

## Ambient Groundwater Quality of the Gila Valley Sub-Basin: A 2004 Baseline Study – November 2009

### INTRODUCTION

A baseline groundwater quality study of the Gila Valley sub-basin, part of the Safford basin, was conducted in 2004 by the Arizona Department of Environmental Quality (ADEQ) Ambient Groundwater Monitoring Program. ADEQ conducted this monitoring pursuant to Arizona Revised Statutes §49-225 that calls for ongoing monitoring of waters of the state including its aquifers. This fact sheet is a synopsis of the ADEQ Open File Report OFR 09-12.<sup>1</sup>

The Safford basin is in eastern Arizona and is divided by the Arizona Department of Water Resources into three sub-basins: the San Simon, Gila Valley and San Carlos Valley. The Gila Valley sub-basin exhibits the greatest water resource development and is the focus of this report. The sub-basin encompasses approximately 1,642 square miles and includes the drainage of the Gila River from the Gila Box Riparian National Conservation Area down gradient to an arbitrary line five miles west of the community of Geronimo (Map 1). It also includes the drainage of the San Simon River down gradient of the railroad siding of Tanque to its confluence with the Gila River.<sup>2</sup>

Safford, Thatcher, Pima, Solomon and other smaller communities are located within the Gila Valley sub-basin where farming is the major industry. About 40,000 acres mostly along the Gila River are irrigated with surface water from the river and groundwater from shallow irrigation wells (Figure 1) which typically produce from 1,000 to over 2,000 gallons per minute.<sup>2</sup> The quantity of groundwater pumped is closely related to the quantity of surface water available as the total water used for irrigation is fairly consistent.

### GROUNDWATER CHARACTERISTICS

The Gila Valley sub-basin is part of a large, sediment-filled, trough-like depression typical of the Mexican Highland section of the Basin and Range physiographic province. Sediments in the sub-basin may be as much as 11,200 feet thick.<sup>2</sup> Basin fill is commonly divided into two units: younger alluvial fill and older alluvial fill that together likely function as a single



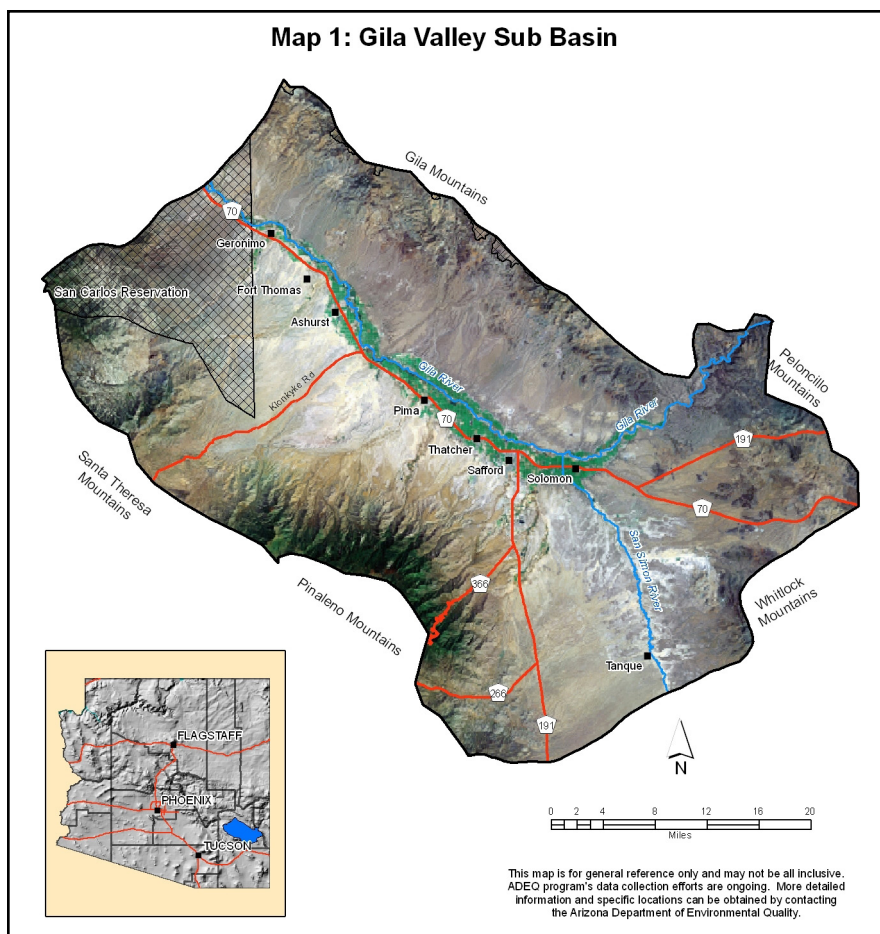
*Figure 1 – An irrigation well pumps water from younger alluvium that has been recharged by flow from the Gila River. Emptying into a ditch, the groundwater eventually irrigates a cotton field near the community of Geronimo, just upstream of the San Carlos Apache tribal lands.*

