Arizona Department of Environmental Quality

FINAL DE-LIST REPORT FOR TOTAL ARSENIC

Reach 15060203-022C

East Verde River –American Gulch to the Verde River

June 9, 2015

Executive Summary

In the 2006-08 305(b) report, reach 15060203-22C of the East Verde River (confluence of American Gulch to the Verde River confluence) was placed by ADEQ on the state of Arizona's 303(d) Impaired Waters List for total arsenic. Based on the best available data collected within the assessment time frame, it continued to be assessed as impaired for arsenic in the 2010 and 2012-14 reports. This listing was based on exceedances that occurred at monitoring point VREVR002.62 (East Verde River near Childs, AZ). Personnel from the TMDL Unit of ADEQ collected additional water samples at multiple monitoring points along the impaired reach outside of the Mazatzal Wilderness Area at various hydrologic conditions, ranging from base flow to flood stage conditions. Personnel from the USGS Tempe office collected monthly samples for a little over a year from monitoring point VREVR002.62 which is located within the Mazatzal Wilderness Area. Analysis of the total arsenic was performed by laboratories that had the ability to analyze to a detection level that was below the strictest applicable total arsenic standard for the drinking water source designated use of 10 µg/L. Data collected at the various sample points since 2009 show further exceedances of the total arsenic standard are still occurring. All of the arsenic detections are once again from samples collected at the VREVR002.62 monitoring site. A review of the available ground and surface water data indicates that surface water in the lower reaches of the East Verde River is being impacted by the mixing of groundwater through upwelling of the local aquifer. Groundwater in the local aquifer has been shown to have high arsenic levels from exposure to a local geologic feature known as the Verde Formation. Reach 15060203-22C is recommended for de-listing for total arsenic impairment based on the documented levels of background arsenic present in the environment. The purpose of this report is to present the rationale for de-listing.

Physiographic Setting

The headwaters for the East Verde are located at an elevation of approximately 7200 feet along the southern face of the Mogollon Rim. The channel drains in a southerly direction to the confluence with Ellison Creek. Below the confluence of Ellison, the East Verde begins to trend in a southwesterly direction to its confluence with the Verde River. The mouth of the East Verde is 3.4 miles downstream of the confluence of the Verde River and Fossil Creek at an elevation of approximately 2480 feet. The entire length of the drainage is contained within the Central Highlands physiographic province, and the majority of the watershed is managed by the Tonto National Forest.

The watershed is located in Gila County which has a population of approximately 51,000. The town of Payson is the largest metropolitan area in the boundaries of the project with a population of about 16,000. Although some mining does occur in the watershed, it makes up a very small portion of the county's industry. Occasional small tailings piles indicate that small mining operations existed in the past. Cattle ranching and logging are the two biggest non-point impacts occurring in the watershed. Outdoor activities such as hunting, fishing, camping, etc., are quite popular, and the National Forest Service maintains camping sites and hiking trails to allow for better access to some of the more remote areas of the watershed.

Geology

Approximately 9 to 10 million years ago the Verde Valley formed along a geologic fault line that is today referred to as the Verde Fault. Over time, land to the northeast of the Verde Fault began to subside as the area in and around the Black Hills rose upward, producing the Verde Valley. Geologic features produced by the subsidence at the downstream portion of the basin formed a natural dam that over time began to collect water from the Verde River and other smaller tributaries. This fault block basin produced an ancient lake that was fairly large in surface area at times, but was also relatively shallow during its existence. The sediments that were deposited over millions of years into Lake Verde produced the Verde Alluvium Formation. This formation consists of numerous layers of mainly limestone and red mudstone. Conglomerates, evaporates, sandstones, and volcanic materials have also been identified within the formation. Many of the materials have been interbedded and layered on top of one another. Geologists believe this is due to the changes in climate which over time led to a series of shrinking and expansions of the lake. Areas that had been eroding were over time covered with water, leading to erosion in differing areas of the basin. The converse is also true; as the lake contracted, submerged areas were exposed to the forces of erosion. Geologists have shown that erosion of the Supai Formation contributed heavily to the composition of the Verde Formation. The Supai Formation is a red-colored sandstone feature that gives the Oak Creek Canyon area its famous reddish hues. It is typically overlain with the cross-bedded desert dune features of the Coconino Sandstone Formation. Analysis of the Supai Formation has shown that it contains high levels of arsenopyrite (FeAsS). Verde Lake existed for about 7 million years. Fossil records in the youngest deposits indicate that the lake ultimately breached the geologic feature damming the basin approximately 2 to 2.5 million years ago. The presence of evaporites and gypsum deposits indicate that the last portions of the lake were located near the Camp Verde area. The Verde formation covers an area of approximately 300 square miles and in some parts is as thick as 3,000 feet. Figure 1 illustrates the extent of the formation and also shows the highest known deposits that sit atop House Mountain.

