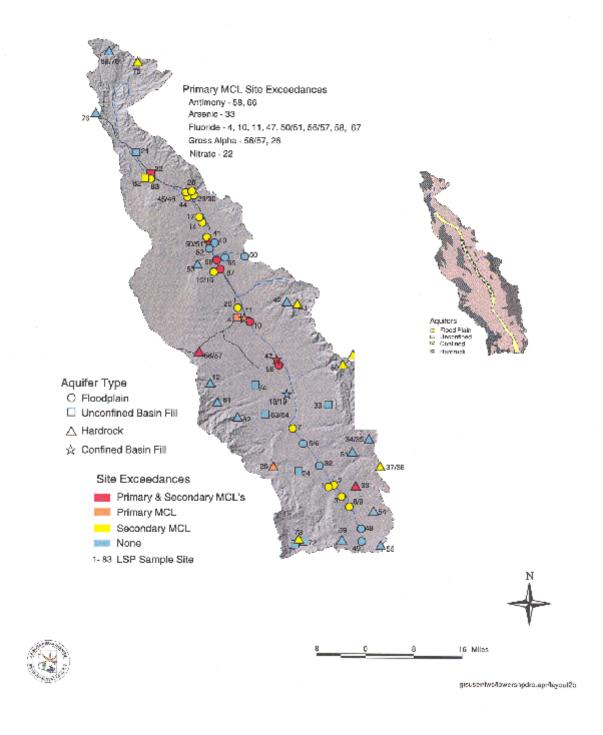
#### Water Quality Standards/Guidelines

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:

- Federal Safe Drinking Water (SDW) **Primary** Maximum Contaminant Levels (MCLs). These enforceable health-based standards establish the maximum concentration of a constituent allowed in water supplied by public systems <sup>54</sup>.
- State of Arizona Aquifer Water-Quality Standards apply to aquifers that are classified for drinking water protected use<sup>5</sup>. 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 nonenforceable 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<sup>54</sup>.

Figure 13 Water Quality Exceedances at Sample Sites



#### Water Quality Standard/Guideline Exceedances

Health-based Primary MCL water quality standards and State aquifer water quality standards were exceeded at 11 of 63 sites (18 percent) (Figure 13)(Table 1). Constituents above Primary MCLs include antimony (2 sites), arsenic (1 site under the current standards; 12 sites under the 2006 standards) (Figure 15), fluoride (8 sites) (Figure 16), nitrate as nitrogen (1 site), gross alpha (2 sites), and uranium (1 site).

In addition, if 2006 arsenic standards are considered, 18 of 63 sites (29 percent) would have exceeded at least one Primary MCL. Potential health effects of these Primary MCL exceedances are also provided in Table 1.

Aesthetics-based Secondary MCL water quality guidelines were exceeded at 31 of 63 sites (49 percent) (Table 2)(Figure 13). Constituents above Secondary MCLs include: chloride (2 sites), fluoride (16 sites) (**Figure 16**), iron (4 sites), manganese (9 sites)

(**Figure 15**), pH (4 sites) (**Figure 17**), sulfate (11 sites)

(Figure 18), and TDS (24 sites) (Figure 18).

Radon is a naturally occurring, intermediate breakdown product from the radioactive decay of uranium-238 to lead-206<sup>20</sup>. There are widely conflicting opinions on the risk assessment of radon in drinking water, with drinking water standards varying from 300 piC/l to 4,000 piC/l<sup>20</sup>. Sixteen of the 19 sites exceeded the 300 piC/l proposed standard; none exceeded the 4,000 proposed standard.

#### **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<sup>56</sup>. Irrigation water may be classified using specific conductivity (SC) and the Sodium Adsorption Ratio (SAR) in conjunction with one another. The majority of sites in the LSP have a low sodium hazard and a low-to-high salinity hazard when used for irrigation (**Figure 19**). Generally, only confined aquifer sites had sodium hazards while floodplain aquifer sites had salinity hazards.

#### **Analytical Results**

Analytical inorganic and radiochemistry results of the 63 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<sub>95%</sub>), 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**.



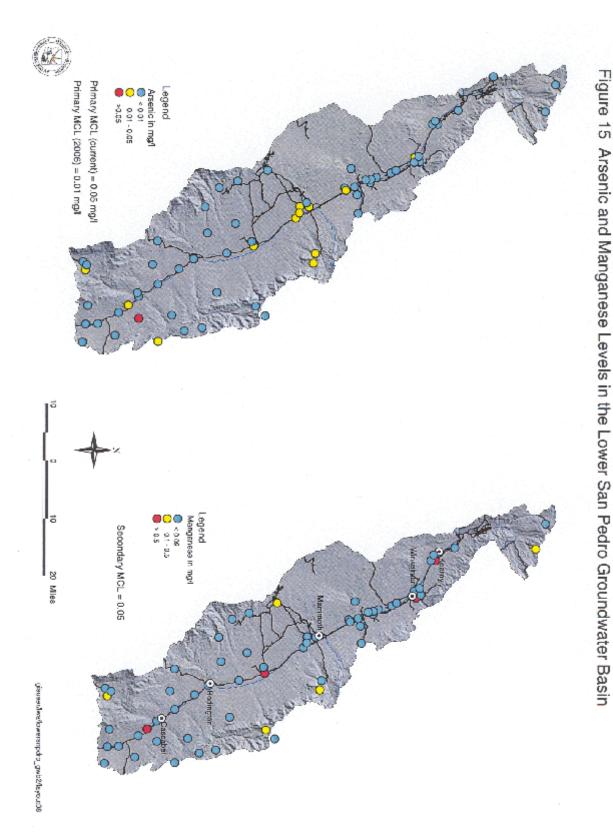
Figure 14. In remote mountainous areas, groundwater samples are often collected from springs as typically few wells exist in these rugged areas. Ranchers use these springs to water their livestock, often developing them so that the water flows out of a pipe into a series of troughs. The flow rate of springs can vary from figuratively drops per minute to higher flows which can sustain their own riparian area. Davis Spring, located on the eastern slope of the Santa Catalina Mountains, is an example of the latter with its valley location clearly marked by an abundance of verdant, water-loving, deciduous tress.

Table 1. LSP 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 <sub>2</sub> -N)	1.0	0		Methemoglobinemia						
Nitrate (NO <sub>3</sub> -N)	10.0	1	30	Methemoglobinemia						
	Trace Elements									
Antimony (Sb)	0.006	2	0.0073 - 0.75	Cancer						
Arsenic (As)	0.05 0.01*	1 12*	0.11 0.011 - 0.11	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						
Fluoride (F)	4.0	8	4.0 - 13	Skeletal damage						
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	2	19 - 68 piC/l	Cancer						
Ra-226 + Ra-228	5 piC/l	0	Bone cancer							
Uranium	30 Fg/l	1	61.5 Fg/l							

All units in mg/l except gross alpha, radium-226+228, and uranium.

<sup>\*</sup> new arsenic primary MCL scheduled to be implemented in 2006 Source: 54 57



**Groundwater Sampling Results** 16



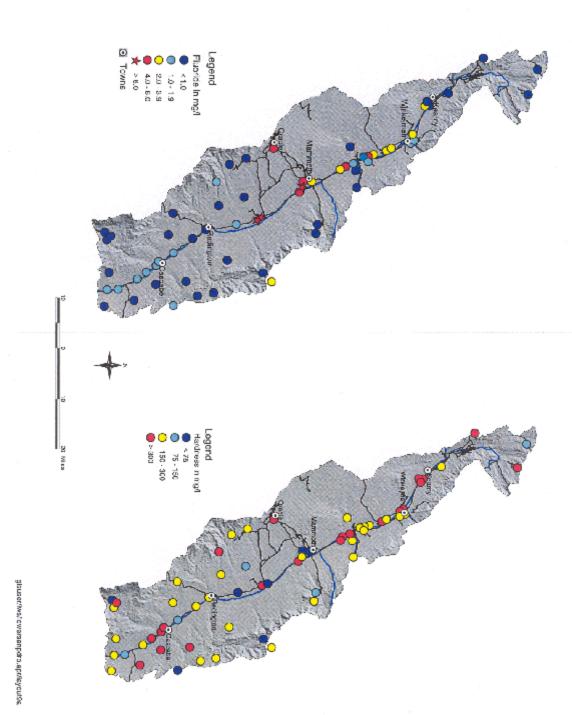


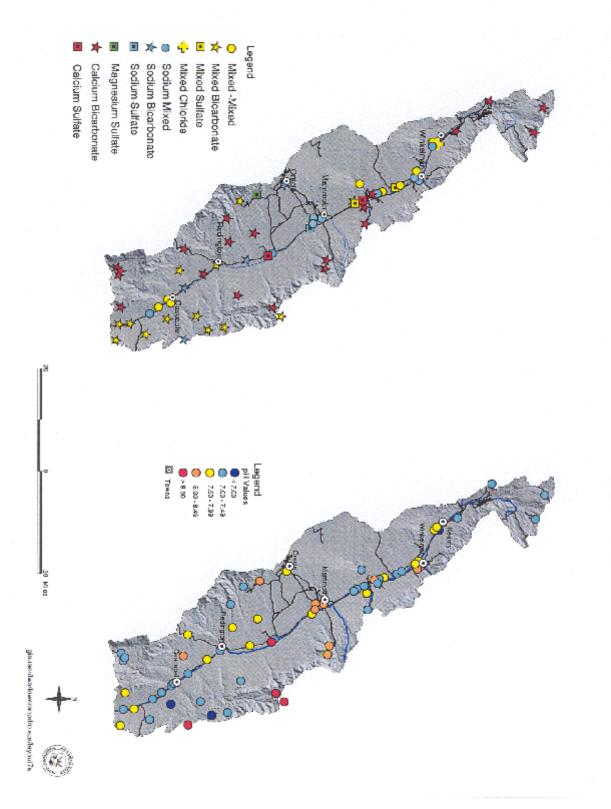
Figure 16 Fluoride and Hardness Levels In the Lower San Pedro Groundwater Basin

Table 2. LSP 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	4	8.53 - 9.24 su	Corrosive water					
	General Mineral Characteristics								
TDS	500	24	500 - 2850 mg/l	Unpleasant taste					
	Major Ions								
Chloride (Cl)	250	2	705 - 810 mg/l	Salty taste					
Sulfate (SO <sub>4</sub> )	250	11	260 - 1100 mg/l	Rotten-egg odor, unpleasant taste, and laxative effect					
		Т	race Elements						
Fluoride (F)	2.0	16	2.0 - 13 mg/l	Mottling of teeth enamel					
Iron (Fe)	0.3	4	0.34 - 2.1 mg/l	Rusty color, reddish stains, and metallic tastes					
Manganese (Mn)	0.05	9	0.056 - 0.76 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:  $^{31\ 54\ 57}$ 

Figure 17 Water Chemistry and pH Levels in the Lower San Pedro Groundwater Basin





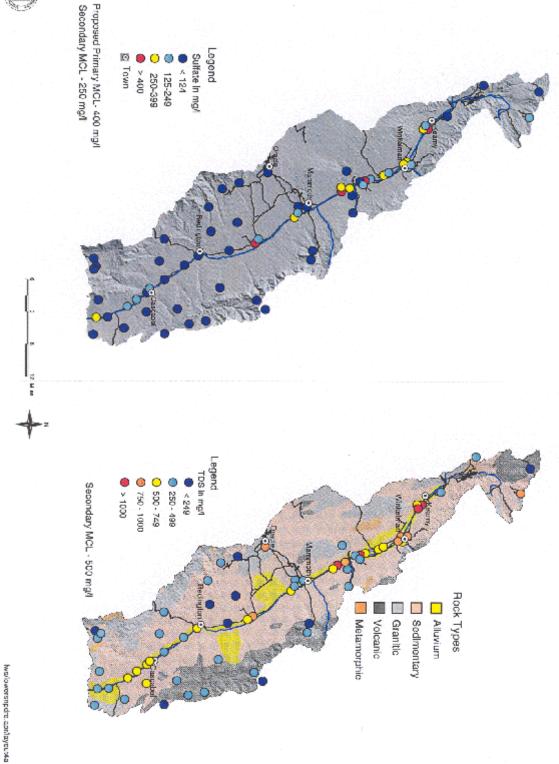


Table 3. Summary Statistics for LSP Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Median	Mean	Upper 95% Confidence Interval	
Physical Parameters							
Temperature (°C)	N/A	60	20.1	20.9	21.3	22.5	
pH-field (su)	N/A	63	7.50	7.45	7.63	7.76	
pH-lab (su)	0.01	63	7.59	7.60	7.69	7.79	
Turbidity (ntu)	0.01	63	- 0.33	0.41	3.18	6.69	
		General Min	eral Characteris	tics			
Total Alkalinity	2.0	63	192	220	209	227	
Phenol. Alkalinity	2.0	5		> 80% of d	ata below MRL		
SC-field (FS/cm)	N/A	63	637	656	810	982	
SC-lab (FS/cm)	N/A	63	684	700	872	1061	
Hardness	10.0	63	219	250	266	312	
TDS	10.0	63	428	440	549	671	
		M	Iajor Ions				
Calcium	5.0	63	61	72	75	89	
Magnesium	1.0	62	14.9	18.0	18.6	22.2	
Sodium	5.0	62	58	51	91	123	
Potassium	0.5	61	2.8	3.0	3.5	4.2	
Bicarbonate	2.0	63	231	270	253	275	
Carbonate	2.0	5	> 80% of data below MRL				
Chloride	1.0	62	21	21	55	90	
Sulfate	10.0	58	101	72	155	209	
Nutrients							
Nitrate (as N)	0.02	54	0.5	0.5	1.5	2.6	
Nitrite (as N)	0.02	3	> 80% of data below MRL				
Ammonia	0.02	11	> 80% of data below MRL				
TKN	0.05	33	0.06	0.06	0.27	0.48	
Total Phosphorus	0.02	38	0.036	0.035	0.054	0.072	

All units mg/l except where noted with physical parameters Source: 43

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

Constituent	Minimum Reporting Limit (MRL)	Number of Samples Over MRL	Lower 95% Confidence Interval	Median	Mean	Upper 95% Confidence Interval			
Trace Elements									
Antimony	0.005	2		> 80% of d	ata below MRL				
Arsenic	0.01	13		> 80% of d	ata below MRL				
Barium	0.1	6		> 80% of d	ata below MRL				
Beryllium	0.0005	0		> 80% of d	ata below MRL				
Boron	0.1	28	0.09	0.05	0.15	0.22			
Cadmium	0.001	1		> 80% of d	ata below MRL				
Chromium	0.01	1		> 80% of d	ata below MRL				
Copper	0.01	2		> 80% of d	ata below MRL				
Fluoride	0.20	61	1.09	0.93	1.62	2.15			
Iron	0.1	8		> 80% of d	ata below MRL				
Lead	0.005	1	> 80% of data below MRL						
Manganese	0.05	9	> 80% of data below MRL						
Mercury	0.0005	0		> 80% of d					
Nickel	0.1	0		> 80% of data below MRL					
Selenium	0.005	11		> 80% of data below MRL					
Silver	0.001	0		> 80% of d	ata below MRL				
Thallium	0.005	0		> 80% of data below MRL					
Zinc	0.05	13		> 80% of data below MRL					
		Radi	ochemical Constitu	ients					
Radon*	Varies	19 (out of 19)	366	385	507	647			
Gross Alpha*	Varies	18 (out of 19)	1.5	4.6	8.8	16.1			
Gross Beta*	Varies	16 (out of 19)	2.1	2.6	4.0	5.9			
Ra-226*	Varies	0 (out of 9)		> 80% of data below MRL					
Uranium**	Varies	2 (out of 2)		> 80% of d	ata below MRL				

All units mg/l except \* = piC/l and \*\* = Fg/l Source:  $^{43}$ 

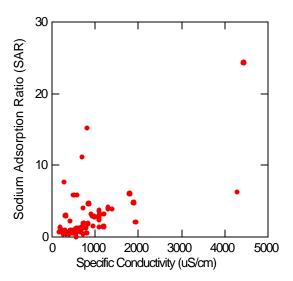


Figure 19. This graph illustrates that salinity is generally more of a hazard than sodium to successful plant growth. The salinity hazard is considered "medium" at SC levels > 250 uS/cm and "high" at > 750 uS/cm. In contrast, the sodium hazard is considered "low" when the SAR is less than 8. This typically only occurs with confined basin-fill aguifer sites<sup>56</sup>.

The VOC and pesticide analytical results are provided in Appendix B and summarized as follows:

**VOC Results** - Analytical results of the VOC samples collected at 25 sites revealed detections at only two sites. Chloroform, an organic disinfection byproduct of drinking water systems using free chlorine, was detected (4.4 Fg/l) in the sample collected from a public water supply well near Kearny. Detections of methylethyl ketone and another unidentified compound occurred in a sample collected from a well located in the floodplain south of Mammoth. These compounds are not target compounds listed by either EPA method 601 or 602 but were identified by the ADHS laboratory. These detections were probably caused by glue used for PVC piping. The well owner added a sample port at the wellhead the day before sampling by ADEQ.

None of the other 34 VOC compounds on the EPA 601/602 VOC list, including the gasoline oxygenate, Methyl tertiary-Butyl Ether (MTBE), were detected at any sites. Analytes on the EPA 601/602 VOC list is found in Appendix C.

**Pesticide Results** - Analytical results of the two samples collected for Groundwater Protection List (GWPL) analysis indicated that none of the 76

pesticides or their products of degradation on the list were detected at any of the sites. Appendix D contains a list of the pesticides on the GWPL.