aquifer system.<sup>2</sup> These units are often separated by a thick, discontinuous blue clay layer though well logs sometimes reveal more complex interbedding with other clay, sand and gravel layers to form the demarcation.<sup>3</sup>

The younger alluvial fill of Holocene age is composed of Gila River sediments that occur in discontinuous lenticular beds consisting of clay and unconsolidated silt, sand, and gravel. This unit is rarely wider than four miles and is thickest near Safford where it averages 85 feet in depth and tapers to about 30 feet thick down gradient near Geronimo.<sup>2</sup> Most groundwater in the sub-basin is pumped from this unit.

Although the older alluvial fill is interfingered with numerous water bearing layers it can be divided into, in descending order, three general sub-units classified by lithologic and paleontologic characteristics: clay-silt, evaporite, and basal-conglomerate. The clay-silt

**Map 1: Gila Valley Sub Basin**



*Map 1 – Map of the Gila Valley sub-basin.*

sub-unit is lacustrine in origin and can be as much as 610 feet thick.<sup>2</sup> The evaporite sub-unit is composed of salt beds, gypsum, limestone, gypsiferous clay, and shale and is thickest near the basin axis. The basal-conglomerate sub-unit is composed of sand and gravel and extends throughout the sub-basin. The clay-silt sub-unit, at the top of the older alluvial unit, restricts vertical movement of groundwater in the underlying sub-units causing artesian conditions that result in flowing wells at ground surface.<sup>2</sup> Hard rock found in the surrounding mountains also yields small amounts of water from local aquifers.

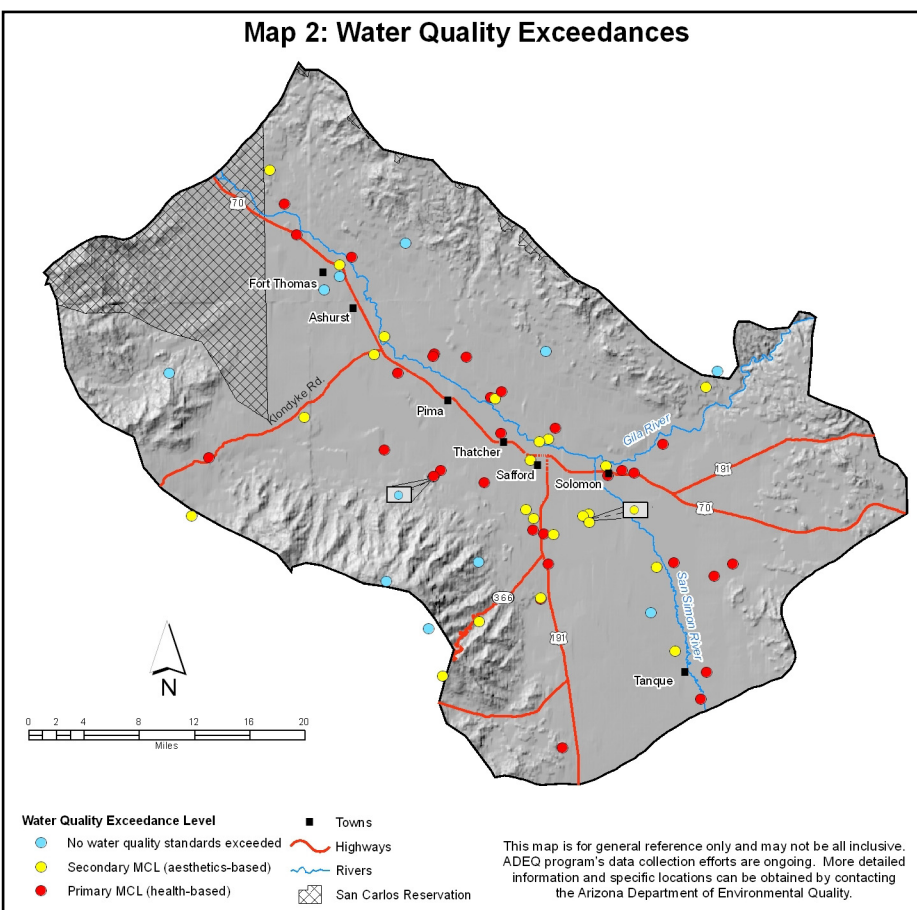
The primary source of recharge in the sub-basin is the Gila River; groundwater levels respond rapidly to increases in surface water flow. Significant amounts of mountain-front recharge from local precipitation occur in stream channels that have cut