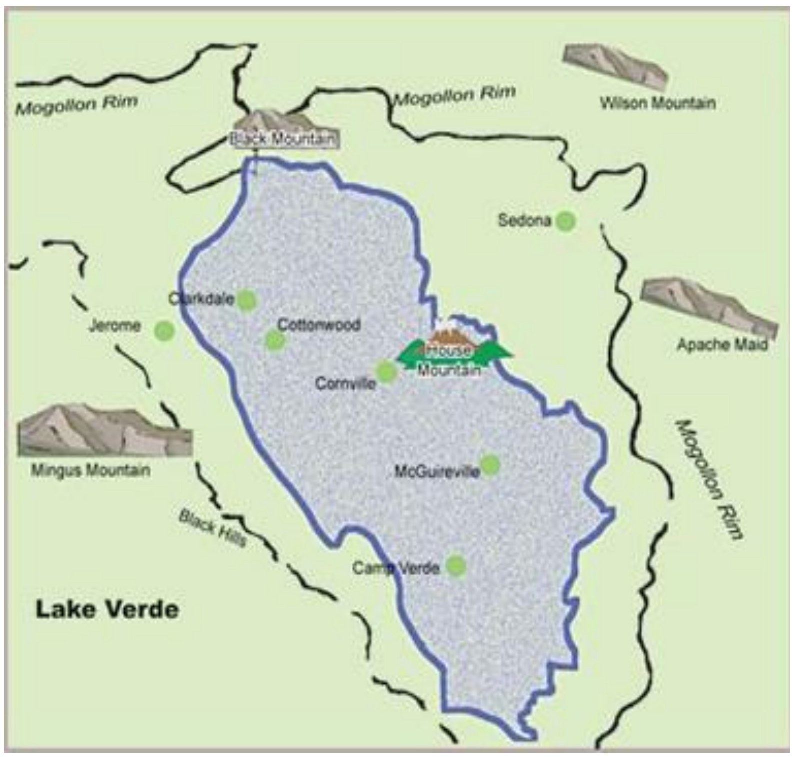


Figure 1: approximate extent of the Verde Formation. Used with permission of Dan Engler, editor, The Verde Independent.

Hydrology

The East Verde River watershed is a sub-watershed of the Verde River. It has a drainage area of 336 square miles and runs perennially along most reaches of the upper to middle sections of its channel. Pine Creek, Ellison Creek and Webber Creek are sub-watersheds of the East Verde River which have spatially-interrupted perennial reaches along the course of their channels. USGS discharge data from gauge # 09507980 (the location of sample site VREVR002.62) near the mouth of the East Verde River does indicate that flows of less than 1.0 cubic feet per second (cfs) were recorded on some site visits, usually during the hottest, driest times of the year. The average daily flow data collected at this gauge show that typically during June and July there are stretches of sometimes several weeks where there are no flow conditions, or a daily average flow of 0 cfs. This would seem to indicate that the flow through the East Verde canyon below the confluence of Pine Creek in the lower reaches of its channel may more correctly be described as intermittent based on the bedrock depth and the thickness of alluvial deposition. The two largest sub-watersheds of the East Verde are Pine Creek (watershed area 48 square miles) and Ellison Creek (watershed area 42 square miles).

The Tonto National Forest has recently completed inventory work on springs located within their boundaries, and the data they have provided indicates that 52 springs have been identified within the East Verde watershed. Some springs vary in discharge quantity based on the rainfall conditions occurring within the watershed, while others can discharge at a fairly consistent rate even in dry weather conditions. Personnel of the Tonto Natural Bridge State Park have indicated that the unnamed spring located south of the parking lot area has discharged at about the same rate for many years. A visit to the park to sample the creek below the natural bridge structure allowed a discharge measurement of the unnamed spring which produced a gauged instantaneous flow rate of approximately 78 gallons per minute, or about 0.17 cfs. Because of the ongoing dry conditions within the watershed, other spring sites have been reduced to discharges of almost zero.