#### **GROUNDWATER COMPOSITION**

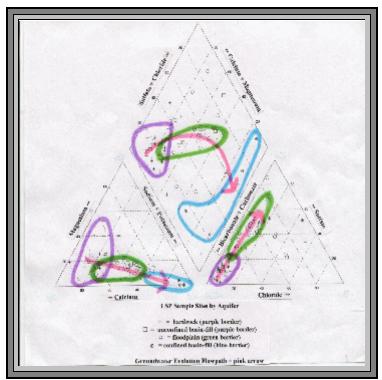
Groundwater in the LSP was characterized by qualitative classifications, chemistry, and crosscorrelation of constituent concentrations.

**General Summary** - Groundwater in the LSP is generally fresh, slightly-alkaline, and varies widely in hardness concentrations. TDS concentrations (**Figure 18**) were considered *fresh* (below 1.000 mg/l) at 59 sites while 4 sites were slightly saline (1,000 to 3,000 mg/l)<sup>27</sup>. Among cations, sodium plays the greatest role in predicting TDS concentrations while among anions, the best predictor is chloride. Overall among major ions, sodium is by far the best predictor of TDS concentrations (multiple regression analysis, p # 0.05). Levels of pH were *slightly-alkaline* (above 7 su) at 60 sites and *slightly-acidic* (below 7 su) at 3 sites <sup>22</sup>. Hardness concentrations (**Figure 16**) were divided into soft (9 sites), moderately hard (5 sites), hard (29 sites), and very hard (20 sites) $^{21}$ .

Nutrient concentrations were generally low with only nitrate, total phosphorus, and total Kjeldahl nitrogen (TKN) detected at more than 20 percent of the sites. Nitrate (as nitrogen) concentrations were divided into natural background (15 sites at < 0.2 mg/l), may or may not indicate human influence (40 sites between 0.2 - 3.0 mg.l), may result from human activities (6 sites between 3.0 - 10 mg/l), and probably result from human activities  $(1 \text{ site} > 10 \text{ mg/l})^{38}$ .

Most trace elements were rarely detected. These include antimony, arsenic, barium, beryllium, cadmium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium. Only boron and fluoride (**Figure 16**) were detected at more than 20 percent of the sites while arsenic (Figure 15), barium, iron, manganese (Figure 15), selenium, and zinc were detected at more than 10 percent of sites.

**Groundwater Chemistry** - The chemical composition of the 63 groundwater sites in the LSP is illustrated using several methods. The groundwater chemistry of each site is mapped in **Figure 18** and plotted using Piper trilinear diagrams in **Figure 20**. These figures revealed several patterns. The cation triangle



**Figure 20**. Sample sites plotted on a Piper tri-linear diagram illustrates that aquifers in the LSP generally have characteristic groundwater chemistries as indicated by the colored borders. The groundwater evolution flowpath is thought to follow the route indicated by the pink arrows.

diagram (lower left in **Figure 20**) shows that the dominant (> 50 percent) cation is calcium at 24 sites, sodium at 23 sites, magnesium at 1 site, and is mixed (no constituent > 50 percent) at 15 sites. The anion triangle diagram (lower right in **Figure 20**) shows that the dominant anion (> 50 percent) is bicarbonate at 38 sites, sulfate at 6 sites, chloride at 1 site, and is mixed (no constituent > 50 percent) at 18 sites. The cationanion diamond diagram (in the center of **Figure 20**) shows that the groundwater chemistry is highly variable in the basin.

Water chemistries found in the LSP include: calciumbicarbonate (22 sites), mixed-bicarbonate (12 sites), sodium-mixed (10 sites), mixed-mixed (8 sites), sodium-bicarbonate (4 sites), calcium-sulfate and mixed-sulfate (2 sites apiece), and mixed-chloride, sodium-sulfate, and magnesium-sulfate (1 site apiece).

The 63 groundwater sites were divided into four aquifers for chemical comparison: hardrock, unconfined basin-fill, floodplain, and confined basin-fill. Empirical patterns appeared with each group and are highlighted in **Figure 20**. Hardrock and

unconfined basin-fill sites (clustered within the purple border) were generally *calcium-bicarbonate*, floodplain sites (clustered within the green border) were generally *mixed-mixed*, and confined basin-fill sites (clustered within the blue border) were generally *sodium-mixed*. Groundwater chemical evolution is hypothesized to follow the pink arrow, changing from *calcium-bicarbonate* to *mixed-mixed* to *sodium-mixed*<sup>46</sup>.

Constituent Covariation - The covariation of constituent concentrations from the 63 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.

The *overall basin* (63 sites) had many significant correlations among constituents (Pearson Correlation Coefficient test, p# 0.05). The most prevalent pattern involved the positive correlation among TDS, SC, hardness, major ions (calcium, magnesium, sodium, potassium, sulfate (Figure 21), and chloride), nitrate, and boron. Other constituents such as pH-field, temperature, and fluoride exhibited unique patterns. With pH-field, a positive correlation occurred with fluoride and temperature: in contrast, negative correlations occurred with hardness (Figure 22), calcium, magnesium, bicarbonate, and nitrate. Temperature was positively correlated with pH-field and fluoride; in contrast, negative correlations occurred with bicarbonate and potassium. Fluoride was positively correlated with temperature, pH-field, sodium, sulfate, boron, gross alpha, and gross beta; negative correlations occurred with bicarbonate. Each of the four aquifers examined separately for significant correlations exhibited different patterns (Pearson Correlation Coefficient test, p# 0.05).

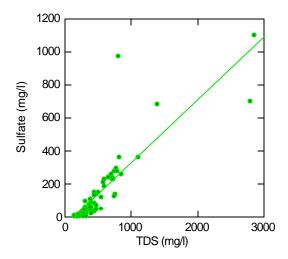


Figure 21. The positive correlation between TDS and sulfate is shown above (Pearson Correlation Coefficient, p # 0.01). The highest sulfate concentrations are typically found in the floodplain aquifer between Mammoth and Kearny and may be the result of elevated sulfate concentrations in surface water flow, gypsum deposits, and extensive mine tailings in the area.

The *floodplain aquifer* (27 sites) showed similar patterns to the overall basin, but with interesting differences. Again the major pattern is the positive correlations among TDS, SC, hardness, major ions, boron and fluoride (instead of nitrate). Very different patterns emerged with pH-field, temperature, and fluoride. With pH-field, a positive correlation occurred with TDS, hardness, calcium, magnesium, bicarbonate, and sulfate. There were no significant correlations with temperature. Fluoride had the above-noted positive correlations.

The hardrock aquifer (23 sites) also exhibited similar patterns to the overall basin but with unique differences. Again the major pattern is the positive correlations among TDS, SC, hardness, major ions, nitrate, and boron. With pH-field, negative correlations occurred with TDS, SC, hardness, calcium, magnesium, and bicarbonate. Temperature had a negative correlation with nitrate. Fluoride was positively correlated with sodium, gross alpha, and gross beta; negative correlations occurred with hardness and calcium.

The *unconfined basin-fill aquifer* (9 sites) had a positive correlation among TDS, SC, hardness, turbidity, the major ions, nitrate, and boron. There were no significant correlations involving pH-field, temperature, and fluoride.

The *confined basin-fill aquifer* (4 sites) had a positive correlation among TDS, SC, hardness, turbidity, the major ions, and boron. The only significant correlations involving pH-field and fluoride was a positive one with each other. Temperature was not correlated to any other constituents.

#### **GROUNDWATER QUALITY PATTERNS**

Groundwater in the LSP was characterized by assessing the spatial variation of groundwater quality among aquifers, geologic classifications, and watersheds as well as the variation of groundwater quality in relation to groundwater depth.

**Aguifer Comparison** - Analytical results were compared between the four major aquifers in the LSP: floodplain (27 sites), unconfined basin-fill (9 sites), confined basin-fill (4 sites), and hardrock (23 sites) to examine for significant differences.

Three constituents, pH-field, sodium, and fluoride (Figure 23), were higher in the confined basin-fill aquifer than in the other three aquifers. Four other constituents had unique patterns. Temperature was higher in the confined basin-fill aquifer than in hardrock. Bicarbonate/total alkalinity was lower in the *confined basin-fill aquifer* than in the *floodplain* 

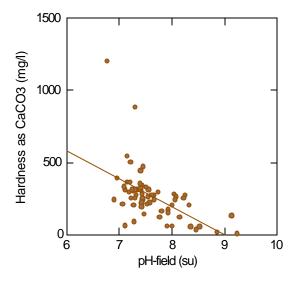


Figure 22. Hardness and pH have a negative correlation (Pearson Correlation Coefficient, p # 0.01). Calcium, a major component of hardness, is typically removed from solution by precipitation of calcium carbonate and formation of smectitie clays while pH typically increases downgradient through silicate hydrolysis reactions<sup>44</sup>.

aguifer and hardrock; and in the unconfined basin-fill aguifer than in the hardrock (Figure 24). Sulfate was lower in hardrock than in the confined basin-fill aguifer and the floodplain aguifer. Finally, potassium was higher in the *floodplain aguifer* than in the hardrock (Kruskal-Wallis test in conjunction with Tukey test, p# 0.05).

In many cases, the *confined basin-fill aquifer* sites were data outliers which may have been masking other patterns. For this reason, the four confined basin-fill aguifer sites were deleted from the data set and analytical results were compared between three LSP aquifers: floodplain, unconfined basin-fill, and *hardrock* to examine for significant differences.

Six constituents--SC, TDS, sodium, potassium, sulfate, and fluoride—were higher in the *floodplain aquifer* than in hardrock. Bicarbonate/total alkalinity was higher in hardrock than in the unconfined basin-fill aquifer (Kruskal-Wallis test in conjunction with Tukey test, p# 0.05).

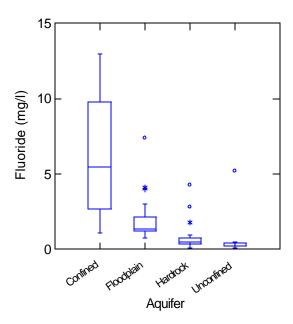


Figure 23. Fluoride concentrations are frequently elevated over Primary and Seconday MCLs in the confined, basin-fill aquifer. At these sites, calcium appears to be an important control on fluoride through precipitation of the mineral, fluorite<sup>44</sup>. These sites had depleted levels of calcium constituting a small percentage of the total cation concentration.

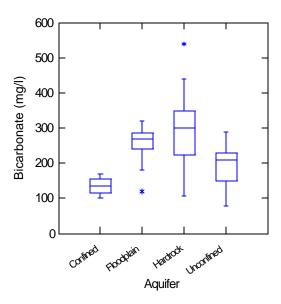


Figure 24. Bicarbonate concentrations are higher in hardrock than in the confined and unconfined-basin fill aguifers and in the floodplain aguifer than in the confined basin-fill aguifer (Kruskal-Wallis test, p # 0.05). These patterns support earlier reports that indicate most recharge occurs in the hardrock mountains and along river floodplains<sup>28</sup>.

Floodplain Aquifer Comparison - Analytical results were compared for groundwater quality data collected in the *floodplain aguifer* between the four watersheds: Redington, Mammoth, Winkelman, and **Kearny** to examine for significant constituent concentration differences along this flowpath

Three patterns were revealed. SC and sodium (**Figure 25**) were higher in the *Kearny watershed* than in the Redington and Winkelman watersheds. Potassium and chloride (**Figure 26**) were higher in the *Kearny watershed* than in the other three watersheds. Finally, fluoride was higher in the Mammoth watershed than in the other three watersheds (Kruskal-Wallis test in conjunction with Tukey test, p# 0.05).

**Geological Comparison** - Hardrock sites in the LSP were divided into four rock types (**Figure 10**): sedimentary (17 sites), volcanic (7 sites), granitic (6 sites), and **metamorphic** (1 site) that are interspersed

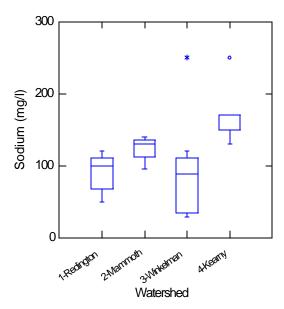


Figure 25. Sodium concentrations in the floodplain aquifer generally increase from upgradient (left) to downgradient (right) watersheds, particularly in the most downgradient, Kearny. This may be partially due to recharge from the Gila River that has higher salt levels than are found in the San Pedro River<sup>7 56</sup>.

throughout mountainous areas of the basin. Analytical results were again examined for concentration differences. No significant patterns were revealed with this geological comparison (Kruskal-Wallis test, p# 0.05).

Geographic Comparison - The LSP was divided into southern (upgradient) and northern (downgradient) sub-basins at the USGS gauging station at Mammoth for further analyses. TDS (Figure 27), SC, hardness, calcium, magnesium, sodium, potassium, chloride, and sulfate had higher concentrations in the northern, downgradient portion than the southern, upgradient portion. In contrast, pH values were higher in the southern, upgradient portion than in the northern, downgradient portion (Kruskal-Wallis test, p# 0.05).

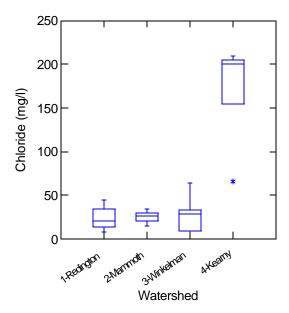
**Groundwater Depth Comparison** - The vertical variation of groundwater quality was examined by comparing constituent concentrations with groundwater depth below land surface (bls) for the 63 sites in the LSP. Many constituent concentrations tended to significantly decrease with increasing groundwater depth bls. Hardness, calcium, magnesium, sodium, chloride, fluoride, and boron followed this pattern. In contrast, pH-field,

temperature (**Figure 28**), and bicarbonate/total alkalinity had concentrations that increased with increasing groundwater depth (regression analysis, p # 0.05).

Constituent concentrations from sample sites in the four aquifers (floodplain, confined basin-fill, unconfined basin-fill, and hardrock) were compared with groundwater depth for significant trends within each aquifer. No significant trends were found within the floodplain, and unconfined basin-fill aquifers as well as hardrock. Total alkalinity concentration was found to decrease with increasing groundwater depth bls (regression analysis, p # 0.05).

#### **Groundwater Quality Time Trend Analysis**

A time-trend analysis (**Table 4**) compared groundwater quality data collected from six ADEQ sites previously sampled in the early 1950s by the USGS<sup>28</sup>.

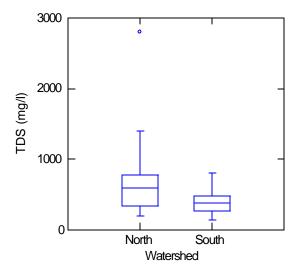


**Figure 26**. Chloride increases in the *Kearny watershed* is even more dramatic than with sodium. Gila River recharge to the floodplain aquifer probably accounts for much of this increase. Degradation of Gila River water quality is caused by irrigation-return flows and highly-mineralized springs and flowing artesian wells, particularly in times of low flows<sup>10</sup>.

**Table 4. Time-Trend Comparison of LSP Sample Sites** 

Constituent	LSP-11	LSP-14	LSP-24	LSP-37/38	LSP-54	LSP-63/64			
	1950/1999 -% Difference	1950/1999 -% Difference	1951/2000 - % Difference	1950/2000 - % Difference	1965/2000 - % Difference	1950 /2000 - % Difference			
Physical Parameters and General Mineral Characteristics									
Temp. ( <sup>0</sup> C)	42 - 38 <b>9%</b>	21 - 20.8 <b>0%</b>	42 - 34 <b>22%</b>	20 - 21.4 <b>7%</b>	20 - 17.7 <b>12%</b>	27 - 22 <b>20%</b>			
SC (FS/cm)	683 - 700 <b>2%</b>	928-1100 <b>17%</b>	287 - 290 1%	457 - 430 <b>6%</b>	614 - 608 <b>1%</b>	338 - 330 <b>2%</b>			
Alk., Total				218 - 180 <b>19%</b>	263 - 270 <b>3%</b>				
Hardness	36 - 32 <b>12%</b>	284 - 310 <b>9%</b>	12 - 9.2 <b>26%</b>		310 - 310 <b>0%</b>	158 - 160 <b>1%</b>			
TDS	441 - 450 <b>2%</b>	624 - 700 <b>6%</b>	218 - 195 <b>11%</b>		376 - 380 <b>1%</b>	205 - 195 <b>5%</b>			
			Major Ions						
Calcium	12 - 12 <b>0%</b>	84 - 95 6%	4 - 3.5 13%		60 - 69 13%	45 - 48 <b>1%</b>			
Magnesium	1.65 <b>105%</b>	18 - 18 <b>0%</b>	0.4 - 0.5 <b>22%</b>		39 - 37 <b>5%</b>	11 - 9.7 6%			
Sodium & Potassium	133 - 142 6%	100 - 116 <b>7%</b>	68 - 65 <b>4%</b>		18 - 26 <b>38%</b>	9 - 14 <b>22%</b>			
Bicarbonate	114 - 104 <b>9%</b>	287 - 270 <b>4%</b>	173 - 135 <b>25%</b>	266 - 220 <b>19%</b>	321 - 330 <b>3%</b>	188 - 180 <b>2%</b>			
Chloride	42 - 41 <b>2%</b>	29 - 33 <b>7%</b>	4 - 3.1 <b>25%</b>	5 - 4.9 <b>2%</b>	20 - 22 10%	4 - 4.5 6%			
Sulfate	152 - 150 <b>1%</b>	209 - 260 11%	4.9 - 3.9 <b>23%</b>		48 - 47 <b>2%</b>	15 - 13 <b>7%</b>			
Nutrients									
Nitrate (as nitrogen)	.2534 30%	.5342 <b>12%</b>	.2907 <b>122%</b>		1.8 - 2.5 33%	.3139 <b>11%</b>			
Trace Elements									
Fluoride	5.6 - 6.6 <b>16%</b>	2.4 - 2.1 <b>7%</b>	2 - 1.8 11%		.70 - 71 <b>1%</b>	0.425 <b>23%</b>			

All units in milligrams per liter (mg/l) except where noted. Historic samples collected by the U.S. Geological Survey  $^{28\,47}$ .