into caliche-capped gravel zones along the Pinaleno and Gila Mountains. Other sources of recharge are percolation from agricultural irrigation and seepage from canals. Groundwater moves from the sub-basin's margins toward, and then parallel, to the Gila River as it flows to the northwest.<sup>2</sup>

## METHODS OF INVESTIGATION

To characterize regional groundwater quality in the Gila Valley sub-basin, 67 groundwater samples were collected from 53 wells and 14 springs that were randomly selected according to a stratified strategy designed to characterize both alluvial units. Many ADEQ requests to sample private wells were denied because of fears the data would influence water rights litigation associated with the Gila River adjudication; other wells were not sampled because they lacked proper sampling ports. Samples were collected for inorganic constituents (65), radon (30), radionuclides (20) and pesticides (4)

**Map 2: Water Quality Exceedances**



*Map 2 – Sample sites in the Gila Valley sub-basin are color-coded according to their water quality standard status.*



at selected sites. All sites were sampled for oxygen and hydrogen isotopes. Nine oxygen and hydrogen isotope samples were also collected from surface water sites and precipitation events to help determine groundwater recharge sources.

Sampling protocol followed the *ADEQ Quality Assurance Project Plan*. The effects of sampling equipment and procedures were not found to be significant based on seven quality assurance/quality control tests.<sup>4</sup>

## WATER QUALITY SAMPLING RESULTS

Groundwater sample results were compared with the Safe Drinking Water Act (SDWA) water quality standards. Public water systems must meet these enforceable, health-based, water quality standards, called Primary Maximum Contaminant Levels (MCLs), when supplying water to their customers. Primary MCLs are based on a daily lifetime (70 years) consumption of two liters of water.<sup>5</sup> Of the 65 sites sampled, 30 sites (46 percent) had concentrations of at least one constituent that exceeded a Primary MCL (Map 2). Constituents exceeding Primary MCLs included arsenic (21 sites), fluoride (20 sites), gross alpha (3 sites), nitrate (4 sites) and uranium (2 sites).

Groundwater sample results were also compared with SDWA water quality guidelines. Public water systems are encouraged to meet these unenforceable, aesthetics-based water quality guidelines, called Secondary MCLs, when supplying water to their customers. Water exceeding Secondary MCLs may be unpleasant to drink and/or create unwanted cosmetic or laundry effects but is not considered a health concern.<sup>5</sup> Of the 65 sites samples, 54 sites (83 percent) had concentrations of at least one constituent that exceeded a Secondary MCL water quality guideline (Map 2). Constituents above Secondary MCLs included chloride (29 sites), fluoride (35 sites), manganese (4 sites), pH (11 sites), sulfate (29 sites), and TDS (43 sites).

Of the 30 sites sampled for radon, none exceeded the proposed 4,000 picocuries per liter (pCi/L) standard that would apply if Arizona establishes an enhanced multimedia program to address the health risks from radon in indoor air. Nineteen (19) sites exceeded the proposed 300 pCi/L radon standard that would apply if Arizona doesn't develop a multimedia program. There were no positive detections of any of the 20 organochlorine compounds analyzed in the four pesticides samples.