SRP currently discharges between 24 and 33 cfs to the East Verde River about two miles downstream of the headwaters near an area known as Washington Park. This water is piped over the rim from the C.C. Cragin Reservoir in the Little Colorado River Watershed, and runs spring, summer and fall. Flows from the reservoir normally continue until the winter snows cut off access to both the lake and the pipeline. The pipeline,which runs about seventeen miles from source to discharge point, and the pumping system were completed in 1965 and began moving water from what was then called the Blue Ridge Reservoir on East Clear Creek into the headwaters of the East Verde River. The original purpose of the pipeline was to replace water that Phelps Dodge was taking from outside of the East Verde watershed. Water was being withdrawn from the Black River, a tributary of the Salt River in eastern Arizona. Because SRP owned the water rights to the Black River, the pumped reservoir water replaced the water being withdrawn. The city of Payson is currently building a pipeline to capture a portion of the water from the reservoir that will be used to augment their drinking water supply which at present comes from pumped groundwater. Water quality data for the reservoir indicates that total arsenic levels are typically very low. A review of the available data showed that the highest total arsenic level collected at the three monitoring sites around the lake was 2 µg/L. The majority of samples indicated non-detect for total arsenic.

Land Use / Ownership

Land ownership in the East Verde River TMDL Project area is mainly federal with some private land and a very small parcel of State Trust Land located near the Payson airport. The US Forest Service manages the federal land through the Tonto National Forest offices. Private land ownership makes up a very small portion of the project area, with the 2 largest parcels of private land falling within the city of Payson and the city of Pine boundaries. There is also a small piece of land south of the town of Payson owned and managed by the Tonto Apache Indian Tribe. This parcel is small, but it does sit on the edge of the TMDL Project area. The lower reaches of the East Verde River run through the Mazatzal Wilderness Area which is managed by the USFS, and is inaccessible by vehicle. The map in Figure 2 illustrates the areas of land ownership within the East Verde watershed, and also shows the location of the impaired reach and those tributaries that were monitored during the course of the project. It also illustrates the extent of the Mazatzal Wilderness area where a good portion of the lower reaches of the East Verde River are located.