**Figure 27**. TDS concentrations are higher in the northern (downgradient) portion than in the southern (upgradient) portion (Kruskal-Wallis test, p # 0.05). Factors related to this pattern may be a combination of natural and cultural impacts such as gypsum deposits, large-scale mining operations, and recharge of saline surface water from the Gila River $^{10}$ .

The six sites are distributed as follows: *confined* basin-fill aquifer (one site), unconfined basin-fill aguifer (two sites), floodplain aguifer (one site), and hardrock (two sites). Analytical results were compared between the two sampling events. Of twelve constituents examined (mainly general mineral characteristics and major ions), only temperature levels significantly varied, being higher in the 1950s (Wilcoxon rank-sum test, p # 0.05). Temperature differences may be due to different equipment and purging requirements. Empirically examining the results provided in Table 4, constituent concentrations appear remarkably stable especially when considering potential differences in sampling and analytical techniques. The largest percentage differences typically involve very low concentrations where the absolute difference is small.

#### **CONCLUSIONS**

Groundwater quality of the LSP was assessed in 2000 by the ADEQ Groundwater Monitoring Unit. Sampling was conducted at 63 sites. Groundwater samples were collected for inorganic analyses at all sites, and for VOCs, radiochemistry, radon, and pesticide analyses at fewer sites.

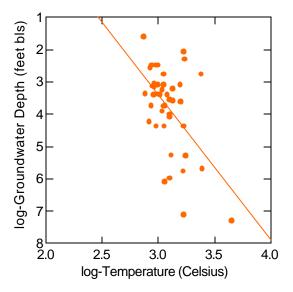
The conclusions of this study are summarized in three different sections:

- Groundwater suitability for domestic use.
- Groundwater quality patterns unique to subareas of the basin.
- Study design and data evaluation.

#### Suitability of Groundwater for Domestic Use

Eighteen (18) percent of sites had at least one constituent exceeding a health-based, Primary MCL standard. Primary MCL exceedances largely involved fluoride in the floodplain and confined basin-fill aquifers generally between the communities of Redington and Dudleyville. Both antimony exceedances were also in this area (Figure 13).

Other Primary MCL exceedances included gross alpha at two sites located in granitic geology near Oracle and Redington Pass, nitrate at one site near Kearny, and arsenic at one site near Cascabel. If the new arsenic standard scheduled to be implemented in 2006 is considered, 11 additional sites near Mammoth and Cascabel (**Figure 15**) would exceed drinking water standards.



**Figure 28**. Temperatures generally increase with increasing groundwater depth bls (regression analysis, p # 0.05). Groundwater temperatures increase approximately 3 degrees Celsius with every 328 feet in depth <sup>13</sup>. This relationship is best displayed using a biphasic method utilizing the log values of both factors.

Similarly, 49 percent of sites had at least one constituent exceeding an aesthetics-based, Secondary MCL guideline. Their spatial distribution is largely constituent-specific:

- TDS exceedances (24 sites), sulfate exceedances (11 sites), and chloride exceedances (2 sites) occurred primarily along the San Pedro-Gila River corridor from the Aravaipa Creek confluence downstream to Kearny.
- Fluoride exceedances (16 sites) occurred primarily along the San Pedro River corridor stretching from north of Redington to Winkelman.
- *Manganese* exceedances (9 sites) and *iron* exceedances (4 sites) were randomly distributed throughout the basin.
- *pH* exceedances (4 sites) occurred primarily in the Gailuro Mountains.

Salinity related exceedances such as TDS, sulfate, and chloride appear to be related to recharge from the Gila and the San Pedro Rivers, dissolution of gypsum deposits, and recharge impacted by mine tailings and farming. Fluoride exceedances may be associated with calcium-depleted, alkaline conditions in the *confined basin-fill aquifer* that leaks groundwater into the *floodplain aquifer*<sup>28</sup>. Iron and manganese exceedances appear to be site specific with no large clusters of elevated concentrations of either constituent evident.

Radon, the naturally occurring, intermediate breakdown product from the radioactive decay of uranium-238 to lead-206, had a mean concentration of 507 piC/l determined from 19 sites in the LSP. Recent radon data collected in three central Arizona basins had a similar mean of 590 piC/l<sup>20</sup>. As with the LSP data, this previous USGS study identified few relations between radon concentrations and various hydrologic factors. There are widely conflicting opinions on the risk assessment of radon in drinking water, with drinking water standards varying from 300 piC/l to 4,000 piC/l<sup>20</sup>.

Based upon comparing the results of this regional study with water quality standards/guidelines, groundwater in large expanses of the LSP appears to be largely suitable for domestic purposes.

Caution should be exercised when using groundwater

from along the San Pedro and Gila River corridors north of Redington because of potentially elevated fluoride concentrations as well as increased salinity levels.

### **Groundwater Quality Patterns Unique to Aquifers**

Individual aquifers were examined for groundwater quality patterns.

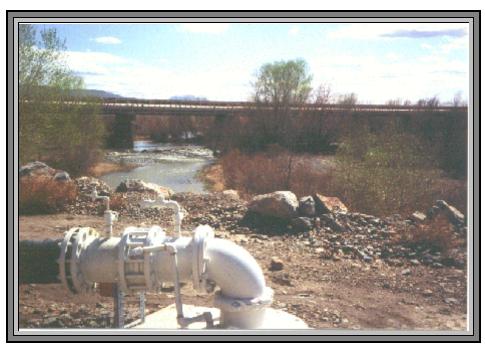
#### Hardrock

Analyses of groundwater samples collected from sites in hardrock areas indicate that water quality typically is suitable for domestic or municipal uses. However, caution should be exercised in wells or springs located in granitic geology as elevated radiochemistry concentrations are often found in this rock type. The limited potential water production in hardrock areas usually makes these sites suitable only for domestic or stock use<sup>35</sup>.

Of the 23 hardrock sample sites, only three had constituents exceeding a Primary MCL which consisted of gross alpha (two sites) and arsenic and fluoride (one site apiece). The 15 piC/l gross alpha standard was exceeded twice, with one site near Oracle having a concentration (69 piC/l) more than four times the MCL. Radiochemistry is typically elevated in areas of granite rocks, with the highest concentrations near mining areas<sup>37</sup>. Mining may effect gross alpha concentrations through increased rock surface exposure. In contrast, four other sample sites were also located in or near granitic rock but did not have gross alpha concentrations over the Primary MCL. This indicates that not all groundwater in areas of granitic geology necessarily have elevated gross alpha concentrations. These patterns have occurred in previous basin studies in Arizona<sup>51 52 53</sup>.

The site near Oracle also exceeded the fluoride Primary MCL standard. This well had a relatively high pH (7.93 su) and a calcium-depleted chemistry (sodium-bicarbonate) often reflective of groundwater with high fluoride concentrations. Groundwater in areas of granitic rock have previously been found to have fluoride concentrations at least twice that of other rock types <sup>59</sup>.

A site in the southern Gailuro Mountains exceeded the current arsenic Primary MCL standard. This spring had a low pH (6.97 su), a mixed-bicarbonate chemistry, and a low concentration of fluoride (0.30 mg/l), unusual for sites with elevated arsenic concentrations<sup>51 53</sup>.



**Figure 29**. The highest sulfate concentrations usually occur in wells withdrawing water from the floodplain aquifer, particularly those between the towns of Mammoth and Kearny. One such well that exceeds the 250 mg/l Secondary MCL is pictured above, which supplies water to ASARCO's milling activities near the town of Hayden. The influence of surface water recharge from the Gila River to nearby shallow wells is evident in this photograph.

Eight (8) of the 24 hardrock sites had constituent concentrations exceeding Secondary MCLs. These exceedances included manganese (five sites), pH (three sites), TDS (two sites), fluoride (one site).

The chemistry of hardrock sites was typically a calcium or mixed-bicarbonate type, which is typical of recharge areas <sup>46</sup>. The occasional site where sodium is the dominant cation are springs associated with fault zones, reversing the typical groundwater chemistry in hardrock areas <sup>28</sup>.

Many constituents (SC, TDS, sodium, potassium, sulfate, and fluoride) have lower concentrations in hardrock than in the *floodplain aquifer*; the opposite pattern occurs with bicarbonate. This indicates that although recharge occurs in both areas, mountain precipitation and runoff is more dilute than surface water flow from the San Pedro and Gila Rivers (**Figure 29**) (Kruskal-Wallis in conjunction with the Tukey test, p # 0.05).

No significant differences were found among different rock types (Kruskal-Wallis in conjunction with the Tukey test, p # 0.05).

# Unconfined Basin-Fill Aquifer

Analyses of groundwater samples collected from sites in the *unconfined basin-fill aquifer* indicate that water quality is typically suitable for domestic or municipal uses. Furthermore, this aquifer appears to have the highest quality groundwater in the LSP as evidenced by the lowest constituent concentrations.

Only two of the nine sites in the *unconfined basinfill aquifer* had water quality standard exceedances. A site near Mammoth had fluoride concentrations exceeding

the Primary MCL; the arsenic concentration also exceeded the 2006 standard.

A site near Kearny exceeded water quality standards for nitrate as well as TDS, sulfate, iron, and manganese. However, caution should be exercised in using data from this well. The analytical results do not match up with previous samples collected by the U.S. Geological Survey in 1980 and seem very out-of-character with other area samples. In particular, the nitrate (as nitrogen) concentration of 30 mg/l seems unusual. Both the ADHS laboratory and the well owner were contacted, but no errors could be found either with sample collection or analytical testing.

Except for the above two sites, the *unconfined basin-fill aquifer* sites had a calcium-bicarbonate chemistry, which is typical of recharge areas <sup>46</sup>. However, bicarbonate concentrations are less than in hardrock, probably indicating less recharge is occurring here than in the mountains (Kruskal-Wallis in conjunction with the Tukey test, p # 0.05). Median concentrations of TDS, hardness, magnesium, sodium, chloride, sulfate, and fluoride were lower in the *unconfined basin-fill aquifer* than in hardrock, the *floodplain aquifer*, and the *confined basin-fill aquifer*, though these differences were not typically statistically-different.

#### Floodplain Aquifer

Analysis of groundwater samples collected from 27 floodplain aguifer sites indicate that while healthbased water quality standards were only exceeded at 4 sites (15 percent), aesthetics-based water quality standards were exceeded at 19 sites (70 percent). Groundwater from this most productive aguifer in the LSP generally can be used for domestic or municipal purposes, but often has aesthetic drawbacks associated with salinity concentrations.

Primary MCL exceedances in the *floodplain aguifer* involved fluoride (three sites) and antimony (two sites). All four sites were located between Redington and Duddleyville. In addition, six sites exceeded the revised arsenic Primary MCL scheduled to be implemented in 2006.

Secondary MCL exceedances included TDS (18 sites), fluoride (10 sites), sulfate (nine sites), and iron and manganese (3 sites apiece). The chemistry of floodplain aquifer sites varied widely. Interestingly, a previous groundwater quality study near Cascabel

also revealed the characteristic clusters of Secondary MCL exceedances in the *floodplain aguifer* that were found in this study<sup>42</sup>.

Many constituents (SC, TDS, sodium, potassium, sulfate, and fluoride) had higher concentrations in the floodplain aquifer than hardrock (Figure 30). Fluoride, sodium, and pH were lower in the *floodplain aguifer* than in the *confined basin-fill aquifer*; the opposite pattern occurred with bicarbonate. These patterns suggest that more dilute recharge occurs in the mountains than along the streams and that little recharge occurs in the confined basin-fill aquifer.

Examining *floodplain aguifer* data by watershed, the most downgradient (Kearny) had significantly higher concentrations of SC, sodium, chloride, and potassium (Kruskal-Wallis in conjunction with the Tukey test, p# 0.05). These patterns may be explained by a combination of factors including impacts from surface water, natural factors, and human activities.

Surface water quality was examined from the four major waterways influencing the LSP:



Figure 30. ADEQ employee Elizabeth Boettcher kicks up her heels in excitement upon discovering a commercial water outlet touted as dispensing "Mountain Water" as compared to the Town of Kearny tanks holding groundwater pumped from the floodplain aquifer in the background. Although precise analytical techniques and proper statistical applications are indispensable to hydrology reports, often a great deal of information about a region's water resources can be discerned from examining the landscape and conversing with the residents. The entrepreneur operating this water stand shows it doesn't take an ADEQ hydrology report to determine that "Mountain Water" tastes better than "Valley Water", although perhaps not coincidently constituents with aesthetic-based standards such as TDS and sulfate were significantly higher in the floodplain aquifer than in hardrock areas (Kruskal-Wallis test in conjunction with the Tukey test, p # 0.05).



**Figure 31**. Coolidge Dam, constructed in 1928, impounds the Gila River upriver of the LSP and creates San Carlos Reservoir. Water is stored here for power generation and irrigation in San Carlos Irrigation Project lands near the Coolidge/Casa Grande area. The USGS collects water quality samples from the river near Calva upgradient of the reservoir. All ready highly mineralized especially during low flows<sup>10</sup>, evaporation from the reservoir adds to the salinity concentrations<sup>32</sup>. This surface water recharges the floodplain aquifer in portions of the LSP. Water is released from San Carlos Reservoir into the Gila River according to regulations contained in the Gila Decree of 1936 for San Carlos Project lands<sup>10</sup>.

- The San Pedro River (upgradient site near Cascabel and a downgradient site near Duddleyville).
- Aravaipa Creek (site upgradient of the LSP).
- The Gila River (site near Calva upgradient of both the LSP and Coolidge Dam).

The San Pedro River sites appear to be closely related to local precipitation levels. Another study has indicated that the groundwater quality of side canyon inflows have a major impact on the quality of the *floodplain aquifer*<sup>42</sup>. This concurs with another study which indicates very little flow from south to north along the axis of the basin <sup>46</sup>. In contrast, Gila River flows are regulated by releases from San Carlos Reservoir <sup>41</sup>. Surface water infiltrates readily from the both rivers into the floodplain deposits and is the source of most groundwater recharge to the *floodplain aquifer* as indicated by rising groundwater levels after periods of high streamflow <sup>41</sup>. As such, this aquifer is considered a *chemically open hydrologic system* <sup>46</sup>.

Bicarbonate patterns support previous statements that considerable recharge occurs from surface flows in the San Pedro and Gila Rivers. Bicarbonate

concentrations in the San Pedro River near Cascabel (288 mg/l), and near Feldman (353 mg/l), as well as the Gila River above Coolidge Dam near Calva (308 mg/l) are all near the median 270 mg/l floodplain aquifer concentration. The shallow groundwater levels the floodplain aquifer may indicate that groundwater is open to soil CO<sub>2</sub> <sup>46</sup>.

Using mean TDS concentrations as a measurement, these waterways may be ranked in the following order from freshest to most saline:<sup>7 56</sup> Aravaipa Creek (261 mg/l), upper San Pedro River (437 mg/l), lower San Pedro River (670 mg/l), and the Gila River (1500 mg/l) (**Appendix E**). TDS concentrations in the stretch of the Gila River

through the LSP are probably even higher after being subjected to evaporation while impounded in the San Carlos Reservoir (**Figure 31**). Recharge of this surface water should contribute both to the generally higher salinity concentrations found in the *floodplain aquifer* in general, and specifically to the most downgradient portion (Kearny) part of the aquifer influenced by the Gila River.

Recharge from surface water also appears to influence specific concentrations of major ions. Comparing *floodplain aquifer* data by watershed, the most downgradient (Kearny) watershed had significantly higher concentrations of sodium, chloride, and potassium (Kruskal-Wallis in conjunction with the Tukey test, p # 0.05). A similar pattern occurred with surface water quality with sodium, chloride, and potassium having much higher concentrations in the Gila River than in the other three noted waterways.

Another major ion, sulfate, exhibits some unique patterns that may indicate a different contributing source. Sulfate was significantly higher in the *floodplain aquifer* than hardrock although no spatial patterns were found within the *floodplain aquifer* (Kruskal-Wallis in conjunction with the Tukey test, p#

0.05). Surface water quality data reveals the highest sulfate concentrations are found at the most downgradient site on the San Pedro River.

A potential source of sulfate in this area is the large gypsum deposit that is mined (**Figure 32**) near the mouth of Aravaipa Creek<sup>41</sup>. Gypsum dissolves readily in contact with water and release sulfate and calcium ions into solution:<sup>17</sup>

$$CaSO_4 C 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$$

Another sulfate source may be the extensive mine tailings found along the San Pedro River near San Manuel. Previous studies indicated much of the groundwater pumped for mining is later recharged to the *floodplain aquifer*<sup>28</sup>. Groundwater quality impacts from mine tailings may include elevated concentrations of both sulfate and radiochemical constituents as well as low, acidic pH values which can leach heavy metals <sup>33 46</sup>. Leachate from tailings ponds is considered the source of elevated sulfate concentrations in the Bisbee-Naco area<sup>36</sup>.

Salinity concentrations in the *floodplain aquifer* could also be impacted by land uses in the area. Though not extensive, irrigated farming is common along the San Pedro River and Gila River floodplains. Seepage from irrigated fields was estimated to be 3,000 af/yr<sup>28</sup>. With groundwater depths typically less than 50 feet bls, it is probable that this shallow aguifer may receive impacts by groundwater recharge from irrigation applications. Deterioration of groundwater quality associated with irrigation development has also been commonly observed worldwide<sup>31</sup>, as well as in other agricultural areas of Arizona<sup>48 53</sup>. Constituents such as TDS become concentrated by evaporation during the irrigation and are subsequently recharged to the aquifer<sup>18</sup>. Best management practices can reduce concentrations of nitrate and pesticides in this recharge water but not salt loadings on the groundwater<sup>14</sup>.