## GROUNDWATER CHEMICAL COMPOSITION

Isotope results indicated that 18 sites appear to produce water from younger alluvium recharged by

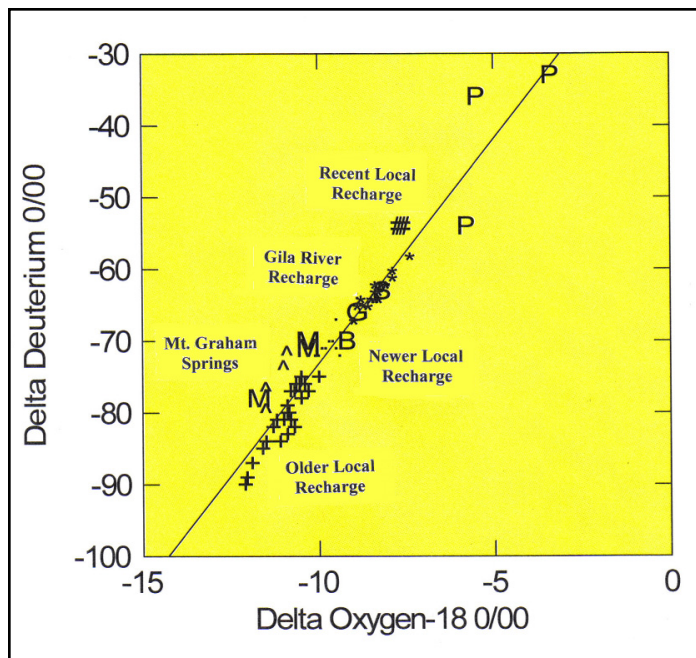


Figure 2 – Along the Local Meteoric Water Line (LMWL), starting from highest on the precipitation trajectory (upper right of graph), the following types of samples plot: precipitation (P), Gila River recharge (\*), San Simon River (S), Gila River (G), newer local recharge (.), Bonita Creek (B), and older local recharge (+). Slightly above the LMWL are recent local recharge (#), Mt. Graham springs (^) and creeks on Mt. Graham (M).

the Gila River while 47 sites produce water predominantly from older alluvium and/or hard rock recharged by local precipitation (Figure 2). The 47 sites recharged by local precipitation can be subdivided into two main groups:

- 29 “older” sites that plot lowest on the precipitation trajectory and consist mostly of deep wells with some having artesian flow (Figure 3) that appear to produce water from the evaporite and/or basal-conglomerate sub-unit and,
- 12 “newer” sites that plot slightly higher on the precipitation trajectory and appear to consist mostly of shallow wells that produce water from the clay-silt sub-unit.

The “older” and “newer” subgroups were statistically demarcated (cluster analysis test, F-ratio = 83). The predominant cation at “older” sample sites were sodium-type waters and the predominant cation at “newer” sample sites were calcium-type waters, except for five sample sites in which the pattern was reversed (Figure 4). These water chemistry anomalies illustrate the hydrologic complexity of the older alluvium and that some wells and springs likely produce a mixture of water from different sub-units.

There are also two other local precipitation subgroups. The “Mt. Graham” sites consist of four



Figure 3 – Artesian flow from 1,000 foot deep Kimball Well has the high arsenic and fluoride concentrations that are characteristic of water from the evaporate/basal-conglomerate sub-units in the older alluvium.

springs that flow from hard rock in the high altitude Pinaleno Mountains. These sites plot above the precipitation trajectory (Figure 2) and appear to produce water mainly from winter precipitation. The two “recent” sites also plot above the precipitation trajectory and are the most enriched groundwater sites sampled in the sub-basin (Figure 2). Both sites are shallow alluvial wells located near ephemeral washes far upgradient of the Gila River and appear to produce water predominantly recharged from summer monsoon precipitation.

Groundwater chemistry also varied by elevation of the sample sites; the highest sites in the Pinaleno Mountains had a calcium-bicarbonate composition. Sites lower in the Pinaleno Mountains and in the Gila Mountains had a mixed-bicarbonate composition. Sites in the Gila Valley predominantly had a sodium-mixed or sodium-chloride composition (Figure 4).

Most groundwater was *slightly alkaline* based on pH-field values, *fresh* or *slightly saline* based on TDS concentrations, and had similar frequencies of *soft*, *moderately hard*, *hard* and *very hard* water. Generally, nitrate concentrations were below 3 milligrams per Liter and, based on a common classification system, did not appear to be definitively influenced by human activities, except for some sites along the Gila River.<sup>5</sup>

Trace elements such as antimony, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium and zinc were rarely, if ever, detected. Of trace elements, only

arsenic, boron, and fluoride were detected at more than 20 percent of the sites.