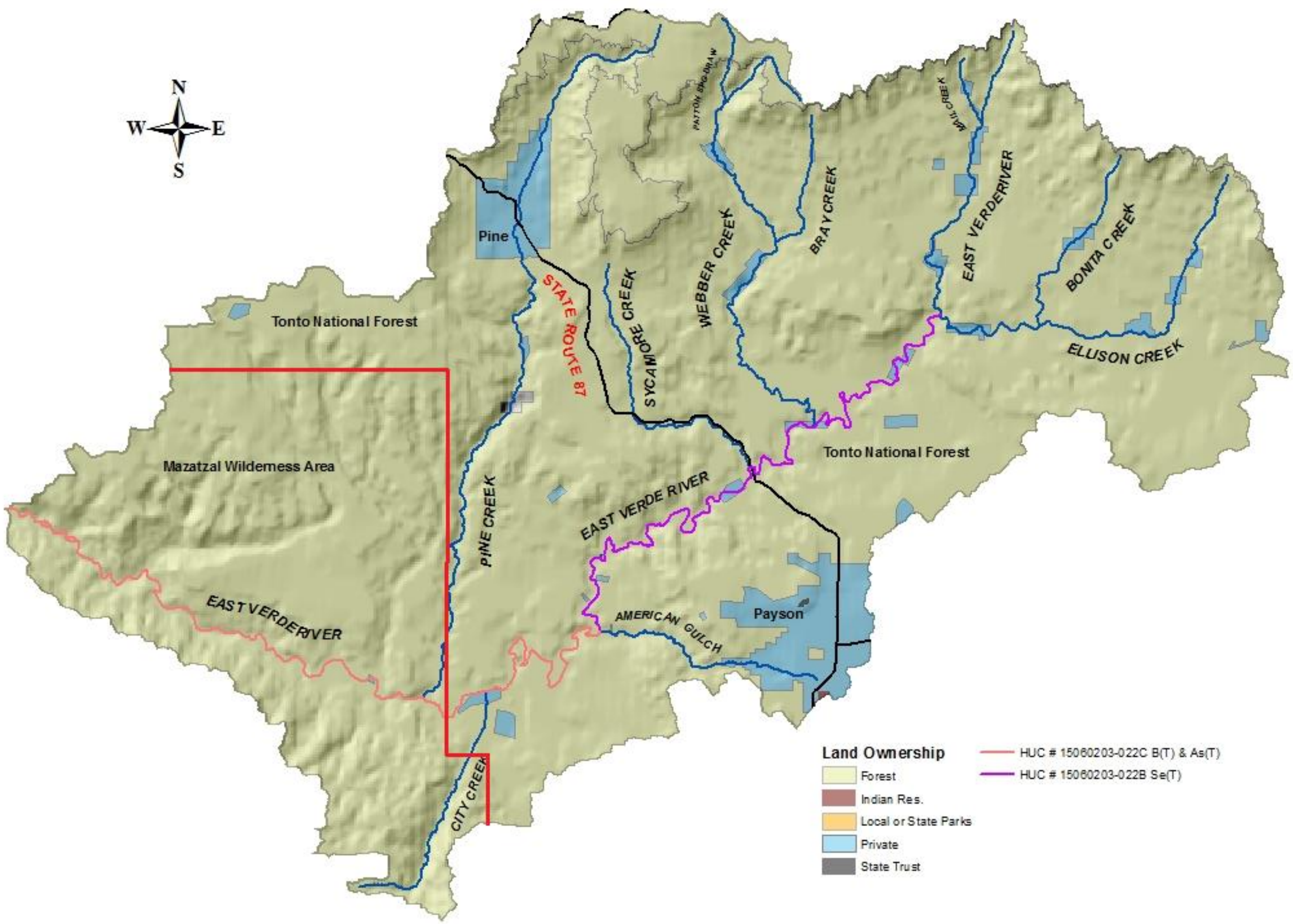
Listing

Water quality standards for the state of Arizona (Arizona Administrative Code Title 18-Chapter 11) have been developed in response to the mandates of the Clean Water Act. These standards define the goals and thresholds for water quality pollution issues and prescribe the criteria necessary to protect the various designated uses ascribed to particular water bodies.

The Arizona Department of Environmental Quality is required under the Clean Water Act Section 305(B) to issue a biennial assessment of the condition and quality of the state's waters. The state also maintains a Section 303(d) list of waters that are not meeting their designated uses. Assessments are based upon all available, credible, and scientifically defensible data collected by ADEQ or received from participating agencies and stake-holder groups.

For the 2006-08 assessment period, based on monitoring data collected between May, 2000 and August, 2004, Reach 15060203-022C (East Verde River –American Gulch to the Verde River) was listed as impaired for total arsenic due to exceedances in 12 of 22 samples collected at VREVR002.62. Figure 2 shows the reach of the East Verde River that is listed as impaired for total arsenic. The reach was identified as water-quality limited for the Domestic Water Source designated use which at the time had a standard of 50 µg/L, and the reach was placed on the State's 303(d) list. It remained on the 2010 and 2012-14 303(d) lists based on the available water quality data. During the last review of Article 1 of Arizona's Water Quality Standards for Surface Waters, the total arsenic criteria for several of the designated uses were revised, while a few remained unchanged. The Domestic Water Source designated use was lowered from 50 µg/L to 10 µg/L. The Fish Consumption use was changed from 1450 µg/L to 80 µg/L. Full Body Contact was revised downward from 50 µg/L to 30 µg/L and the Partial Body Contact designated use dropped from 420 µg/L to 280 µg/L. Both Agricultural Irrigation (2,000 µg/L) and Agricultural Livestock (200 µg/L) remain unchanged.

The listing was based on exceedances that occurred at monitoring site VREVR002.62, located within the Mazatzal Wilderness Area. There are currently four other monitoring sites that are located on this particular reach which have sample results for total arsenic. All are located upstream and outside of the Mazatzal Wilderness Area. No other monitoring site on this reach of the East Verde River produced sample results that exceeded the most stringent applicable standard. Due to the remoteness and difficulty accessing monitoring site VREVR002.62, the sample collection at this site has always been done by personnel of the USGS, who fly in by helicopter. This remoteness has also limited the ability to sample upstream of VREVR002.62, leaving a stretch of the river approximately 13.5 miles in length within the wilderness area that has no available water quality data.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WEBBER CREEK
BRAY CREEK
EAST VERDERIVER
BONITA CREEK
ELLISON CREEK
Mazatzal Wilderness Area
PINE CREEK
EAST VERDE RIVER
Tonto National Forest
EAST VERDERIVER
AMERICAN GULCH
Payson
CITY CREEK
Land Ownership
Forest
Indian Res.
Local or State Parks
Private
State Trust
HUC # 15060203-022C B(T) & As(T)
HUC # 15060203-022B Se(T)