Other human activities such as domestic and municipal wastewater treatment systems do not appear to have an extensive impact on th *floodplain aquifer* at this time, a conclusion also reached in previous reports <sup>42</sup>. Nitrate concentrations were generally low. When elevated over 3 mg/l which may indicate impacts from human activities <sup>38</sup>, these sites were generally located in hardrock or the *unconfined basin-fill aquifer*.

In the *floodplain aquifer*, fluoride concentrations were significantly higher in the Mammoth watershed than in the other three (one upgradient, two downgradient) watersheds. This may be because this portion of the *floodplain aquifer* largely overlies the *confined basin-fill aquifer*. Through both natural fault zones and inadequately sealed wells, groundwater high in fluoride concentrations migrates upwards into the *floodplain aquifer*<sup>28-45</sup>. This relationship could potentially reverse in the future if the continued discharge of deep artesian aquifer water reduces the head below water table levels <sup>41</sup>. Sulfate and chloride variability in the *floodplain aquifer* could be impacted by upward leakage through gypsum or halite deposits, materials which are less common in the stream alluvium<sup>46</sup>.

### **Confined Basin-Fill Aquifer**

The four sites from which samples were collected from this artesian aquifer represent three areas of confined conditions previously detailed<sup>46</sup>. The confined basinfill aquifer averaging around 300 feet in depth near Redington is represented by LSP-18/19 and is significant for dilute groundwater which indicates an absence of gypsum deposits found at the other artesian sites 46. This is the beginning and the shallowest part of the artesian aquifer. The deeper Mammoth-area artesian wells are represented by LSP-11. Artesian conditions near Feldman are represented by LSP-50/51. The fourth site, LSP-47 appears to be transitional, having a depth similar to Redington-area wells but a chemical composition reflective of Mammoth-area wells. Robertson<sup>46</sup> notes that recharge for the artesian aquifer occurs as precipitation and runoff in the Galiuro Mountains and moves toward the center of the basin, eventually discharging along the line of dense phreatophytes near the San Pedro River with very little moving downgradient.

Analysis of groundwater samples collected from four sites in the *confined basin-fill aquifer* indicate that health-based and aesthics-based water quality standards were exceeded at 3 sites (75 percent). Thus, groundwater from this artesian aquifer, especially away from shallow depths near Redington generally shouldn't be relied upon for domestic or municipal purposes without treatment for elevated fluoride concentrations. Irrigation use is also not recommended because of sodium hazards since the sites are sodiumdominated with an almost complete lack of calcium ions.

Water quality standard exceedances in the *confined* basin-fill aquifer involved fluoride (three sites), TDS (two sites), and pH, chloride, and sulfate (one site apiece). Two sites had arsenic concentrations exceeding the new 2006 arsenic standard. Another artesian site sampled (LSP-77/78) located just outside the LSP in the Donnelly Wash Basin had a pH exceedance as well as arsenic concentrations exceeding the 2006 standards. The elevated fluoride concentrations as well prevailing sodium-bicarbonate chemistry of the confined basin-fill aquifer have been noted in previous studies <sup>16</sup>.

The chemistry of *confined basin-fill aquifer* sites were of a sodium-bicarbonate/mixed type and represent a chemically closed hydrologic system in which the aqueous chemistry is determined solely by the reactions of the initial recharge water with the various minerals as it moves downgradient 46. The high sodium concentrations are likely the result of ion exchange of calcium for sodium 46. Ion exchange is a significant reaction in basins having high TDS and sulfate concentrations caused by the dissolution of gypsum. The additional sulfate concentrations caused by the dissolution of gypsum are made up by the exchange of calcium for sodium. In other areas of Arizona where groundwater is more dilute, high sodium concentrations are usually caused by silicate hydrolysis <sup>46</sup>. *Chemically closed hydrologic systems* favor high pH values and the removal of calcium, factors that may produce large fluoride concentrations<sup>46</sup>.

Calcium is an important control of higher fluoride concentrations (> 5 mg/l) through precipitation of the mineral fluorite<sup>44</sup>. In a chemically *closed hydrologic system*, calcium is removed from solution by precipitation of calcium carbonate and formation of smectite clays, which may result in large fluoride concentrations<sup>45</sup>. High concentrations of dissolved fluoride may occur if the groundwater is depleted in calcium and a source of fluoride ions is available for dissolution<sup>45</sup>. Results from this study support this finding. The three of the four sites with fluoride concentrations greater than 5 mg/l had corresponding depleted calcium concentrations.

Constituents such as pH, fluoride, and sodium were higher in the *confined basin-fill aquifer* than in the other three LSP aquifers. Sulfate and temperature were higher in the *confined basin-fill aquifer* than in hardrock. In contrast, bicarbonate was lower than in the *floodplain aquifer* and hardrock (Kruskal-Wallis

in conjunction with the Tukey test, p # 0.05). These patterns indicate that groundwater in the *confined* basin-fill aquifer is probably highly evolved and receives little recent recharge.

#### **Overview of Basin**

Interestingly, few significant relationships were found between groundwater depth and constituent concentrations. Although previous studies had found TDS concentrations increasing with depth in the floodplain aquifer<sup>46</sup>, this study did not reveal a significant relationship between these two indices (regression analysis, p # 0.05). In other ADEQ studies in Arizona basins, many significant relationships were typically present 50 51 52 53. The LSP is similar to the Virgin River basin in extreme northwestern part of the state on the Arizona Strip 49. In this basin, there were significant relationships between groundwater depth and constituent concentrations; however, few relationships existed within individual aguifers. Thus in the Virgin River basin, as well as in the LSP basin, it was thought that groundwater depth relationships were the result of differences in constituent concentrations and groundwater depth between aquifers than any actual relationship within aquifers.

# Study Design and Data Evaluation

**Methods of Investigation** - The 63 groundwater sample sites were selected using a stratified, random sampling strategy. The sample collection methods for this study conformed to the *Quality Assurance Project Plan*<sup>4</sup> and the *Field Manual for Water Quality Sampling* <sup>11</sup>.

**Data Evaluation** - 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 by SC-lab and turbidity; however, the extent of the contamination by these parameters was not considered significant. Analysis of duplicate and split samples revealed excellent correlations; those constituents with large percent differences typically had only minor absolute differences. Data validation was also examined in six QA/QC correlations that validated the acceptability of the groundwater quality data for further analysis. Overall, the effects of sampling procedures and laboratory methods on the samples were not considered significant.

Data analysis for this study was conducted using Systat software 58. The non-normality of both the nontransformed data and the log-transformed data was determined by using the Kolmogorov-Smirnov onesample test with the Lilliefors option <sup>15</sup>. Spatial variations in constituent concentrations were investigated using the non-parametric Kruskal-Wallis test. Constituent concentration changes over time were investigated using the non-parametric Wilcoxon rank-sum test<sup>29</sup>. Vertical (groundwater depth) variations were examined using three regression models. Correlations among constituent concentrations were analyzed using the Pearson Correlation Coefficient test. Determining the most important major ion influences on TDS concentrations was conducted using multiple regression <sup>29</sup>.

### RECOMMENDATIONS

Recommendations for domestic well owners, public water supply systems, and future groundwater quality studies are provided in this section. These recommendations 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 LSP.

- < 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 interested in less expensive and more targeted testing of their water source should include the following constituents in their sampling and analysis: fluoride and arsenic particularly at sites located along the San Pedro and Gila River corridor between San Manuel and Kearny and in wells drawing groundwater from the confined basin-fill aquifer, and gross alpha in areas of granite rock, especially near Oracle. Primary MCL exceedances may occur in other areas of the LSP; however, based upon the results of this regional groundwater quality report, their occurrence should not be widespread on a basin-wide basis. Again, it should be stressed that for full assurance that groundwater pumped by a

- private well meets all water quality standards for domestic use, tests should be conducted on a range of 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.

The following recommendations are provided for public water systems within the LSP.

< Groundwater quality data collected during this study should assist in the site selection process of new public supply wells. Some sample sites exceeded health-based, water quality standards and caution should be used in developing new public water supplies in these aquifers and areas.

The following recommendations are provided for future groundwater quality studies within the LSP.

Resampling of the ADEQ index wells appears to be unnecessary at intervals of less than approximately ten years. Although a comprehensive time-trend analysis was not able to be conducted, limited historical data in conjunction with other studies in Arizona suggests that most of the constituents are largely controlled by natural factors and are not prone to vary significantly over time in the near term.

#### REFERENCES

- <sup>1</sup> American Smelting and Refining Company Website, 2001, www.asarcocu.com/ray/ray2.htm
- <sup>2</sup> Arizona Department of Environmental Quality, 1989. Engineering Bulletin No. 12: Minimum Requirements for the Design and Installation of Septic Tank Systems and Alternative on-Site Disposal Systems. ADEQ: Phoenix, Arizona.
- <sup>3</sup> Arizona Department of Commerce Website, 2001,www.commerce.state.az.us/publications/comm unity\_profile\_index.htm
- <sup>4</sup> Arizona Department of Environmental Quality, 1991. Quality Assurance Project Plan. ADEQ Water Quality Standards Unit: Phoenix, Arizona.

- Arizona Department of Environmental Quality, 1998. Arizona Laws Relating to Environmental Quality. West Group: St. Paul, Minnesota.
- <sup>6</sup> Arizona Department of Environmental Quality, 1998b. *Drinking Water Section Fact Sheet #3*. ADEQ Fact Sheet 98-16, Phoenix, Arizona.
- Arizona Department of Environmental Quality, 2001. Surface Water Quality Database. ADEQ Surface Water Quality Unit: Phoenix, Arizona.
- <sup>8</sup> Arizona Department of State Lands, 1997. Arizona Land Resource Information Systems. ADSL: Phoenix, Arizona.
- <sup>9</sup> Arizona Department of Water Resources, 1990. Preliminary Hydrographic Survey Report for the San Pedro River Watershed: Volume 1 - General Assessment. ADWR: Phoenix, Arizona.
- Arizona Department of Water Resources, 1994.
  Arizona Water Resources Assessment. ADWR: Phoenix, Arizona.
- Arizona Water Resources Research Center, 1995.
  Field Manual for Water-Quality Sampling.
  University of Arizona College of Agriculture:
  Tucson, Arizona.
- <sup>12</sup> Bedient, P.B., H.S. Rifai., and C.J. Newell, 1994. Ground Water Contamination: Transport and Remediation. Prentice Hall, Inc: Englewood Cliffs, New Jersey.
- Bitton, Gabriel and C.P. Gerba, 1994. GroundwaterPollution Microbiology. Krieger PublishingCompany: Malabar, Florida.
- <sup>14</sup> Bouwer, Herman, 1997. Arizona's Long-Term Water Outlook: From NIMTO to AMTO-Part II. Arizona Hydrologic Newsletter, Vol. 14, Issue 5.
- <sup>15</sup> Brown, S.L., W.K. Yu, and B.E. Munson, 1996. The Impact of Agricultural Runoff on the Pesticide Contamination of a River System - A Case Study on the Middle Gila River. ADEQ Open File Report 96-1: Phoenix, Arizona.
- <sup>16</sup> Bryan, Kirk, G.E.P. Smith, and G.A.Waring, 1934. Ground-Water Supplies and Irrigation in San Pedro Valley, Arizona. U.S. Geological Survey Open File Report, 167 p.

- <sup>17</sup> Coes, A. L., D.J. Gellenbeck, and D.C. Towne, 1999. Ground-Water Quality in the Sierra Vista Subbasin, Arizona, 1996-97. U.S. Geological Survey Water-Resources Investigations Report 99-4056: Tucson, Arizona.
- <sup>18</sup> Coes, A.L., D.J. Gellenbeck, D.C. Towne, and M.C. Freark, 2000. *Ground-Water Quality in the Upper Santa Cruz Basin, Arizona, 1998.* U.S. Geological Survey Water-Resources Investigations Report 00-4117: Tucson, Arizona.
- <sup>19</sup> Cohen, P., W.A. Alley, and W.G. Wilber, 1988. National Water-Quality Assessment: Future Directions of the U.S. Geological Survey. *Water Resources Bulletin* 24: 1047-1051.
- <sup>20</sup> Cordy, G.E., H.W. Sanger, and D.J. Gellenbeck, 2000. Radon in Ground Water in Central and Southern Arizona: A Cause for Concern? Paper Presented at ASH 2000, Annual Symposium of the Arizona Hydrologic Society, Phoenix, Arizona, September 20th to 23rd.
- <sup>21</sup> Crockett, Janet K., 1995. *Idaho Statewide* Groundwater Quality Monitoring Program -Summary of Results, 1991 Through 1993. Idaho Department of Water Resources: Boise, Idaho.
- <sup>22</sup> Del Mar Laboratory, 2000. *Personal communication* from Del Mar laboratory staff member.
- <sup>23</sup> Ducote, Richard, 2002. San Manuel's Mining Hopes Fade, BHP Copper to Trim More Jobs, Allow Underground Mine to Flood. Arizona Daily Star, January 17: Tucson, Arizona.
- <sup>24</sup> Duncan, J.T. and J.E. Spencer, 1993. "Uranium and Radon in Southeastern Arizona" in *Radon in Arizona*, Spencer, Jon. E. ed, Geological Survey Bulletin 1999, p. 40-42.
- <sup>25</sup> Freethey, G.W. and T.W. Anderson, 1986. Predevelopment Hydrologic Conditions in the Alluvial Basins of Arizona and Adjacent Parts of California and New Mexico. U.S. Geological Survey Hydrologic Investigations Atlas HJA-664.
- <sup>26</sup> Graf, Charles, 1990. An Overview of Groundwater Contamination in Arizona: Problems and Principals. ADEQ Seminar: Phoenix, Arizona.

- <sup>27</sup> Heath, Ralph C., 1989. *Basic Ground-Water Hydrology*. U.S. Geological Survey Water-Supply Paper 2220.
- <sup>28</sup> Heindl, L.A., 1952. Groundwater in the Gila River Basin and Adjacent Areas, Arizona—A Summary, Halpenny, L.C., ed. USGS Open File Report: Tucson, Arizona.
- <sup>29</sup> Helsel, D. R., and R.M. Hirsch, 1997. *Statistical Methods in Water Resources*. Elsevier Publishing: New York, New York.
- <sup>30</sup> Hem, John D., 1947. "Section on Quality of the Water" in *Geology and Ground-Water Resources* of the Willcox Basin, Cochise and Graham Counties, Arizona, Jones, R.S. and Cushman, R.L. eds. U.S. Geological Survey in conjunction with the Arizona State Land Department.
- <sup>31</sup> Hem, John D., 1970. Study and Interpretation of the Chemical Characteristics of Natural Water. USGS Water-Supply Paper 1473: Washington, D.C.
- <sup>32</sup> Hem, John D., 1985. Study and Interpretation of the Chemical Characteristics of Natural Water, Third Edition. USGS Water-Supply Paper 2254: Washington, D.C.
- 33 Henderson, Timothy R., 1984. *Groundwater Strategies for State Action*. The Environmental Law Institute: Washington, D.C.
- <sup>34</sup> Hood, Wayne K, III., 1991. A Plan To Establish Ambient Groundwater Quality Monitoring Networks in Arizona. ADEQ: Phoenix, Arizona.
- <sup>35</sup> Jones, S.C., 1980. Maps Showing Ground-Water Conditions in the Lower San Pedro Basin Area, Pinal, Cochise, Pima, and Graham Counties, Arizona–1979. USGS Water-Resources Investigations Open-File Report 80-954.
- <sup>36</sup> Littin, G.R., 1987. Groundwater Resources of the Bisbee-Naco Area, Cochise County, Arizona. USGS Water-Resources Investigations Reprt 87-4103: Denver, Colorado.
- <sup>37</sup> Lowry, J.D. and S.B. Lowry,, 1988. "Radionuclides in Drinking Waters," in *American Water Works Association Journal*. July 1988.

- <sup>38</sup> Madison, R.J. and J.O. Brunett, 1984. "Overview of the Occurrence of Nitrate in Ground Water of the United States," in *National Water Summary 1984 -Water Quality Issues*.
- <sup>39</sup> Muffley, Bernard W., 1938. The History of the Lower San Pedro Valley in Arizona. Masters Thesis, University of Arizona: Tucson, Arizona.
- <sup>40</sup> Nature Conservancy, Arizona Chapter Website, 2001, www.tncarizona.org/
- <sup>41</sup> Page, Harry G., 1963. Water Regimen of the Inner Valley of the San Pedro River near Mammoth, Arizona (A Pilot Study). USGS Water-Supply Paper 1699-1: Washington, D.C.
- <sup>42</sup> Riverside Technology, Inc, 1992. An Assessment of Well and Stream Water Quality along the San Pedro River near the town of Cascabel, Arizona. Riverside Technology: Fort Collins, Colorado..
- <sup>43</sup> Roberts, Isaac, 2000. *Personal communication from ADHS laboratory staff member*.
- <sup>44</sup> Robertson, F. N., 1986. "Occurrence and Solubility Controls of Trace Elements in Groundwater in Alluvial Basins of Arizona" Anderson, T. W., and Johnson, A. I., eds., Regional Aquifer Systems of the United States, Southwest Alluvial Basins of Arizona. American Water Resources Association Monograph Series No. 7, p. 69-80.
- <sup>45</sup> Robertson, F. N. and W.B. Garrett, 1988.
  Distribution of Fluoride in Ground Water in the Alluvial Basins of Arizona and Adjacent Parts of California, Nevada, and New Mexico. U.S.
  Geological Survey Hydrologic Investigations Atlas HA-665.
- <sup>46</sup> Robertson, F. N., 1991. Geochemistry of Ground Water in Alluvial Basins of Arizona and Adjacent Parts of Nevada, New Mexico, and California. U.S. Geological Survey Professional Paper 1406-C.
- <sup>47</sup> Roeske, R.H. and W.L. Werrell, 1973. *Hydrologic Conditions in the San Pedro River Valley, Arizona*, 1971. Arizona Water Commission Bulletin #4.