## GROUNDWATER PATTERNS

Many statistically significant groundwater quality patterns were found between younger alluvium recharged by the Gila River and older alluvium and/or hard rock recharged by local precipitation. TDS (Figure 5), major ions, nitrate (Figure 6), and boron concentrations were higher in younger alluvium than older alluvium and/or hard rock; the opposite pattern occurred with pH levels (Kruskal-Wallis test,  $p \leq 0.05$ ). Despite the higher salinity in the younger alluvium, there were no significant patterns involving arsenic and fluoride, the two most frequent constituents exceeding Primary MCLs in the sub-basin.

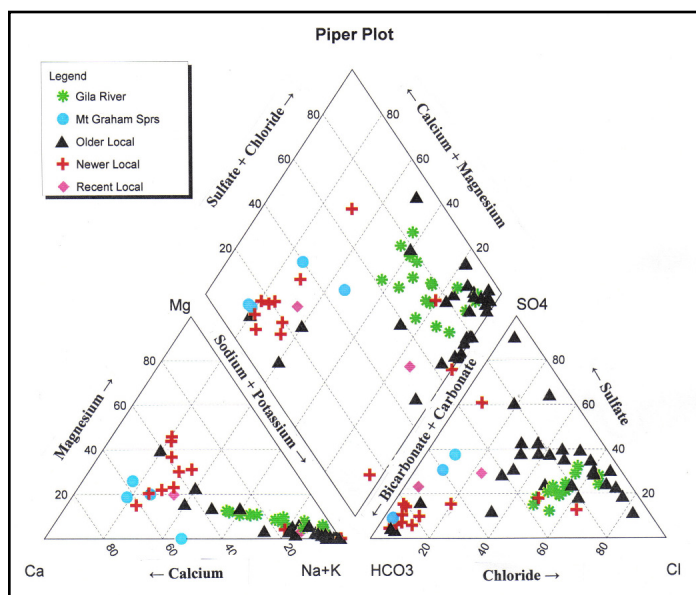


Figure 4 – Water chemistry often varies by recharge source. Sodium is the dominant cation for samples of recharge from the Gila River and from “older” local precipitation. Samples of “newer” local precipitation recharge are typically of calcium or mixed cation composition.

Additional statistical tests were conducted among the various isotopic subgroups with the most important being the comparison between “older” and “newer” local precipitation sites that produce water from the older alluvium. Older local precipitation sites had significantly higher temperature, TDS, sodium, potassium, chloride, sulfate, arsenic, boron and fluoride (Figure 7) concentrations than newer local precipitation sites (Kruskal-Wallis test,  $p \leq 0.05$ ).

## GROUNDWATER CHANGES OVER TIME

In 1995, ADEQ conducted an extensive groundwater quality study of the Upper Gila watershed that sampled 81 targeted sites within the Gila Valley sub-basin.<sup>7</sup> Despite different sampling strategies, the frequency of

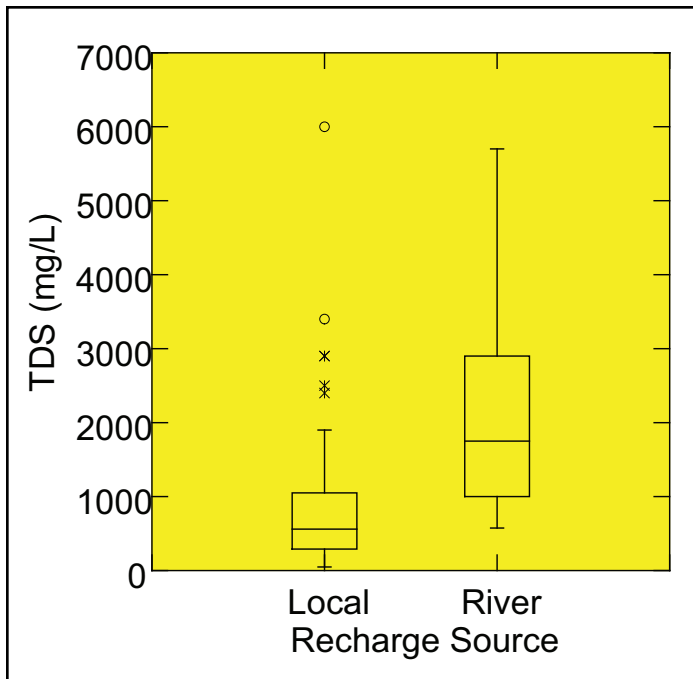


Figure 5 – This box plot illustrates that sample sites of groundwater derived from Gila River recharge have significantly higher TDS concentrations than sample sites derived from recharge from local sources (Kruskal-Wallis test,  $p \leq 0.01$ ). The box plots central vertical line marks the median of the data, the edges of the box mark the first and third quartiles, and the horizontal lines connect all points outside the box with the exception of mild and extreme outliers which are marked respectively by asterisks and open circles.