Figure 2

Designated Uses

Arizona applies designated uses to waterways in the state to serve as the foundation for applying numeric water quality standards. Designated uses may be broadly grouped into human health uses, fish and wildlife uses, and agricultural uses. Parameter standards are then developed based on existing research on toxicity and deleterious effects for each combination of parameter and designated use. Designated uses in Arizona include the following:

- Aquatic and Wildlife uses, cold water (above 5000 feet elevation) – acute and chronic (A&Wc)
- Aquatic and Wildlife uses, warm water (below 5000 feet) – acute and chronic (A&Ww)
- Aquatic and Wildlife uses, ephemeral (A&We)
- Aquatic and Wildlife uses, effluent dependent (A&Wedw)
- Full Body Contact (FBC)
- Partial Body Contact (PBC)
- Domestic Water Source (DWS)
- Agricultural Irrigation (AgI)
- Agricultural Livestock Watering (AgL)
- Fish Consumption (FC)

Any number of these may be combined to adequately and reasonably cover the uses Arizona waters may be put to, excepting the mutually exclusive pairings that might result (e.g., A&Ww and A&Wc would not be found together, nor would FBC and PBC). Typically, any defined Arizona stream reach might have from three to six uses associated with it. Each use has its own set of numeric water quality thresholds or standards associated with it. Dependent upon the parameter, standards may be more or less strict in certain uses than in others, and the limiting use can vary from constituent to constituent based upon the toxicity and natural distribution, among other factors, of the element in question. Designated uses for 15060203-022C include A&Ww, FBC, DWS, FC, AgI, and AgL. The limiting use for total arsenic is the DWS use. DWS is also the use of concern for the field investigation on Reach 15060203-022C.