- <sup>48</sup> Towne, D.C. and W.K. Yu, 1998. Ambient Groundwater Quality of the Yuma Basin: A 1995 Baseline Study. ADEQ Open File Report 98-07: Phoenix, Arizona.
- <sup>49</sup> Towne, D.C. 1999. Ambient Groundwater Quality of the Virgin River Basin: A 1997 Baseline Study. ADEQ Open File Report 99-4: Phoenix, Arizona.
- Towne, D.C. 1999. Ambient Groundwater Quality of the Douglas Basin: A 1995-1996 Baseline Study. ADEQ Open File Report 99-11: Phoenix, Arizona.
- 51 Towne, D.C. and M.C. Freark, 2000. Ambient Groundwater Quality of the Prescott AMA: A 1997-98 Baseline Study. ADEQ Open File Report 00-01: Phoenix, Arizona.
- <sup>52</sup> Towne, D. C. and M.C. Freark, 2001. Ambient Groundwater Quality of the Sacramento Valley Basin: A 1999 Baseline Study. ADEQ Open File Report 01-04, Phoenix, Arizona.
- <sup>53</sup> Towne, D. C. and M.C. Freark, 2001. Ambient Groundwater Quality of the Willcox Basin: A 1999 Baseline Study. ADEQ Open File Report 01-09, Phoenix, Arizona.
- <sup>54</sup> U.S. Environmental Protection Agency, 1993. The Safe Drinking Water Act - A Pocket Guide to the Requirements for the Operators of Small Water Systems. USEPA Region 9: San Francisco, CA.
- <sup>55</sup> U.S. Geological Survey, 2001. Water Resources Data Arizona Water Year 2000. USGS Water-Data Report AZ-00-1: Springfield, VA.
- <sup>56</sup> U.S. Salinity Laboratory, 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. USDA Agriculture Handbook No. 60: Washington, D.C.
- <sup>57</sup> Water Quality Association, 2002, www.wqa.org/
- <sup>58</sup> Wilkinson, L. and M.A. Hill, 1994. *Using Systat*. Systat, Inc: Evanston, IL.
- <sup>59</sup> White, D.E., J.D. Hem, and G.A. Waring, 1963. "Chemical Composition of Sub-Surface Waters," in *Data of Geochemistry*, 6<sup>th</sup> Edition. USGS Professional Paper 440-F: Washington, D.C.

<sup>60</sup> Childs, Craig, 2001. The Secret Knowledge of Water: Discovering the Essence of the American Desert. Little, Brown & Company.

Appendix A. Data for Sample Sites, Lower San Pedro Basin, 1999-2000

Sample #	Cadastral	Latitude - Longitude	ADWR#	ADEQ#	Samples Collected	Well Depth	Water Depth	Watershed	Aquifer
		1st Field Trip, Novem	ber 30-Decemb	er 2, 1999 - To	wne & Boettcher (	Equipment B	lank, LSP-13)		
LSP-01	(D-13-19)23dba	32°17'16.210" 110°22'22.452"	513520	58167	Inorganic	98'	30'	Redington	Floodplain
LSP-02	(D-13-19)23dab	32°17'21.662" 110°22'08.235"	629462	58168	Inorganic VOC Radon	122'	60'	Redington	Floodplain
LSP-03	(D-13-20)31bcc	32°15'41.795" 110°20'50.617"	645667	58169	Inorganic	90'	29.7'	Redington	Floodplain
LSP-04	(D-08-17)31acd	32°41'43.911" 110°38'27.999"	532355	58170	Inorganic VOC	501'	295'	Mammoth	UBF
LSP-05/06	(D-12-18)13bda	32°23'24.428" 110°27'20.607"	608218	58171	Inorganic VOC Radon	150'	80'	Mammoth	Floodplain
LSP-07	(D-12-18)03aaa	32°25'37.421" 110°29'06.186"	608217	58172	Inorganic	127'	42'	Mammoth	Floodplain
LSP-08/09	(D-14-20)08bbd	32°14'12.964" 110°19'32.787"	608065	58173	Inorganic VOC Radon	100'	42'	Redington	Floodplain
LSP-10	(D-09-17)04aaa	32°41'05.891" 110°36'20.791"	607862	58174	Inorganic VOC Radon	150'	80'	Mammoth	Floodplain
LSP-11	(D-08-17)32add	32°41'38.803" 110°37'17.996"	624632	58175	Inorganic VOC Radon	1485'	Artesian	Mammoth	CBF
LSP-12	(D-10-16)28bdb	32°32'17.997" 110°43'01.918"	806798	58176	Inorganic Radiochem	97'	25'	Mammoth	Hardrock
		2 <sup>nd</sup> Field Trip,	December 15-1	7, 1999 - Towr	ne & Lucci (Equipm	nent Blank, L	SP-23)		
LSP-14	(D-06-16)08cbb	32°55'26.917" 110°44'26.234"	612036	58218	Inorganic	120'	26'	Winkelman	Floodplain
LSP-15/16	(D-07-16)22ddd	32°48'29.594" 110°41'45.509"	618760	58219	Inorganic VOC Radon	140'	43'	Winkelman	Floodplain
LSP-17	(D-06-16)06dbc	32°56'14.895" 110°44'55.955"	612039	58220	Inorganic	90'	23.7'	Winkelman	Floodplain
LSP-18/19	(D-11-18)03bbc	32°30'38.356" 110°30'08.518"	600350	58221	Inorganic VOC Radon	195'	Artesian	Mammoth	CBF
LSP-20	(D-08-17)19ddd	32°43'05.789" 110°38'22.355"	643305	58222	Inorganic VOC Radon	130'	10'	Mammoth	Floodplain
LSP-21	(D-04-14)08ddc	33°05'40.824" 110°55'44.306"	540818	58223	Inorganic VOC	320'	200'	Kearny	UBF
LSP-22	(D-04-14)35bad	33°02'32.863" 110°53'09.233"	607497	27719	Inorganic Radon	500'	22'	Kearny	UBF
			3 <sup>rd</sup> Field Trip,	January 12-13	, 2000 - Towne & 1	Flora			
LSP-24*	(D-13-18)11aad	32°19'24.679" 110°28'05.914"	613547	36630	Inorganic Radiochem	230'	80'	Redington	UBF

<sup>\* =</sup> LSP-25 and LSP-26 were splits for the City of Tucson that were never analyzed.

Appendix A. Data on Sample Sites, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Cadastral	Latitude - Longitude	ADWR#	ADEQ#	Samples Collected	Well Depth	Water Depth	Watershed	Aquifer
LSP-26*	(D-13-18)06adb	32°20'10.370" 110°32'19.596"	613550	58789	Inorganic VOC Radiochem	300'	150'	Redington	Hardrock
LSP-28	(D-05-15)24baa	32°59'24.905" 110°45'55.803"	616618	28881	Inorganic VOC	120'	23'	Kearny	Floodplain
LSP-29/30	(D-05-15)24baa	32°59'23.856" 110°45'56.091"	616694	28882	Inorganic Radon	412'	22'	Kearny	Floodplain
		4 <sup>th</sup>	Field Trip, Fo	ebruary 2-4, 2	000 - Towne & Bo	ettcher			
LSP-31	(D-12-20)21cca	32°22'16.985" 110°18'58.924"	648764	58271	Inorganic VOC Radiochem	147'	30'	Redington	Hardrock
LSP-32	(D-13-19)04bad	32°20'11.779" 110°24'34.277"	545407	58272	Inorganic	100'	55'	Redington	Floodplain
LSP-33	(D-13-20)21dbb	32°17'16.200" 110°18'27.225"	none	58273	Inorganic	spring	spring	Redington	Hardrock
LSP-34/35	(D-12-20)11dad	32°24'08.554" 110°16'09.585"	648765	58274	Inorganic VOC Radiochem	140'	50'	Redington	Hardrock
LSP-36	(D-11-20)26cab	32°26'49.398" 110°16'42.644"	none	58275	Inorganic	spring	spring	Redington	Hardrock
LSP-37/38	(D-13-21)06abd	32°20'09.108" 110°14'18.338"	none	58276	Inorganic VOC Radiochem	spring	spring	Redington	Hardrock
LSP-39	(D-11-19)15aaa	32°29'06.282" 110°23'02.569"	none	58277	Inorganic Radiochem	spring	spring	Mammoth	UBF
LSP-40	(D-06-16)33bbc	32°52'22.482" 110°42'45.447"	617384	55093	Inorganic Radon Pesticide	101'	13'	Winkelman	Floodplain
LSP-41	(D-06-16)29aba	32°53'18.790" 110°43'40.869"	617385	58278	Inorganic Pesticide	100'	22'	Winkelman	Floodplain
		5 <sup>th</sup>	Field Trip, F	ebruary 24-25	5, 2000 - Towne & l	Freark			
LSP-42	(D-08-18)14dad	32°44'02.189" 110°29'59.461"	none	58449	Inorganic Radiochem	spring	spring	Mammoth	Hardrock
LSP-43	(D-08-18)23aba	34°43'44.453" 110°28'13.814"	none	58786	Inorganic	spring	spring	Mammoth	Hardrock
LSP-44	(D-05-15)23bda	32°59'07.361" 110°47'17.739"	617374	28877	Inorganic VOC Radion	80'	21'	Kearny	Floodplain
LSP-45/46	(D-05-15)23bda	32°59'08.325" 110°46'59.328"	617367	58450	Inorganic VOC Radion	100'	29'	Kearny	Floodplain

<sup>\* =</sup> LSP-25 and LSP-26 were splits for the City of Tucson that were never analyzed.

Appendix A. Data on Sample Sites, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Cadastral	Latitude - Longitude	ADWR#	ADEQ#	Samples Collected	Well Depth	Water Depth	Watershed	Aquifer
		6 <sup>th</sup>	Field Trip, M	arch 29-31, 2	000 - Towne & Bo	ettcher			
LSP-47	(D-10-18)08cbb	32°34'43.288" 110°31'24.910"	561754	58542	Inorganic VOC Radion	400'	artesian	Mammoth	CAF
LSP-48	(D-14-20)27ccc	32°34'43.705" 110°31'24.585"	none	58546	Inorganic VOC Radion	90'	16'	Redington	Floodplain
LSP-49	(D-15-20)03ccd	32°09'13.435" 110°17'31.815"	none	58590	Inorganic	90'	16'	Redington	Floodplain
LSP-50/51	(D-06-16)33bbb	32°11'59.845" 110°14'35.475"	526520	58591	Inorganic Radon	1250'	artesian	Winkelman	CBF
LSP-52	(D-06-16)	32°52'27.525" 110°43'22.425"	none	58592	Inorganic	spring	spring	Winkelman	Floodplain
LSP-53	(D-07-16)18bcd	32°49'28.145" 110°45'16.675"	none	31851	Inorganic Radiochem	spring	spring	Winkelman	Hardrock
LSP-54	(D-14-20)12cac	32°13'39.665" 110°15'25.255"	651298	38003	Inorganic Radiochem	14'	5'	Redington	Hardrock
LSP-55	(D-15-21)07bcd	32°08'43.245" 110°14'23.285"	none	58593	Inorganic Radiochem	spring	spring	Redington	Hardrock
LSP-56/57	(D-09-16)31bad	32°36'50.515" 110°44'58.225"	575608	33951	Inorganic Radiochem	300'	70'	Mammoth	Hardrock
LSP-58	(D-10-18)08abc	32°34'48.125" 110°31'25.825"	542755	58594	Inorganic VOC	80'	30'	Mammoth	Floodplain
LSP-59	(D-15-19)01add	32°09'31.035" 110°20'50.900"	none	38952	Inorganic	spring	spring	Redington	Hardrock
		7 <sup>tt</sup>	Field Trip, A	pril 19-21, 20	000 - Towne & Boe	ttcher			
LSP-60	(D-07-17)09bcb	32°50'32.207" 110°37'12.000"	806142	58652	Inorganic	65'	12'	Winkelman	Floodplain
LSP-61	(D-11-16)10dda	32°29'32.877" 110°41'50.930"	none	58653	Inorganic	spring	spring	Mammoth	Hardrock
LSP-62	(D-11-17)19ddd	32°27'22.477" 110°38'23.126"	none	58654	Inorganic Radiochem	spring	spring	Mammoth	Hardrock
LSP-63/64	(D-11-17)24cac	34°27'42.985" 110°33'43.919"	624301	58655	Inorganic VOC Radon		32'	Mammoth	UBF
LSP-65	(D-07-16)11adc	32°50'21.925" 110°40'31.823"	538345	58656	Inorganic	108'	12'	Mammoth	Floodplain
LSP-66	(D-07-16)10cdd	32°49'59.352" 110°41'57.569"	636185	58657	Inorganic	157'	12'	Mammoth	Floodplain
LSP-67	(D-07-16)22add	32°48'41.820" 110°41'20.280"	none	58658	Inorganic	100'	25'	Mammoth	Floodplain

Appendix A. Data on Sample Sites, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Cadastral	Latitude - Longitude	ADWR#	ADEQ#	Samples Collected	Well Depth	Water Depth	Watershed	Aquifer
		8 <sup>th</sup> Field Trip, J	une 28-30, 200	00 - Towne & 1	Boettcher (Equip	nent Blank, LS	P-68)		
LSP-69/70	(D-01-13)14dbd	32°34'43.705" 110°31'24.585"	526188	58806	Inorganic VOCs Radiochem	545'	450'	Kearney	Hardrock
LSP-71	(D-15-18)11bbd	32°09'13.435" 110°17'31.815"	604357	58807	Inorganic Radon	300'	36'	Redington	UBF
LSP-72	(D-15-18)01dbc	32°11'59.845" 110°14'35.475"	645893	58808	Inorganic VOCs	40'	35'	Redington	UBF
LSP-73	(D-15-19)06ada	32°52'27.525" 110°43'22.425"	none	58819	Inorganic Radiochem	spring	spring	Redington	Hardrock
LSP-74	(D-10-17)27dbd	32°31'57.632" 110°35'24.659"	629393	58820	Inorganic	360'	320'	Mammoth	UBF
LSP-75	(D-01-14)27caa	33°18'48.703" 110°55'31.160"	none	58818	Inorganic Radiochem	spring	spring	Kearney	Hardrock
		9th Field Trip, J	uly 10-12, 200	00 - Towne & 1	Boettcher (Equipm	nent Blank, LS	P-84)		
LSP-76	(D-03-13)08ba	33°11'27.34" 111°02'40.12"	633774	55034	Inorganic VOCs Radiochem	30'	8'	Kearney	Hardrock
LSP-77/78**	(D-03-12)24bcb	33°09'25.604" 111°04'47.346"	none	58801	Inorganic Radon	deep'	artesian	Kearney	CBF
LSP-80	(D-10-20)07bdd	32°34'48.125" 110°31'25.825"	none	58802	Inorganic Radiochem	spring	spring	Redington	Hardrock
LSP-81	(D-09-20)33cbb	32°36'23.559" 110°18'47.704"	none	58803	Inorganic	spring	spring	Redington	Hardrock
LSP-82	(D-05-14)03adb	32°50'32.207" 110°37'12.000"	none	58804	Inorganic Radiochem	spring	spring	Kearney	Hardrock
LSP-83	(D-05-14)02bba	32°29'32.877" 110°41'50.930"	615376	58805	Inorganic VOCs Radon	45'	37'	Kearney	Floodplain

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash groundwater basin.