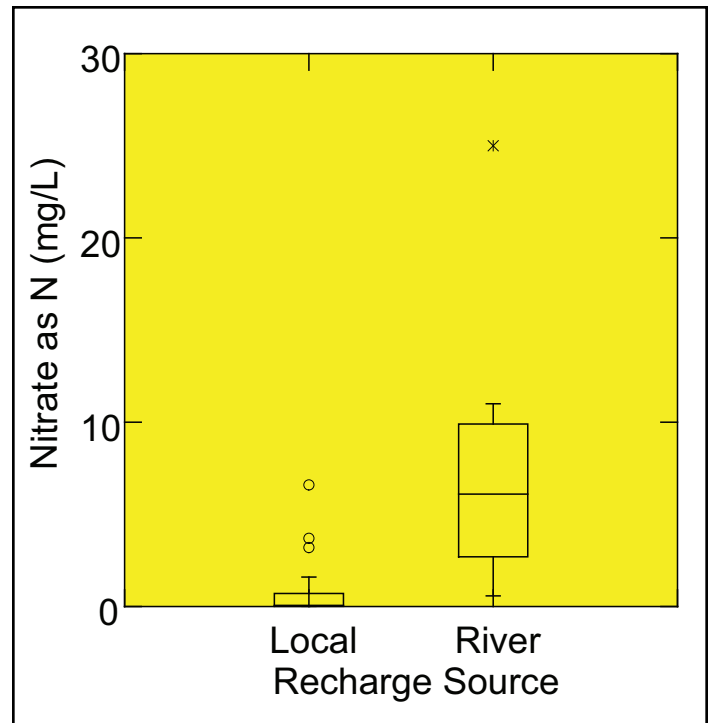


Figure 6 - Sample sites of recharge from the Gila River had significantly higher nitrate concentrations than sample sites of recharge from local precipitation sources (Kruskal-Wallis test,  $p \leq 0.01$ ). The elevated nitrate concentrations found in the younger alluvium likely result from both septic system effluent and nitrogen fertilizer applications.

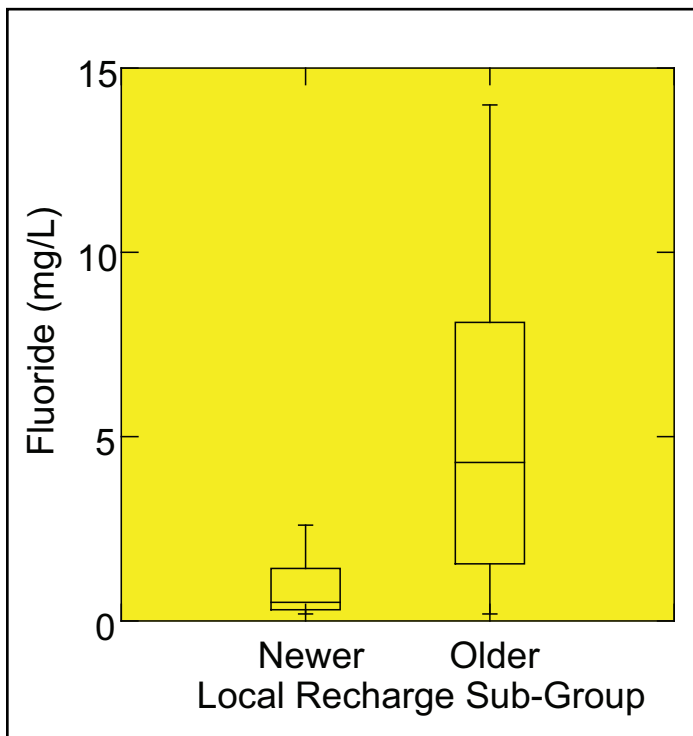


Figure 7 – Sample sites of “older” local precipitation recharge sites have significantly higher fluoride concentrations than sample sites derived from “newer” local precipitation recharge sites (Kruskal-Wallis with Tukey test,  $p \leq 0.05$ ). Elevated fluoride concentrations commonly occur in confined aquifers throughout southeastern Arizona.