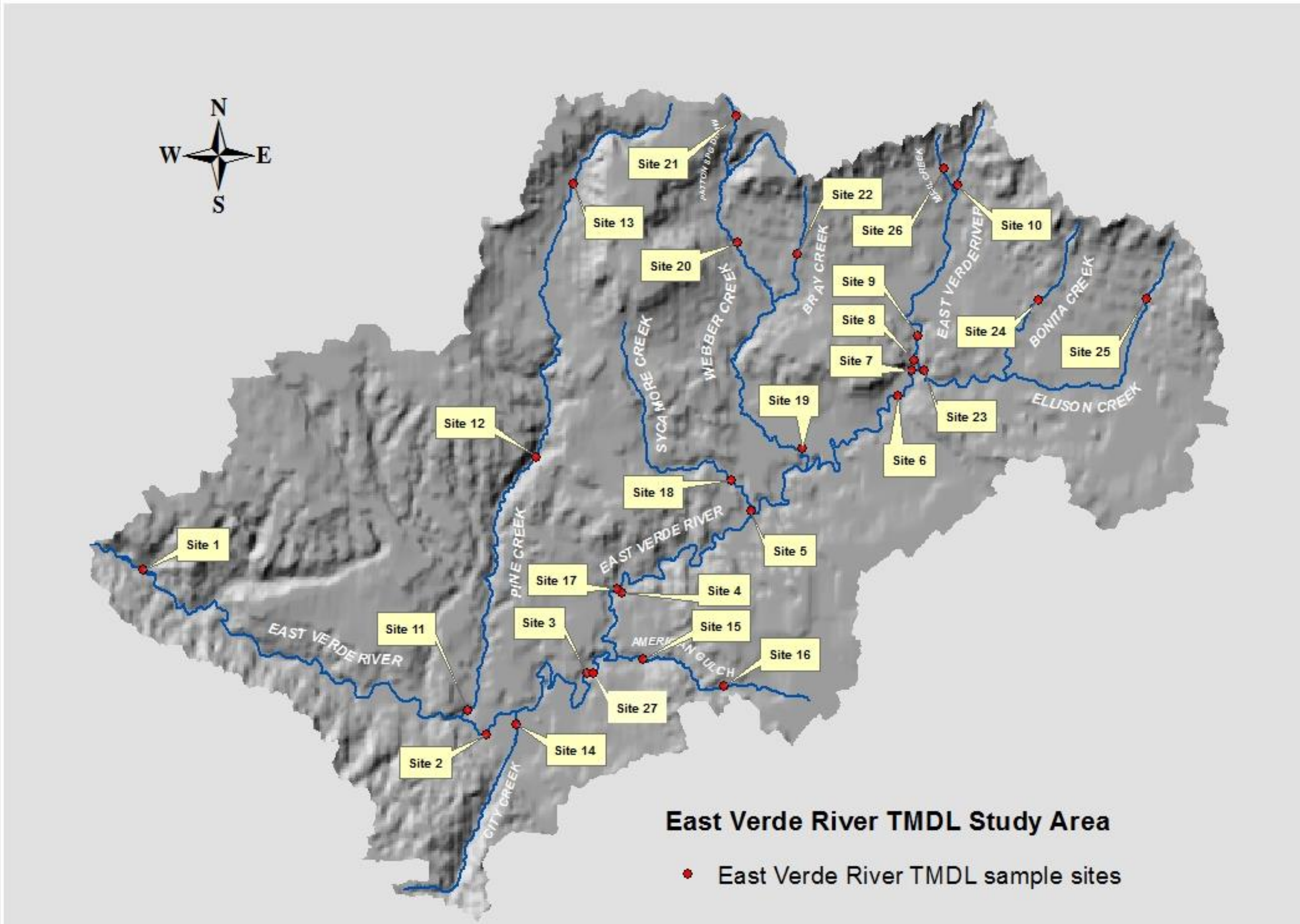
Arsenic

The chemical element arsenic is typically found in many minerals, and also as a pure elemental crystal. Chemical elements fall within three classes: metals, nonmetals, and metalloids. Arsenic is defined as a metalloid, which means that it has properties found somewhere between those of metals and nonmetals. Most soils contain about one to ten parts per million of arsenic. Arsenic levels in the ocean are usually much lower, averaging about 1.6 parts per billion. Mineral forms of arsenic usually occur in combination with sulfur and metals such as iron, nickel, and cobalt. Minor arsenic minerals are known to exist, along with various organic forms. One aspect of organic arsenic is that it is not toxic when ingested in the organic chemically-bound form, even in high concentrations that would be toxic in the dissolved un-bound form. Inorganic forms of arsenic are considered especially toxic to living organisms, although there are some species of bacteria found in oxygen-poor or reducing environments that are able to use arsenic compounds as respiratory metabolites. Arsenate and arsenite salts, which are formed through oxidation of arsenic, are considered to be the most toxic forms of arsenic. The presence of arsenic in groundwater supplies is a serious problem in various parts of the world. It has been estimated that in the Bengal Basin of India alone there are around 57 million people utilizing aquifers contaminated with arsenic above the 10 parts per billion standard established by the World Health Organization.

The most stringent applicable Arizona water quality standard for total arsenic exceedances is 10 µg/L for the DWS designated use. The standard for total arsenic is slightly higher for the Full Body Contact designated use at 30 µg/L. The Fish Consumption designated use standard is 80 µg/L. The Partial Body Contact designated use standard is just under 10 times the FBC use at 280 µg/L. The Agricultural Livestock use standard has been set at 200 µg/L, with the Agricultural Irrigation use established at 2,000 µg/L. All Aquatic and Wildlife designated uses have standards for dissolved arsenic only, as this is the biologically available and most toxic form of arsenic. Of the 13 sample results collected most recently by the USGS at VREVR002.62, 11 exceeded the DWS standard and 4 exceeded the FBC standard

Sampling History

The listing of the impaired reach in Arizona's 2006-08 305(b) report was based solely on samples that were collected at site VREVR002.62 (East Verde River near Childs, AZ; USGS gauge 09507980). Between May of 2000 and August of 2004, 22 sampling events took place. Analysis for total arsenic resulted in twelve exceedances of the DWS and FBC designated uses. At that time both uses had an established standard of 50 µg/L. Five exceedances of the AgL use (200 µg/L) also were observed. ADEQ's TMDL monitoring of the reach for total arsenic impairment began in December of 2009. Monitoring sites on the East Verde River were sampled on and above the impaired reach, as well as sites within the sub-basins that make up the overall East Verde River basin. In February of 2013 an auto-sampler was installed at site VREVR023.39 (East Verde River above Forest Service Road 502) in order to collect storm water samples. This site is near the top of the impaired reach, and is located approximately 1.63 miles below the confluence of American Gulch at a bedrock outcrop. Figure 3 indicates the location of the sample sites within the East Verde watershed, and Table 1 provides the corresponding site ID, site description, and map coordinates for each site. Sample sites located within the Mazatzal Wilderness Area are high-lighted in red. Sample collection at the USGS gauge site (VREVR002.62) was conducted by the personnel from the USGS office in Tempe. The gauge is cooperatively funded by SRP and is calibrated on a monthly basis. It was on these trips to calibrate the gauge that the samples were collected. No field data other than discharge was documented. It was also stipulated that samples could only be taken when there was continuous stream flow present in the channel. Monitoring of the established sampling sites within the East Verde watershed was carried out with the intent to gather data that would represent any seasonal variations in water quality. Sampling of storm events that typically occur in the winter or summer was also part of the monitoring regime, in order to collect samples of storm water flood stage events.