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000

Sample #	ADEQ#	MCL Exceedances	Temp (°C)	pH-field (su)	SC-lab (FS/cm)	TDS (mg/l)	Hardness (mg/l)	Total Alk (mg/l)	Turbidity (ntu)
LSP-01	58167	TDS, Fe	19.35	7.43	1100	720	340	250	1.3
LSP-02	58168	TDS	22.26	7.34	1000	690	310	210	2.5
LSP-03	58169	TDS, Fe, Mn, As*	19.99	7.41	1100	710	310	260	8.1
LSP-04	58170	F, As*	29.70	8.01	590	390	58	110	0.45
LSP-05/06	58171		19.77	7.58	725	375	220	220	0.05
LSP-07	58172	TDS	18.92	7.27	840	550	300	260	0.33
LSP-08/09	58173	TDS	21.34	7.45	905	600	240	230	1.0
LSP-10	58174	TDS, SO4, F, As*	25.21	7.55	1100	740	260	210	6.6
LSP-11	58175	F, As*	38.60	8.47	700	450	32	92	0.15
LSP-12	58176			8.33	400	220	200	180	0.08
LSP-14	58218	TDS, SO4, F	20.80	7.31	1100	700	310	220	0.60
LSP-15/16	58219	TDS, SO4, F	21.16	7.15	1100	775	360	235	1.6
LSP-17	58220	TDS, F	19.37	7.44	930	600	280	210	1.3
LSP-18/19	58221		22.55	7.91	320	200	57	140	0.06
LSP-20	58222	F, As*	26.50	8.36	510	310	53	100	2.2
LSP-21	58223		25.53	7.19	670	400	290	190	0.12
LSP-22	27719	TDS,SO4,NO3,Fe,Mn	24.45	6.78	4300	2800	1200	220	16
LSP-24	36630		21.21	8.01	430	260	200	180	0.30
LSP-26	58789	Gross Alpha		7.67	690	440	270	260	1.1
LSP-28	28881	TDS, Mn	19.09	8.05	1300	760	280	190	0.09
LSP-29/30	28882	TDS	19.99	8.08	1300	740	260	190	0.32
LSP-31	58271		20.46	7.25	723	460	310	300	0.22
LSP-32	58272		22.28	7.48	720	450	140	260	2.2
LSP-33	58273	TDS, As	11.52	6.97	960	550	390	440	9.0
LSP-34/35	58274		20.81	6.91	505	335	240	225	0.90
LSP-36	58275		13.75	7.07	460	310	210	200	0.75
LSP-37/38	58276	pH, As*	34.37	9.24	290	195	9.2	130	0.04
LSP-39	58277		11.77	7.45	560	310	250	240	0.12
LSP-40	55093		18.74	7.33	660	470	270	200	0.18

**bold** = constituent level exceeds Primary or Secondary MCL

<sup>\*</sup> = concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-01	85	30	100	2.37	3.6	300	ND	41	230
LSP-02	82	24	110	2.75	3.6	260	ND	45	240
LSP-03	83	22	120	3.03	6.1	320	ND	30	240
LSP-04	20	1.7	100	5.76	3.1	130	ND	34	110
LSP-05/06	64.5	12.5	49	1.50	4.05	269	ND	12.5	75.5
LSP-07	85	20	71	1.80	4.6	320	ND	21	120
LSP-08/09	60.5	19	110	3.15	3.85	280	ND	34	185
LSP-10	78	12	130	3.62	5.0	260	ND	34	280
LSP-11	12	ND	140	11.12	1.9	100	4.2	41	150
LSP-12	34	28	9.6	0.30	0.82	210	3.1	9.0	20
LSP-14	95	18	110	2.71	5.3	270	ND	33	260
LSP-15/16	100	23	120	2.81	5.3	285	ND	33	295
LSP-17	83	16	110	2.89	4.6	260	ND	28	230
LSP-18/19	18	2.8	50	2.93	2.8	170	ND	4.3	18
LSP-20	16	2.6	95	5.81	2.5	120	ND	26	95
LSP-21	84	20	29	0.74	3.0	230	ND	31	91
LSP-22	330	95	500	6.24	15	270	ND	810	700
LSP-24	67	9.8	15	0.45	1.2	220	ND	4.9	26
LSP-26	79	17	46	1.22	1.9	320	ND	30	34
LSP-28	79	20	150	3.91	6.4	230	ND	200	140
LSP-29/30	74	19	150	4.03	6.2	230	ND	205	125
LSP-31	56	41.5	51	1.26	2.7	370	ND	39	43
LSP-32	37	11	120	4.01	3.05	320	ND	18	86
LSP-33	72	49.5	67.5	1.48	1.45	540	ND	28	51
LSP-34/35	48	31.5	19	0.52	0.91	275	ND	5.45	40.5
LSP-36	47	26	20	0.57	0.845	240	ND	4.9	41
LSP-37/38	3.5	ND	64.5	7.60	0.63	107	28	3.1	3.9
LSP-39	73	18	20	0.54	5.6	290	ND	9.7	47
LSP-40	91	12	36	0.94	3.4	240	ND	10	140

 $\boldsymbol{bold} = constituent \ level \ exceeds \ Primary \ or \ Secondary \ MCL$ 

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Nitrate-Nitrite-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Total Phosphorus (mg/l)
LSP-01	0.72	0.72	ND	0.085	ND	ND
LSP-02	0.71	0.71	ND	0.080	ND	ND
LSP-03	ND	ND	ND	0.15	0.078	0.052
LSP-04	0.90	0.90	ND	ND	ND	ND
LSP-05/06	0.92	0.92	ND	ND	ND	0.061
LSP-07	2.3	2.3	ND	ND	ND	0.042
LSP-08/09	1.3	0.77	ND	ND	ND	0.022
LSP-10	0.45	0.45	ND	ND	ND	ND
LSP-11	0.34	0.34	ND	ND	ND	ND
LSP-12	0.52	0.52	ND	ND	0.024	0.032
LSP-14	0.42	0.42	ND	ND	ND	0.027
LSP-15/16	0.70	0.70	ND	ND	ND	0.055
LSP-17	0.25	0.25	ND	ND	ND	0.10
LSP-18/19	0.18	0.18	ND	ND	ND	ND
LSP-20	0.96	0.96	ND	ND	ND	0.033
LSP-21	3.9	3.9	ND	ND	ND	ND
LSP-22	30	29.78	0.22	0.30	ND	ND
LSP-24	2.3	2.3	ND	ND	ND	ND
LSP-26	6.8	6.8	ND	0.11	ND	ND
LSP-28	0.04	0.04	ND	0.30	0.17	0.042
LSP-29/30	0.05	0.05	ND	0.10	0.052	0.067
LSP-31	3.4	3.4	ND	ND	ND	ND
LSP-32	0.99	0.99	ND	ND	ND	ND
LSP-33	2.2	2.2	ND	0.070	ND	0.086
LSP-34/35	0.585	0.585	ND	1.2	ND	0.05
LSP-36	ND	ND	ND	4.2	ND	0.054
LSP-37/38	0.31	0.31	ND	ND	ND	0.034
LSP-39	0.24	0.24	ND	0.082	ND	0.19
LSP-40	0.40	0.40	ND	ND	ND	0.068

**bold** = constituent level exceeds Primary or Secondary MCL

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-01	ND	ND	ND	ND	0.15	ND	ND	0.013	1.3
LSP-02	ND	ND	ND	ND	0.16	ND	ND	ND	1.3
LSP-03	ND	0.012*	ND	ND	0.18	ND	ND	ND	1.2
LSP-04	ND	0.016*	ND	ND	0.14	ND	ND	ND	5.2
LSP-05/06	ND	ND	ND	ND	ND	ND	ND	ND	0.825
LSP-07	ND	ND	ND	ND	0.13	ND	ND	ND	0.82
LSP-08/09	ND	ND	ND	ND	0.205	ND	ND	ND	1.4
LSP-10	ND	0.013*	ND	ND	0.17	ND	ND	ND	4.0
LSP-11	ND	0.020*	ND	ND	0.17	ND	ND	ND	6.6
LSP-12	ND	ND	ND	ND	ND	ND	ND	ND	0.13
LSP-14	ND	ND	ND	ND	0.13	ND	ND	ND	2.1
LSP-15/16	ND	ND	ND	ND	0.14	ND	ND	ND	2.45
LSP-17	ND	ND	ND	ND	0.14	ND	ND	ND	2.2
LSP-18/19	ND	ND	ND	ND	ND	ND	ND	ND	1.1
LSP-20	ND	0.048*	ND	ND	0.10	ND	ND	ND	3.0
LSP-21	ND	ND	ND	ND	ND	ND	ND	ND	0.51
LSP-22	ND	ND	ND	ND	0.72	0.001	ND	ND	0.45
LSP-24	ND	ND	ND	ND	ND	ND	ND	ND	0.32
LSP-26	ND	ND	ND	ND	ND	ND	ND	ND	0.86
LSP-28	ND	ND	ND	ND	0.18	ND	ND	ND	1.2
LSP-29/30	ND	ND	ND	ND	0.20	ND	ND	ND	1.2
LSP-31	ND	ND	0.20	ND	0.38	ND	ND	0.007	0.78
LSP-32	ND	ND	ND	ND	0.13	ND	ND	ND	1.6
LSP-33	ND	0.11	0.185	ND	0.30	ND	ND	ND	0.30
LSP-34/35	ND	ND	ND	ND	ND	ND	ND	ND	0.555
LSP-36	ND	ND	ND	ND	ND	ND	ND	ND	0.33
LSP-37/38	ND	0.021*	ND	ND	ND	ND	0.0052	ND	1.8
LSP-39	ND	ND	ND	ND	ND	ND	ND	ND	0.22
LSP-40	ND	ND	ND	ND	ND	ND	ND	ND	1.2

**bold** = constituent level exceeds Primary or Secondary MCL

<sup>\* =</sup> concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-01	0.34	ND	ND	ND	ND	ND	ND	ND	ND
LSP-02	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-03	0.81	ND	0.76	ND	ND	0.0069	ND	ND	ND
LSP-04	ND	ND	ND	ND	ND	ND	ND	ND	0.11
LSP-05/06	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-07	ND	ND	ND	ND	ND	0.0077	ND	ND	ND
LSP-08/09	ND	ND	ND	ND	ND	0.0074	ND	ND	ND
LSP-10	ND	ND	ND	ND	ND	0.0089	ND	ND	ND
LSP-11	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-12	ND	ND	ND	ND	ND	ND	ND	ND	0.059
LSP-14	ND	ND	ND	ND	ND	0.0060	ND	ND	ND
LSP-15/16	ND	0.0055	ND	ND	ND	0.0074	ND	ND	0.095
LSP-17	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-18/19	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-20	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-21	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-22	1.2	ND	0.58	ND	ND	0.007	ND	ND	ND
LSP-24	ND	ND	ND	ND	ND	ND	ND	ND	0.11
LSP-26	ND	ND	ND	ND	ND	ND	ND	ND	0.34
LSP-28	ND	ND	0.056	ND	ND	ND	ND	ND	ND
LSP-29/30	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-31	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-32	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-33	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-34/35	ND	ND	ND	ND	ND	ND	ND	ND	0.195
LSP-36	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-37/38	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-39	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-40	ND	ND	ND	ND	ND	ND	ND	ND	ND

 $\boldsymbol{bold} = constituent \ level \ exceeds \ Primary \ or \ Secondary \ MCL$ 

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000-Continued

Sample #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	<b>Ra-226</b> (pCi/L)	Uranium (μg/l)	VOCs (μg/l)	GWPL Pesticides	Type of Chemistry
LSP-01								mixed-mixed
LSP-02	430+/-83					ND		mixed-mixed
LSP-03								mixed-mixed
LSP-04						ND		sodium-mixed
LSP-05/06	384+/-55					ND		mixed-bicarbonate
LSP-07								mixed-bicarbonate
LSP-08/09	925+/-94					ND		sodium-mixed
LSP-10	350+/-65					ND		sodium-sulfate
LSP-11	550+/-77					ND		sodium-mixed
LSP-12/13		0.76+/-0.4	< 1.25					magnesium-bicarbonate
LSP-14								mixed-mixed
LSP-15/16	375+/-68					ND		mixed-sulfate
LSP-17								mixed-mixed
LSP-18/19	1050+/-93					ND		sodium-bicarbonate
LSP-20	910+/-88					ND		sodium-mixed
LSP-21						ND		calcium-bicarbonate
LSP-22/23	1080+/-95							mixed-chloride
LSP-24		7.3+/-1.0	3.3+/-0.88	< LLD				calcium-bicarbonate
LSP-26		19+/-1.4	4.0+/-0.94	< LLD	6.9+/-1.8	ND		calcium-bicarbonate
LSP-28						ND		sodium-mixed
LSP-29/30	295+/-58							sodium-mixed
LSP-31		12+/-0.96	5.9+/-1.1	< LLD		ND		bicarbonate-mixed
LSP-32						ND		sodium-bicarbonate
LSP-33								mixed-bicarbonate
LSP-34/35		1.5+/-0.72	< LLD					mixed-bicarbonate
LSP-36								mixed-bicarbonate
LSP-37/38		10.85+/-1.	2.25+/-0.9	< LLD		ND		sodium-bicarbonate

**bold** = Primary MCL Exceedance

LLD = Lower Limit of Detection

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	ADEQ #	MCL Exceedances	Temp (°C)	<b>pH-field</b> (su)	SC-lab (FS/cm)	TDS (mg/l)	Hardness (mg/l)	Total Alk (mg/l)	Turbidity (ntu)
LSP-41	28278	TDS, F	21.07	7.75	980	650	290	240	0.03
LSP-42	58449	As*	13.80	8.15	310	220	120	140	0.97
LSP-43	58786	As*, Mn	11.21	8.07	590	400	240	220	0.63
LSP-44	28877	TDS, SO4, As*, F	19.39	7.56	1200	790	310	230	0.13
LSP-45/46	58450	TDS, SO4, As*	17.88	7.52	1400	855	325	225	0.38
LSP-47	58542	pH, TDS, As*, F	22.27	8.86	820	500	14	140	0.04
LSP-48	58546		29.46	7.77	430	250	120	180	0.03
LSP-49	58590		21.14	7.30	740	450	250	220	0.03
LSP-50/51	58591	TDS, Cl, SO4, F	25.21	8.26	4450	2850	257	110	2.5
LSP-52	58592		21.51	8.23	560	320	220	220	0.59
LSP-53	31851		24.91	7.43	580	330	220	240	0.67
LSP-54	38003		17.67	7.41	670	380	320	270	0.06
LSP-55	58593		20.18	7.62	640	380	270	250	0.11
LSP-56/57	33951	F, Mn, Gross Alpha	18.55	7.93	850	480	170	300	2.35
LSP-58	58594	TDS,SO4,Sb,F,Fe,Mn	21.74	7.31	1940	800	880	150	110
LSP-59	38952		16.95	7.67	550	320	240	250	0.34
LSP-60	58652		19.61	7.43	440	270	190	200	0.24
LSP-61	58653		17.88	7.23	524	290	250	250	3.1
LSP-62	58654		19.77	7.12	560	310	310	260	0.13
LSP-63/64	58655		21.95	7.81	330	195	160	150	0.33
LSP-65	58656		19.01	7.53	490	310	210	180	0.10
LSP-66	58657	TDS, SO4, Sb	20.11	7.22	1100	820	500	200	0.26
LSP-67	58658	TDS, SO4, As*, F	22.90	7.16	1900	1400	540	240	0.11
LSP-69/70	58806		21.33	7.29	240	190	87	100	0.64
LSP-71	58807		22.91	7.12	170	140	60	65	3.8
LSP-72	58808		22.23	7.28	420	280	200	170	0.40
LSP-73	58819	Mn	20.67	7.10	780	480	330	360	0.54
LSP-74	58820		25.13	7.94	270	200	150	120	8.8
LSP-75	58818	TDS, Mn	19.52	7.41	810	580	440	248	0.66

**bold** = constituent level exceeds Primary or Secondary MCL

<sup>\*</sup> = concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-41	89	17	110	2.80	4.0	290	ND	30	240
LSP-42	45	6.6	22	0.81	1.1	170	ND	6.4	ND
LSP-43	66	19	28	0.78	3.3	270	ND	15	61
LSP-44	94	22	130	3.14	5.3	280	ND	66	280
LSP-45/46	92.5	24	170	3.84	6.25	270	ND	155	260
LSP-47	9.6	ND	170	15.11	2.4	140	13	31	150
LSP-48	32	11	55	2.14	2.5	220	ND	8	28
LSP-49	73	18	68	1.85	3.0	270	ND	14	130
LSP-50/51	70.5	20	895	24.30	14.5	130	ND	705	1100
LSP-52	70	11	34	1.00	5.1	270	ND	9.4	57
LSP-53	63	17	42	1.21	0.79	290	ND	21	21
LSP-54	69	37	24	0.58	2.4	330	ND	22	47
LSP-55	72	23	42	1.11	0.53	300	18	18	58
LSP-56/57	39.5	17.5	140	4.62	2.65	370	ND	37	71.5
LSP-58	310	27	140	2.05	4.0	180	ND	15	970
LSP-59	84	8.9	30	0.83	2.6	300	ND	18	ND
LSP-60	60	11	29	0.90	3.0	244	ND	9.3	34
LSP-61	80	14	22	0.60	1.7	305	ND	11	28
LSP-62	100	15	ND	0.00	ND	320	ND	4.6	39
LSP-63/64	48	9.7	12	0.41	2.05	180	ND	4.5	13
LSP-65	65	12	29	0.87	2.9	220	ND	9.5	62
LSP-66	160	23	68	1.33	3.2	240	ND	34	360
LSP-67	170	24	250	4.76	5.0	290	ND	64	680
LSP-69/70	27	3.8	17	0.81	2.1	120	ND	6.3	ND
LSP-71	20	2.5	11	0.62	1.1	79	ND	3.4	11
LSP-72	69	3.2	15	0.48	1.5	210	ND	8.8	ND
LSP-73	89	26	48	1.15	3.8	440	ND	26	46
LSP-74	37	6.8	9.8	0.38	1.8	150	ND	3.6	15
LSP-75	120	26	23	0.50	4.2	300	ND	4.8	210

 $\boldsymbol{bold} = constituent \ level \ exceeds \ Primary \ or \ Secondary \ MCL$ 

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Nitrate-Nitrite-N (mg/l)	Nitrate -N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Total Phosphorus (mg/l)
LSP-41	0.85	0.85	ND	ND	ND	0.036
LSP-42	ND	ND	ND	0.067	ND	0.059
LSP-43	ND	ND	ND	0.21	0.050	0.18
LSP-44	0.22	0.22	ND	0.077	ND	0.045
LSP-45/46	0.375	0.375	ND	0.12	ND	0.052
LSP-47	0.37	0.37	ND	0.09	ND	0.029
LSP-48	1.0	1.0	ND	0.057	ND	ND
LSP-49	0.99	0.99	ND	ND	ND	ND
LSP-50/51	ND	ND	ND	ND	ND	ND
LSP-52	N/A	N/A	ND	1.1	ND	N/A
LSP-53	3.7	3.7	ND	0.20	0.023	0.047
LSP-54	2.5	2.5	ND	ND	ND	ND
LSP-55	0.90	0.90	ND	ND	ND	0.036
LSP-56/57	ND	ND	ND	ND	0.0225	ND
LSP-58	0.23	0.166	0.064	0.068	0.074	0.35
LSP-59	1.2	1.2	ND	ND	0.022	0.044
LSP-60	0.26	0.26	ND	ND	ND	0.046
LSP-61	ND	ND	ND	0.65	0.026	0.10
LSP-62	0.35	0.35	ND	0.05	ND	0.044
LSP-63/64	0.39	0.39	ND	ND	ND	ND
LSP-65	0.42	0.42	ND	ND	ND	0.057
LSP-66	2.8	2.8	ND	0.084	ND	0.026
LSP-67	0.74	0.74	ND	0.15	ND	ND
LSP-69/70	0.94	0.94	ND	ND	ND	0.14
LSP-71	0.17	0.17	ND	0.095	ND	0.12
LSP-72	6.4	6.4	ND	0.20	ND	0.26
LSP-73	0.44	0.44	ND	0.24	ND	ND
LSP-74	0.37	0.35	0.022	0.54	ND	ND
LSP-75	0.052	0.052	ND	0.13	ND	ND