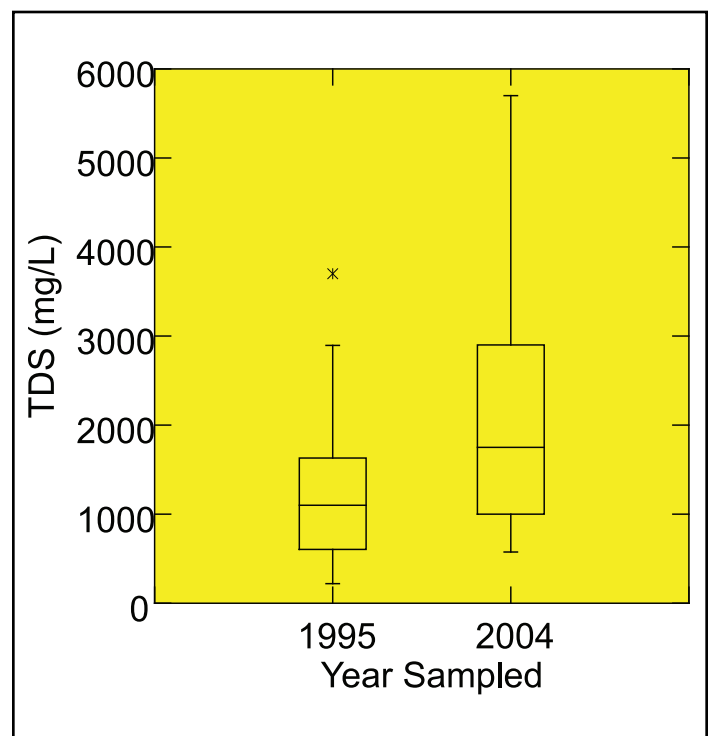


Figure 8 – Sites sampled in 1995 of groundwater derived from Gila River recharge in the younger alluvium have significantly lower TDS concentrations than sites sampled in 2004 (Mann-Whitney test,  $p \leq 0.01$ ). This pattern is likely influenced by saline water inputs from upward leakages and irrigation recharge.



water quality exceedances for each ADEQ study was remarkably similar. Primary MCLs were exceeded at 49 percent of the sites sampled in 1995 and at 46 percent of sites sampled in 2004. Secondary MCLs were exceeded at 75 percent of sites sampled in 1995 and at 83 percent of sites sampled in 2004. Specific constituents with MCLs such as arsenic (using the current 0.01 milligram per Liter standard in evaluating both studies), nitrate, gross alpha, TDS, chloride, sulfate and pH-field also had comparable frequency exceedances. Fluoride had alike frequencies with Secondary MCL exceedances but the 1995 Primary MCL frequency (15 percent) was lower than the 2004 frequency (31 percent).

Examination of the 1995 data revealed deficiencies with sampling protocol and data validation but the data are still considered suitable for making some types of general groundwater quality comparisons between the studies. Although there were 13 duplicate sites for both studies, QA/QC correlations indicated that samples were mismatched to two sites in 1995. Statistical analysis of the eleven remaining duplicate sites found that pH-lab, chloride and arsenic increased significantly between 1995 and 2004 (Wilcoxon test,  $p \leq 0.05$ ).

Another time-trend comparison was made by classifying the 1995 sample sites by alluvial unit using well characteristics. Further sub-classifying older alluvium without actual isotope data was not possible and no time trend analyses were done with data from this alluvial unit. Using the data from the younger alluvium, 49 sites sampled in 1995 were compared with 18 sites sampled in 2004. Concentrations of TDS (Figure 8), sodium, chloride, sulfate and pH-lab increased significantly between 1995 and 2004 (Mann-Whitney test,  $p \leq 0.05$ ).

Additional groundwater quality comparisons were made with the 1995 sample sites between younger alluvium recharged by the Gila River and older alluvium and/or hard rock recharged by local precipitation. The statistically significant groundwater quality patterns found were almost identical to those revealed using the 2004 data. TDS, major ions, nitrate, and boron concentrations were higher in younger alluvium than older alluvium and/or hard rock; the opposite pattern occurred with temperature and pH levels (Kruskal-Wallis test,  $p \leq 0.05$ ).

## CONCLUSIONS

The Gila River is an important influence on groundwater quality in the Gila Valley sub-basin. Salinity in the Gila River seasonally fluctuates, varying in an

inverse, nearly linear fashion versus flow rate.<sup>3</sup> In 2002, the river's average TDS concentration increased from 594 mg/L at Solomon located at the head of the Gila Valley to 2,150 mg/L at Calva located 62.6 river miles away just down gradient from the sub-basin.<sup>8</sup> While TDS concentrations at Solomon aren't highly variable, those at Calva can fluctuate from several hundred mg/L when flood events dilute the salinity during high flows of the Gila River to many thousand mg/L during low flows of the Gila River.

River flow, especially during flood stages, recharges the younger alluvium with fresh water that usually has no detectable amounts of nitrate.<sup>8</sup> However much of the Gila River is diverted for irrigation use above Solomon (Figure 9). The excess water applied for irrigation that is unused by the crops recharges the



Figure 9 – Carrying a heavy silt load from summer rains, the Gila River flows from the Gila Box Riparian National Conservation area toward the town of Solomon at the head of the Gila Valley. Mt Graham is in the distance.

groundwater carrying a large salt load as well as nitrogen from fertilizer applications. The irrigation recharge contributes to the elevated TDS and nitrate concentrations found in the younger alluvium. Nitrate concentrations in irrigation recharge can be reduced by utilizing best management practices while salt loading can be decreased by changing irrigation methods to reduce the volume of water, and the associated salt, applied to farmland.

While the salinity from irrigation recharge contributes to the significant increase in TDS concentrations found in the younger alluvium between the two ADEQ studies, recent research suggests it's not the most important factor. Another major natural source, determined using isotope analysis, is upward leakages of saline groundwater along faults and through abandoned irrigation and oil exploration wells drilled prior to the 1930s. This deep groundwater, impacted by

evaporite deposits and under artesian pressure, is particularly prevalent in the lower portion of the sub-basin.<sup>9</sup>

Effluent from faulty septic systems and waste associated with livestock in corrals adjacent to sample sites such as windmills are probably responsible for the occasionally elevated nitrate concentrations not associated with farming.

Other water quality exceedances in the Gila Valley sub-basin appear to be the result of natural sources. Elevated gross alpha and uranium concentrations were usually located in or near areas of granite, or alluvial areas of eroded granite, a common pattern for these constituents.<sup>10</sup> Elevated fluoride and arsenic concentrations are generally associated with an oxidizing environment, an abundance of trace elements in the sediments, and the long residence time characteristic of waters in chemically closed systems such as the evaporate and basal conglomerate sub-units.<sup>11</sup>

Fluoride water quality exceedances occur both in the older and younger alluvium. Fluoride concentrations above 5 mg/L are controlled by calcium through precipitation or dissolution of the mineral fluorite. In a chemically closed hydrologic system, such as can be found in the older alluvium, calcium is removed from solution by precipitation of calcium carbonate and the formation of smectite clays. High concentrations of dissolved fluoride may occur in groundwater depleted in calcium if a source of fluoride ions is available for dissolution.<sup>11</sup> Exchange of sorption-desorption reactions are an important control for lower (< 5 mg/L) fluoride concentrations. In recharge areas, weathering of rocks releases fluoride ions into solution. As pH levels increase down gradient, more hydroxyl ions may exchange for fluoride ions, thereby increasing the fluoride in solution.<sup>11</sup> Elevated fluoride concentrations in the younger alluvium may result from both upward leakages from the older alluvium and from the high average fluoride concentration (1.2 mg/L) found in the Gila River.<sup>8</sup>

Arsenic concentrations may be influenced by similar reactions as fluoride, including exchange on clays or with hydroxyl ions. Other factors such as aquifer residence time, an oxidizing environment, and lithology likely effect arsenic concentrations.<sup>11</sup>

## **PUBLIC WATER PLANNING RECOMMENDATIONS**

An effective strategy for developing public water supplies in the Gila Valley sub-basin, from a water quality perspective, appears to be drilling shallow wells in the older alluvium along the mountain front up from the Gila River. Such wells generally have

lower TDS, arsenic, and fluoride concentrations compared to wells drilled deeper into the older alluvium that penetrate the evaporite and/or basal conglomerate sub-units. Wells in the older alluvium also generally have lower TDS and nitrate concentrations than are commonly found in the younger alluvium.

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Maps by Jean Ann Rodine

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