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

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-41	ND	ND	ND	ND	0.16	ND	ND	ND	2.2
LSP-42	ND	0.011*	ND	ND	ND	ND	ND	ND	0.53
LSP-43	ND	0.018*	ND	ND	ND	ND	ND	0.014	0.54
LSP-44	ND	0.011*	ND	ND	0.22	ND	ND	ND	2.0
LSP-45/46	ND	0.0043	0.032	ND	0.25	ND	ND	ND	1.35
LSP-47	ND	0.022*	ND	ND	0.30	ND	ND	ND	13
LSP-48	ND	ND	ND	ND	ND	ND	ND	ND	1.3
LSP-49	ND	ND	ND	ND	0.18	ND	ND	ND	1.0
LSP-50/51	ND	ND	ND	ND	2.0	ND	ND	ND	4.3
LSP-52	ND	ND	ND	ND	ND	ND	ND	ND	1.4
LSP-53	ND	ND	ND	ND	ND	ND	ND	ND	0.68
LSP-54	ND	ND	0.13	ND	ND	ND	ND	ND	0.71
LSP-55	ND	ND	0.12	ND	ND	ND	ND	ND	0.93
LSP-56/57	ND	ND	ND	ND	0.225	ND	ND	ND	4.25
LSP-58	0.0073	ND	ND	ND	0.30	ND	ND	ND	7.4
LSP-59	ND	ND	ND	ND	ND	ND	ND	ND	0.48
LSP-60	ND	ND	ND	ND	ND	ND	ND	ND	0.86
LSP-61	ND	ND	ND	ND	ND	ND	ND	ND	0.35
LSP-62	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-63/64	ND	ND	ND	ND	ND	ND	ND	ND	0.25
LSP-65	ND	ND	ND	ND	ND	ND	ND	ND	0.78
LSP-66	0.75	ND	ND	ND	ND	ND	ND	ND	1.1
LSP-67	ND	0.013*	ND	ND	0.42	ND	ND	ND	4.1
LSP-69/70	ND	ND	ND	ND	ND	ND	ND	ND	0.22
LSP-71	ND	ND	ND	ND	ND	ND	ND	ND	0.20
LSP-72	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-73	ND	ND	ND	ND	ND	ND	ND	ND	0.51
LSP-74	ND	ND	ND	ND	ND	ND	ND	ND	0.24
LSP-75	ND	ND	ND	ND	ND	ND	ND	ND	0.40

 $\boldsymbol{bold} = constituent\ level\ exceeds\ Primary\ or\ Secondary\ MCL$ 

<sup>\* =</sup> concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-41	ND	ND	ND	ND	ND	0.0070	ND	ND	ND
LSP-42	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-43	0.15	ND	0.12	ND	ND	0.008	ND	ND	ND
LSP-44	ND	ND	ND	ND	ND	0.014	ND	ND	ND
LSP-45/46	ND	ND	ND	ND	ND	0.010	ND	ND	ND
LSP-47	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-48	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-49	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-50/51A	0.27	ND	ND	ND	ND	ND	ND	ND	ND
LSP-51B	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-53	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-54	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-55	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-56/57	ND	ND	0.10	ND	ND	ND	ND	ND	0.285
LSP-58	2.1	ND	0.50	ND	ND	ND	ND	ND	ND
LSP-59	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-60	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-61	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-62	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-63/64	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-65	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-66	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-67	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-69/70	ND	ND	ND	ND	ND	ND	ND	ND	0.058
LSP-71	0.12	ND	ND	ND	ND	ND	ND	ND	0.064
LSP-72	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-73	ND	ND	0.12	ND	ND	ND	ND	ND	ND
LSP-74	ND	ND	ND	ND	ND	ND	ND	ND	0.18
LSP-75	ND	ND	0.13	ND	ND	ND	ND	ND	0.22

 $\boldsymbol{bold} = constituent \ level \ exceeds \ Primary \ or \ Secondary \ MCL$ 

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000-Continued

Sample #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	<b>Ra-226</b> (pCi/L)	Uranium (μg/l)	VOCs (µg/l)	GWPL Pestidicdes	Type of Chemistry
LSP-39		2.9+/-0.84	4.9+/-1.0					calcium-bicarbonate
LSP-40	374+/-48						ND	calcium-sulfate
LSP-41							ND	calcium-bicarbonate
LSP-42		3.5 +/10.76	< LLD					calcium-bicarbonate
LSP-43								calcium-bicarbonate
LSP-44	317+/-48					ND		mixed-bicarbonate
LSP-45/46	300+/-47					ND		mixed-mixed
LSP-47	554+/-45					ND		sodium-bicarbonate
LSP-48	577+/-46					ND		mixed-bicarbonate
LSP-49								mixed-bicarbonate
LSP-50/51	601+/-43							sodium-mixed
LSP-52								calcium-bicarbonate
LSP-53		7.0+/-1.1	2.5+/-0.84	< LLD				mixed-mixed
LSP-54		6.1+/-1.1	3.7+/-0.86	< LLD				mixed-bicarbonate
LSP-55		7.4+/-1.1	1.8+/-0.82	< LLD				mixed-bicarbonate
LSP-56/57		68+/-3.0	16.5+/-1.1	< LLD	61.5+/-4.7			sodium-bicarbonate
LSP-58a						ND*		calcium-sulfate
LSP-59								calcium-bicarbonate
LSP-58b						ND*		calcium-sulfate
LSP-60								calcium-bicarbonate
LSP-61								mixed-bicarbonate
LSP-62		< LLD	< LLD					calcium-bicarbonate
LSP-63/64	80+/-20					ND		calcium-bicarbonate
LSP-65								calcium-bicarbonate
LSP-66								calcium-sulfate
LSP-67								mixed-sulfate

**bold** = Primary MCL Exceedance

LLD = Lower Limit of Detection

 $italics = {\tt constituent} \ {\tt exceeded} \ {\tt holding} \ {\tt time}$ 

\* = methylethyl ketone and another unidentified VOC detected

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	ADEQ #	MCL Exceedances	Temp (°C)	<b>pH-field</b> (su)	SC-lab (FS/cm)	TDS (mg/l)	Hardness (mg/l)	Total Alk (mg/l)	Turbidity (ntu)
LSP-76	55034		25.18	7.21	720	400	360	330	0.07
LSP-77/78**	58801	pH, As*	29.40	9.31	505	300	17	194	0.05
LSP-80	58802	pH, Mn	22.95	9.14	320	290	130	103	2.5
LSP-81	58803	pH, F	18.66	8.53	190	150	53	88	0.41
LSP-82	58804	TDS	N/A	7.46	1200	730	470	310	0.05
LSP-83	58805	TDS, SO4, F	24.63	7.40	1800	1100	350	260	1.7

**bold** = constituent level exceeds Primary or Secondary MCL

italics = constituent exceeded holding time

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-76	78	38	15	0.35	2.0	400	ND	30	26
LSP-77/78	7	ND	120	52.20	ND	230	ND	14.5	35
LSP-80	38	6.2	14	0.56	11	126	ND	7.1	46
LSP-81	20	1.3	21	1.23	ND	110	ND	ND	ND
LSP-82	120	39	68	1.38	0.65	380	ND	51	230
LSP-83	90	26	250	5.98	5.9	320	ND	210	360

 $\boldsymbol{bold} = constituent\ level\ exceeds\ Primary\ or\ Secondary\ MCL$ 

italics = constituent exceeded holding time

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	Nitrate-Nitrite-N (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)	TKN (mg/l)	Ammonia-N (mg/l)	Total Phosphorus (mg/l)
LSP-76	0.94	0.94	ND	ND	ND	ND
LSP-77/78**	0.64	0.64	ND	ND	ND	0.022
LSP-80	0.032	0.032	ND	5.2	0.096	0.31
LSP-81	0.19	0.19	ND	0.14	ND	ND
LSP-82	6.6	6.6	ND	0.13	ND	0.040
LSP-83	ND	ND	ND	0.090	ND	0.056

 $\boldsymbol{bold} = constituent \ level \ exceeds \ Primary \ or \ Secondary \ MCL$ 

<sup>\* =</sup> concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash groundwater basin.

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash groundwater basin.

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash groundwater basin.

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-76	ND	ND	0.14	ND	ND	ND	ND	ND	0.38
LSP-77/78**	ND	0.011*	ND	ND	0.32	ND	ND	ND	1.95
LSP-80	ND	ND	ND	ND	ND	ND	ND	ND	0.36
LSP-81	ND	ND	ND	ND	ND	ND	ND	ND	2.8
LSP-82	ND	ND	ND	ND	0.11	ND	ND	ND	0.30
LSP-83	ND	ND	ND	ND	ND	ND	ND	ND	2.0

**bold** = constituent level exceeds Primary or Secondary MCL

italics = constituent exceeded holding time

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000--Continued

Sample #	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)
LSP-76	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-77/78**	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-80	0.28	ND	0.23	ND	ND	ND	ND	ND	ND
LSP-81	ND	ND	ND	ND	ND	ND	ND	ND	ND
LSP-82	ND	ND	ND	ND	ND	ND	ND	ND	0.052
LSP-83	ND	ND	ND	ND	ND	ND	ND	ND	0.064

**bold** = constituent level exceeds Primary or Secondary MCL

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash grondwater basin.

<sup>\* =</sup> concentration exceeds the revised arsenic SDW Primary MCL of 0.01 mg/l which becomes effective in 2006

<sup>\*\*</sup> Reported for information purposes only as the sample site was in the Donnelly Wash groundwater basin.

Appendix B. Groundwater Quality Data, Lower San Pedro Basin, 1999-2000-Continued

Sample #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	<b>Ra-226</b> (pCi/L)	Uranium (μg/l)	VOCs (µg/l)	GWPL Pestidicde	Type of Chemistry
LSP-69/70		0.75+/-0.50	1.9+/-0.86			ND		calcium-bicarbonate
LSP-71	128+/-15							calcium-bicarbonate
LSP-72						ND		calcium-bicarbonate
LSP-73		4.6+/-0.68	4.6+/-0.98					calcium-bicarbonate
LSP-74								calcium-bicarbonate
LSP-75		8.7+/-0.82	6.0+/-1.0	< LLD				calcium-bicarbonate
LSP-76		2.1 +/- 0.62	2.6 +/- 0.09			Chloroform 4.4		calcium-bicarbonate
LSP-77/78*	536+/-55							sodium-bicarbonate
LSP-80		0.96+/-0.58	11+/-1.1					calcium-bicarbonate
LSP-81								mixed-bicarbonate
LSP-82		3.1+/-0.62	1.5+/-0.98					mixed-mixed
LSP-83	348+/-35					ND		sodium-mixed

**bold** = Primary MCL Exceedance

LLD = Lower Limit of Detection

 $<sup>{\</sup>rm *Reported\ for\ information\ purposes\ only\ as\ the\ sample\ site\ was\ in\ the\ Donnelly\ Wash\ groundwater\ basin.}$ 

Appendix C. Groundwater Quality Data by Aquifer, Lower San Pedro Basin, 1999-2000

	Hardrock				Unconfined	Basin-Fill		Flood	plain		Confined Basin-Fill			
Constituent	# of sites	Median	95% CIs	# of sites	Median	95% CIs	# of sites	Median	95% CIs	# of sites	Median	95% CIs		
	Physical Parameters and General Mineral Characteristics													
Temp.	20	19.7	17.1 to 21.9	9	22.9	19.0 to 26.5	27	20.8	20.2 to 22.2	4	23.9	14.8 to 39.5		
pH-field	23	7.43	7.38 to 7.94	9	7.45	7.16 -to 7.86	27	7.44	7.41 to 7.66	4	8.37	7.74 to 9.01		
Turbidity	23	0.6	0.3 to 1.9	9	0.4	-0.9 to 7.6	27	0.4	-3.1 to 13.6	4	0.1	-1.2 to 2.6		
Total Alk.	23	250	200 to 275	9	170	118 to 203	27	220	200 to 209	4	125	83 to 158		
SC-lab	23	580	484 to 695	9	430	- 139 to 1859	27	1000	850 to 1178	4	760	-1499 to 4644		
Hardness	23	240	194 to 296	9	200	15 to 556	27	280	242 to 362	4	45	-96 to 283		
TDS	23	335	307 to 427	9	280	-98 to 1204	27	690	534 to 741	4	475	-974 to 2974		
						Major I	ons							
Calcium	23	66	50 to 76	9	67	10 to 156	27	83	68 to 111	4	15	-18 to 73		
Magnesium	23	19	16 to 27	9	10	-4 to 41	27	19	16 to 21	4	2	-9 to 21		
Sodium	23	24	24 to 49	9	15	-44 to 202	27	110	85 to 130	4	155	-308 to 936		
Potassium	23	1.7	1.1 to 3.1	9	2.1	0.4 to 7.2	27	4.1	3.9 to 4.9	4	2.6	-4.2 to 15.1		
Bicarbonate	23	300	239 to 334	9	210	143 to 248	27	270	244 to 279	4	135	89 to 181		
Chloride	23	15	11 to 23	9	8.8	-103 to 306	27	30	27 to 76	4	36	-345 to 737		
Sulfate	23	41	25 to 74	9	26	-58 to 285	27	230	150 to 309	4	150	-442 to 1152		

Appendix C. Groundwater Quality Data by Aquifer, Lower San Pedro Basin, 1999-2000-Continued

		Hardr	ock	ı	Unconfined	Basin-Fill		Floodp	lain	Confined Basin-Fill		
Constituent	# of sites	Median	95% CIs	# of sites	Median	95% CIs	# of sites	Median	95% CIs	# of sites	Median	95% CIs
						Nutrien	ıts					
Nitrate (N)	23	0.52	0.52 to 2.24	9	0.9	-2.4 to 12.4	26	0.56	0.44 to 0.96	4	0.26	-0.04 to 0.49
Phosphorus	23	0.04	0.03 to 0.09	9	0.01	0.00 to 0.14	26	0.04	0.02 to 0.08	4	0.01	0.00 to 0.03
TKN	23	0.07	-0.02 to 1.14	9	0.08	0.01 to 0.28	27	0.25	0.02 to 0.19	4	0.03	-0.01 to 0.09
						Trace Elem	nents					
Boron	23	0.05	0.05 to 0.12	9	0.05	-0.04 to 0.31	27	0.14	0.11 to 0.18	4	0.24	-0.83 to 2.09
Fluoride	23	0.51	0.38 to 1.21	9	0.25	-0.43 to 2.10	27	1.35	1.34 to 2.46	4	5.45	-1.76 to 14.3
					F	Radiochemistry (	Constitue	ents				
Gross Alpha	17	4.6	1.1 to17.4	2	5.1	-22.9 to 33.1						
Gross Beta	17	2.5	1.9 to 6.1	2	4.1	-6.1 to 14.3						
Radon				3	128	-972 to 1830	12	374	323 to 608	4	576	304 to 1074
						Well Charact	eristics					
GW Depth	8	40	-26 to 224	7	80	22 to 260	26	26	23 to 39	4	825	-171 to 1836
Well Depth	8	144	49 to 345	8	310	135 to 436	26	100	91 to 144	4	825	-171 to 1836

# Appendix D. 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 \*

<sup>\* =</sup> 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  $^{43}$ .

Appendix E. MRLs of Groundwater Protection List (GWPL) Pesticides

GWPL Carbamates	Diuron (Fragment) - 10	Pebulate - 5
Aldicarb - 1	DPX-M6316 - 25	Permethrin - 5
Carbaryl - 1	Endosulfan - 10	Phosmet - 10
Carbofuran - 1	EPTC - 5	Phosphamidon - 5
Methiocarb - 1	Ethofumesate - 10	Piperonyl Butoxide - 10
Methomyl - 1	Ethoprop - 10	Profenofos - 25
Oxamyl - 1	Fenamiphos - 25	Prometon - 10
GWPL Herbicides	Fenarimol - 5	Prometryn - 10
2,4-D - 0.5	Fluazifop-p-butyl - 10	Pronamide - 10
Dacthal (Acids) - 0.5	Flucythrinate - 10	Propiconazole - 10
Dicamba - 0.5	Fluometuron (Fragment) - 10	Pyrazon - 10
<b>GWPL Pesticides</b>	Fluridone - 10	Sethoxydim (Fragment) - 10
Ametryn - 10	Hexazinone - 5	Sulfometuron-methyl - 10
Azinphos-methyl - 10	Imazalil - 10	Sulprofos - 10
Bromacil - 10	Isaazophos - 10	Tebuthiuron - 25
Butylate - 10	Linuron - 10	Terbacil - 5
Captan - 25	Metalaxyl - 10	Terbufos - 10
Carboxin - 5	Metaldehyde - 5	Thidiazuron (Fragment) - 10
Chlorothalonil - 5	Methyl Parathion - 10	Triadimefon - 10
Cyanazine - 10	Metolachlor - 5	Vernolate - 5
Cycloate - 5	Metribuzin - 10	Vinclozolin - 10
Dacthal - 5	Mevinphos - 10	<b>GWPL Pesticides - SIM</b>
Diazinon - 10	Myclobutanil - 10	Alachlor - 1
Dichloran - 10	Napropamide - 5	Atrazine - 1
Diethatyl ethyl - 10	Norflurazon - 10	Lindane 0.1
Dimethoate - 10	Parathion - 10	Simzine - 1
Diphenamid - 5		

All units in Fg/l Source 43

Appendix F. Surface Water Quality Data Related to the LSP Study

Constituent	San Pedro River near Cascabel <sup>1</sup> San Pedro River near Feldman <sup>2</sup>		Aravaipa Creek in Aravaipa Canyon³	Gila River near Calva <sup>4</sup>			
Quantity of Surface Water							
Flow Rate (cfs)	2.5	12.5	19.0	141.8			
	Physical Paramet	ters and General Mine	ral Characteristics				
Temperature	18.1	20.5	18.5	18.6			
pH-field	8.08	8.19	8.45	8.09			
Turbidity	1.4	299	8	2810			
Alkalinity, total	238	293	175	257			
SC-lab	661	997	391	2506			
Hardness	257	407	166	287			
TDS	437	670	261	1500			
		Major Ions					
Calcium	73	130	52	79			
Magnesium	17	22	9	22			
Sodium	53	110	25	425			
Potassium	4.6	6.3	3.0	7.5			
Bicarbonate	288	353	203	308			
Chloride	18	31	7	521			
Sulfate	106	268	29	239			
Fluoride	0.82	1.96	0.76	1.7			

<sup>&</sup>lt;sup>1</sup> Mean of eight samples collected between November 1991 and May 2000 (7).

<sup>&</sup>lt;sup>2</sup> Mean of nine samples collected between May 1998 and April 2001 (7).

<sup>&</sup>lt;sup>3</sup> Mean of ten samples collected between April 1992 and May 2001 (7).

<sup>&</sup>lt;sup>4</sup> Mean of four samples collected between November 1999 and August 2000 (55).

Appendix G. Drillers' Logs of Selected Wells Representative of Each LSP Aquifer

Stratum	Thickness (ft)	Depth (ft)	Stratum	Thickness (ft)	Depth (ft)	
	Confin	ed Basin-Fill (A	rtesian) Aquifer - LSP-1	1		
Floodplain Alluvium			Brown shale with sand	10	1,015	
Sand and gravel	80	80	Red clay and gravel	15	1,030	
	Basin-Fill Deposits		Sticky black clay	5	1,035	
Sand	5	85	Sticky brown shale	5	1,040	
Sand and boulders	55	140	Red clay and gravel	65	1,105	
Sand	20	160	Gypsum	5	1,110	
Gravel	45	205	Red clay and gravel	25	1,135	
Hard sand	15	220	Brown lime	9	1,144	
Gravel	65	285	Red clay and gravel	16	1,160	
Sand	30	315	Hard sand (some water)	35	1,195	
Sand and boulders	136	451	Red clay	2	1,197	
Sand	144	595	Hard brown sand	8	1,205	
Sand and gravel	10	605	Hard clay lime	15	1,220	
Gravel	20	625	Conglomerate w/ lime	37	1,257	
Sand and gravel	35	660	Red clay	8	1,265	
Running gravel	5	665	Hard conglomerate	2	1,267	
Sand	80	745	Red clay	8	1,275	
Clay and gravel	10	755	Sandstone (artesian water)	95	1,370	
Sand and clay	10	765	Hard sandstone	70	1,440	
Consolidated to	Semi-Consolidated Sedimen	tary Rocks	Red beds	45	1,485	
Red clay and gravel	240	1,005				
		Floodplain A	quifer - LSP-14			
	Floodplain Alluvium		Basin-Fill Deposits			
Clay	15	15	Clay	8	119	
Sand and gravel	96	111				
	Uı	nconfined Basin-	Fill Aquifer - LSP-71			
	Floodplain Alluvium		Hard conglomerate	40	205	
Sandy soil	10	10	Hard rock ledge	10	215	
Gravel, water at 35 feet	26	36	Sticky clay	20	235	
	Basin-Fill Deposits		Medium hard conglomerate	55	290	
Hard and soft conglomerate	109	145	Crystalline and	l Consolidated Sedimenta	ry Rocks	
Soft conglomerate, water	20	165	Very hard rock	10	300	

## INVESTIGATION METHODS

Various groundwater sites were sampled by the ADEQ Groundwater Monitoring Program to characterize regional groundwater quality in the LSP. Samples were collected at all sites for inorganic (physical parameters, major ions, nutrients, and trace elements) analyses. At many sites VOCs, radon, and radiochemistry samples were collected for analysis. At limited sites, samples were collected for GWPL pesticide analyses.

No bacteria sampling was conducted since microbiological contamination problems in groundwater are often transient and subject to a variety of changing environmental conditions including soil moisture content and temperature.<sup>26</sup>

# **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.

Sampling in the LSP conducted by ADEO 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. The main benefit of a statistically-designed sampling plan is that it allows much greater groundwater quality assumptions than would be allowable with a nonstatistical 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 clearlydefined point of egress, and if the sample point had minimal surface impacts (Figure 33). Well information compiled from the ADWR well registry and spring characteristics are found in Appendix A.



Figure 32. Springs that rise along fault planes are an often overlooked source of groundwater samples and are especially useful in lightly developed mountainous areas such as the LSP. ASARCO's Kip Gambee observes ADEQ hydrologist Douglas Towne collect a sample from a headgate used to control inflow from a spring into Cooks Lake. Water is stored in this shallow reservoir until sufficient head is available to distribute the water in irrigation ditches.16

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:31

- 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 LSP study were also responsible for the collection and interpretation of the data<sup>16</sup>. 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)*<sup>4</sup> and the *Field Manual For Water Quality Sampling* <sup>11</sup>. While these sources should be consulted as references to specific sampling questions, a brief synopsis of the procedures involved in collecting a groundwater sample is provided.

After obtaining permission from the 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 Hydrolab 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 aguifer 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. Pesticide
- 4. Inorganic
- 5. Radiochemistry

Radon samples were collected in 2, unpreserved, 40-ml clear glass vials. Radon samples were filled so there was no air trapped within the bottles.

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.

Pesticide samples were collected in two bottles: an unpreserved, one-gallon, amber glass container; and, for carbamates which break down at higher pH levels, a 60 ml glass container preserved with 1.8 ml monochloro (13.3 percent) - acedicitic acid (5.6 percent) and potassium hydroide (5.1 percent).

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

- 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.

All samples were kept at 4°C using ice in an insulated cooler, with the exception of the radiochemistry samples. Chain of custody procedures were followed in sample handling. Samples for this study were collected between November 1999 and July 2000.

## **Laboratory Methods**

The inorganic, VOC, and pesticide 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 5**.

Radon samples were analyzed by Lucas Laboratories of Sedona, AZ with the one split analyzed by Bolin Laboratories of Phoenix, AZ. Radiochemistry samples

ADHS/Del Mar Laboratory Methods Used for the LSP Study Table 5.

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				
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				
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<sup>22 43</sup>

ADHS/Del Mar Laboratory Methods Used for the LSP Study--Continued Table 5.

Constituent	t 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<sup>22 43</sup>

were analyzed by the Arizona Radiation Regulatory Agency (ARRA) laboratory in Phoenix, AZ with the one split analyzed by Lucas Laboratories of Sedona, AZ.

The analysis of radiochemistry samples was treated according to the following SDW protocols <sup>6</sup>. 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.

# Sample Numbers

Sixty-three (63) sites - 46 wells and 17 springs - were sampled for the study. Various numbers and types of samples were collected and analyzed:

- 63 inorganic
- 25 VOC <
- 19 radon <
- 19 radiochemistry
- 2 pesticide

#### **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 LSP study. The design of the QA/QC plan was based on recommendations included in the Quality Assurance Project Plan (QAPP) 4 and the Field Manual For Water Quality Sampling<sup>11</sup>. The types and numbers of QC samples collected for this study are as follows:

(6 duplicates, 7 splits, 4 blanks). Inorganic: VOC: (4 duplicates, 0 splits, 9 blanks). (3 duplicates, 1 splits, 0 blanks). Radiochemical: (4 duplicates, 1 splits, 0 blanks). Radon: (0 duplicates, 0 splits, 0 blanks). Pesticide:

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. 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. 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 four equipment blanks. SC had a mean level of 2.3FS/cm which was less than 1 percent of the SC median 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<sup>31</sup>. Similarly, turbidity had a mean level of 0.11 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<sup>43</sup>. The only other constituent detections were calcium (9.4 mg/l) and hardness (15 mg/l) in one equipment blank.

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

**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. 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 26 constituents examined, the maximum difference between duplicate constituents rarely exceeded 17 percent (Table 6). Median differences were within 6 percent except for gross beta (17 percent), turbidity (25 percent), total phosphorus (58 percent), and TKN (78 percent). Gross beta concentrations were not large in absolute difference levels. Turbidity values can be impacted by the exceedance of this parameter's holding time <sup>43</sup>; this occurred frequently during the study due to turbidity's short holding time. Phosphorus and TKN differences might be related to the analysis of these nutrients, which are particularly difficult and sensitive<sup>43</sup>.

One pair of duplicate samples involving arsenic, total phosphorus, and TKN had a constituent concentration exceeding the MRL in one sample while its duplicate sample was a non-detect. In each of the three cases, the measurable concentration was at or close to the MRL resulting in little variation between the duplicate samples.

Six pairs of duplicate samples were also submitted to test for differences between field and lab filtering of cations and trace elements. The results indicated that with 126 pairs of duplicate constituents, all but 4 pairs had concentrations within 10 percent of each other. One pair involving sodium had a 17 percent difference while copper, iron, and zinc each had a pair in which there was a concentration above the MRL in one sample while the other sample was a non-detect.

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. 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 18 constituents examined, the maximum difference between split constituents rarely exceeded 20 percent (Table 7).

Median differences were within 8 percent except for nitrate as nitrogen (31 percent). This nutrient only had a 0.05 mg/l median absolute difference however. 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 <sup>29</sup>. Results of the Sign test showed that none of the 13 constituents examined had significantly different concentrations between the laboratories.

In addition, 24 pairs of split samples had a constituent concentration exceeding the MRL in one sample while there was a non-detection in its split sample. In all but five cases this discrepancy was due to different constituent MRLs between laboratories. The other five cases involved calcium (twice), hardness, selenium, and TKN. With the exception of TKN, these cases involved the measurable concentration close to the MRL resulting in little sample variation.

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<sup>25</sup>. Overall, cation/anion balances of LSP samples were significantly correlated (regression analysis, p # 0.01) and within acceptable limits (90 - 110 percent) with the exception of three samples (LSP-35, 42, and 63) all which barely exceeded the acceptable limits. In each of the above instances, the cation sum was greater than the anion sum. Laboratory personnel indicated that other parameters not tested for, such as bromide and iodine, could have effected the cation/anion balances 43.

Table 6. Summary Results of LSP Duplicate Samples from ADHS/ARRA Laboratories

_		Difference in Percent			Difference in Concentrations		
Parameter	Number	Minimum	Maximum	Median	Minimum	Maximum	Median
		Physical	Parameters and Ger	neral Mineral Cha	racteristics		
Alkalinity, Total	6	0%	4%	0%	0	10	0
SC (FS/cm)	6	0%	3%	0%	0	30	0
Hardness	6	0%	17%	0%	0	15	0
pH (su)	6	0%	3%	1%	0	0.2	0.1
TDS	6	0%	9%	0%	0	30	0
Turbidity (ntu)	5	1%	160%	25%	0.01	1.6	0.09
			Majo	r Ions			
Bicarbonate	6	0%	10%	0%	0	10	0
Calcium	6	0%	6%	0%	0	3	0
Magnesium	6	0%	6%	0%	0	2	0
Sodium	6	0%	1%	0%	0	1	0
Potassium	6	0%	12%	1%	0	0.3	0.01
Chloride	6	0%	8%	0%	0	10	0
Sulfate	5	1%	8%	5%	1	10	10
			Nutr	ients			
Ammonia	2	4%	8%		0.001	0.004	
Nitrate (as N)	5	0%	16%	1%	0	0.01	0.008
Total Phosphorus	4	7%	94%	58%	0.01	0.051	0.038
ΓKN	1	78%			0.084		
			Trace E	lements			
Boron	4	0%	5%	0%	0	0.1	0
Fluoride	6	0%	4%	0%	0	0.1	0
Lead	1	2%			0.001		
Manganese	1	0%			0		
Selenium	2	8%	14%		0.0006	0.001	
Zinc	4	3%	16%	5%	0.003	0.03	0.009
			Radiochemica	l Constituents			
Gross Alpha	31	5%	21%	6%	0.04	4	2.3
Gross Beta	31	6%	67%	17%	0.3	1.5	1.0
Radon-222	$4^{2}$	2%	17%	3%	10	50	10

All units are mg/l except as noted with certain physical parameters

<sup>1</sup> ARRA Laboratory

<sup>2</sup> Lucas Laboratory

Table 7. Summary Results of LSP Split Samples From ADHS/Del Mar Labs

Constituents	**	Difference in Percent		Difference in Levels			Signif-	
	Number	Minimum	Maximum	Median	Minimum	Maximum	Median	icance
	Physi	cal Parameter	s and General	Mineral Cl	naracteristics			
Alkalinity, total	7	0%	5%	0%	0	10	0	ns
SC (FS/cm)	7	0%	32%	2%	0	230	10	ns
Hardness	5	0%	11%	0%	0	10	0	ns
pH (su)	7	1%	14%	1%	0.8	1.24	0.2	ns
TDS	7	1%	13%	5%	10	100	20	ns
Turbidity (ntu)	1	8%			0.2			ns
			Major Ion	s				
Calcium	5	1%	11%	2%	1	3	1	ns
Magnesium	5	0%	8%	7%	0	.2	1	ns
Sodium	7	0%	12%	5%	0	20	3	ns
Potassium	5	0%	18%	7%	0	1.1	0.3	ns
Chloride	7	1%	27%	8%	0.4	10	1	ns
Sulfate	6	0%	18%	1%	0	20	1	ns
			Nutrients	1				
Nitrate as N	6	3%	86%	31%	0.01	0.78	0.05	ns
Phosphorus, total	1	35%			0.026			ns
TKN	1	167%			0.98			ns
			Trace Eleme	ents				
Fluoride	7	4%	22%	7%	0.01	0.6	0.1	ns
Iron	1	30%			0.08			ns
			Radiochemic	al Constitue	ents			
Radon-222 <sup>1</sup>	1	44%			171			ns

All units are mg/l except as noted with certain physical parameters

<sup>&</sup>lt;sup>1</sup> = Split conducted between Lucas Laboratory (LSP-5) and Bolin Laboratory (LSP-6)

ns = No significant (p # 0.05) difference between labs

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<sup>32</sup>. 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 <sup>31</sup>. The relationship of TDS to SC becomes indefinite for groundwater both with very high and low concentrations of dissolved solids<sup>31</sup>.

**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 Hydrolab 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<sup>31</sup>. Even so, the pH values measured in the field using a Hydrolab at the time of sampling were significantly correlated with laboratory pH values (regression analysis, p # 0.01).

### 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<sup>13</sup>. Groundwater temperature and well depth were significantly correlated (regression analysis, p # 0.01).

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

## **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 21 constituents were tested for both non-transformed and log-transformed normality using the Kolmogorov-Smirnov one-sample test with the Lilliefors option<sup>15</sup>.

Results of this test using non-transformed data revealed that only bicarbonate was normally distributed. The distribution of many groundwater quality parameters is often not Gaussian or normal, but skewed to the right.

The results of the log-transformed test revealed that 7 of the 21 log-transformed constituents were 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 <sup>29</sup>.

Various aspects of LSP 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 groundwater aquifers, geologic types, and/or watersheds of the LSP were the same. The Kruskal-Wallis test uses the differences, but also incorporates information about the magnitude of each difference. 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 aquifers (floodplain, basin-fill, confined basin-fill, and hardrock), basin watersheds (Redington, Mammoth, Winkleman, and Kearny), and geologic (alluvium, granite rock, metamorphic rock, volcanic rock, and sedimentary rock).

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 <sup>29</sup>.

Both the Kruskal-Wallis and Tukey tests are not valid for data sets with greater than 50 percent of the

constituent concentrations below the MRL<sup>29</sup>. Consequently, the Kruskal-Wallis test was not calculated for trace parameters such as antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc as well as phenolphthalein alkalinity, carbonate, nitrite, ammonia, and TKN. Highlights of these statistical tests are summarized in the groundwater quality section.

**Groundwater Level Relationships:** Simple regression was used to examine relationships between constituent concentrations and groundwater depth. Groundwater depth was determined using a sounder in the field when possible or obtained from well driller's logs. Comparisons were conducted using three distinct methods:

- Linear Model [P] = md + b[P] vs d
- Exponential Model  $[P]_d = [P]_{d=0}$ e-rd ln[P] vs d
- Biphasic Model [P] = a(d)-bln[P] vs lnd

The null hypothesis of no association between variables was rejected if the probability of obtaining the correlation by chance was less than or equal to 0.05. Significant correlations between the data sets 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.

The Pearson test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL<sup>29</sup>. Consequently, Pearson Correlation Coefficients were not calculated for trace parameters such as antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc as well as phenolphthalein alkalinity, carbonate, nitrite, ammonia, and TKN. Significant highlights from this statistical test are summarized in the groundwater

quality section.

Time-Trend Analysis: Changes in constituent concentrations over time were examined utilizing data collected from the same wells by the USGS in 1950/1951 and ADEQ in 1999/2000<sup>28</sup>.

The Wilcoxon rank-sum statistic, which is a nonparametric measure of association between two independent sets of data, was used to determine any significant changes in constituent concentrations between the different time periods. The Wilcoxon test was used to test the null hypothesis that constituent concentrations collected in 1950/1951 were the same as constituent concentrations collected during 1999/2000. The null hypothesis of identical median values for each data set was rejected if the probability of obtaining identical medians by chance was less or equal to 0.05.

The Wilcoxon test is not valid for data sets with greater than 50 percent of the constituent concentrations below the MRL<sup>29</sup>. Consequently, the Wilcoxon test was not calculated for trace parameters such as antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, as well as phenolphthalein alkalinity, nitrite, ammonia, and total phosphorus. Highlights from these statistical tests are summarized in the groundwater quality section.