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Site 26
Site 27
EAST VERDE RIVER
PINE CREEK
CITY CREEK
SYCAMORE CREEK
WEBBER CREEK
BRAY CREEK
BONITA CREEK
ELLISON CREEK
AMERICAN GULCH
East Verde River TMDL Study Area
East Verde River TMDL sample sites

Figure 3

Table 1 East Verde TMDL sample site information

Site #	Site Description	Site ID	Latitude	Longitude
1	East Verde River at USGS gauge # 09507980	VREVR002.62	34 16 35	111 38 20
2	East Verde River above the wilderness area boundary	VREVR016.28	34 12 55.1	111 28 47.5
3	East Verde River below the confluence with American Gulch	VREVR023.23	34 14 17.8	111 26 01.3
4	East Verde River above the confluence with American Gulch	VREVR027.67	34 16 07.6	111 25 04.4
5	E Verde River below the State Route 87 bridge (Class 1 Long Term Site)	VREVR034.80	34 17 57.4	111 21 30.2
6	East Verde River at the Forest Service Road 199 bridge	VREVR043.98	34 20 32.5	111 17 24.5
7	East Verde River below the confluence of Ellison Creek	VREVR044.96	34 21 07.4	111 17 03
8	East Verde River above 2nd crossing on Houston Mesa Road	VREVR045.50	34 21 20.9	111 16 59.1
9	E Verde River above the confluence with Willow Spring Canyon	VREVR046.18	34 21 53.8	111 16 52.6
10	East Verde River below Washington Park	VREVR051.15	34 25 16	111 15 47.8
11	Pine Creek above the confluence with the East Verde River	VRPIE000.29	34 13 27.6	111 29 18.7
12	Pine Creek at the Tonto Natural Bridge State Park	VRPIE008.19	34 19 09.2	111 27 27
13	Pine Creek above the City of Pine drinking water intake structure	VRPIE016.49	34 25 15.7	111 26 27.2
14	City Creek, just above Forest Service Road 406	VRCIT000.37	34 13 09.7	111 27 58.8
15	American Gulch, just above Forest Service Road 67	VRAMG000.76	34 14 37.5	111 24 28.1
16	American Gulch, appx 0.25 miles downstream of the Payson WWTP	VRAMG003.62	34 14 02.5	111 22 14.2
17	Dripping Springs, just above the confluence with the East Verde River	VRDRP000.01	34 16 11.5	111 25 13.1
18	Sycamore Creek, just below the unnamed springs	VRSYE000.95	34 18 39.7	111 22 01.7
19	Webber Spring, just above the confluence with Webber Creek	VRWES000.03	34 19 22.5	111 20 04.8
20	Webber Creek, below the boy scout camp	VRWEB009.13	34 23 57.6	111 21 53.5
21	Patton Spring Draw; north of the rim road, west of Baker Butte	VRPSD001.63	34 26 49.1	111 21 55.5
22	Bray Creek; upstream of the Fire Control Rd, west of Holbert Rd	VRBRA001.82	34 23 43.7	111 20 13.8
23	Ellison Creek, just above the confluence with the East Verde River	VRELL000.18	34 21 06.6	111 16 42.3
24	Bonita Creek, above the confluence of Fuller Creek	VRBON002.71	34 22 41.7	111 13 32.1
25	Ellison Creek; near the headwaters area, just east of Forest Service Rd 1922	VRELL009.02	34 22 44	111 10 31.9
26	Mail Creek, just above the Forest Service Road 32 crossing	VRMAI000.78	34 25 39.4	111 16 09.3
27	East Verde River above Forest Service Road 502 (auto-sampler site)	VREVR023.39	34 14 19.0	111 25 51.3

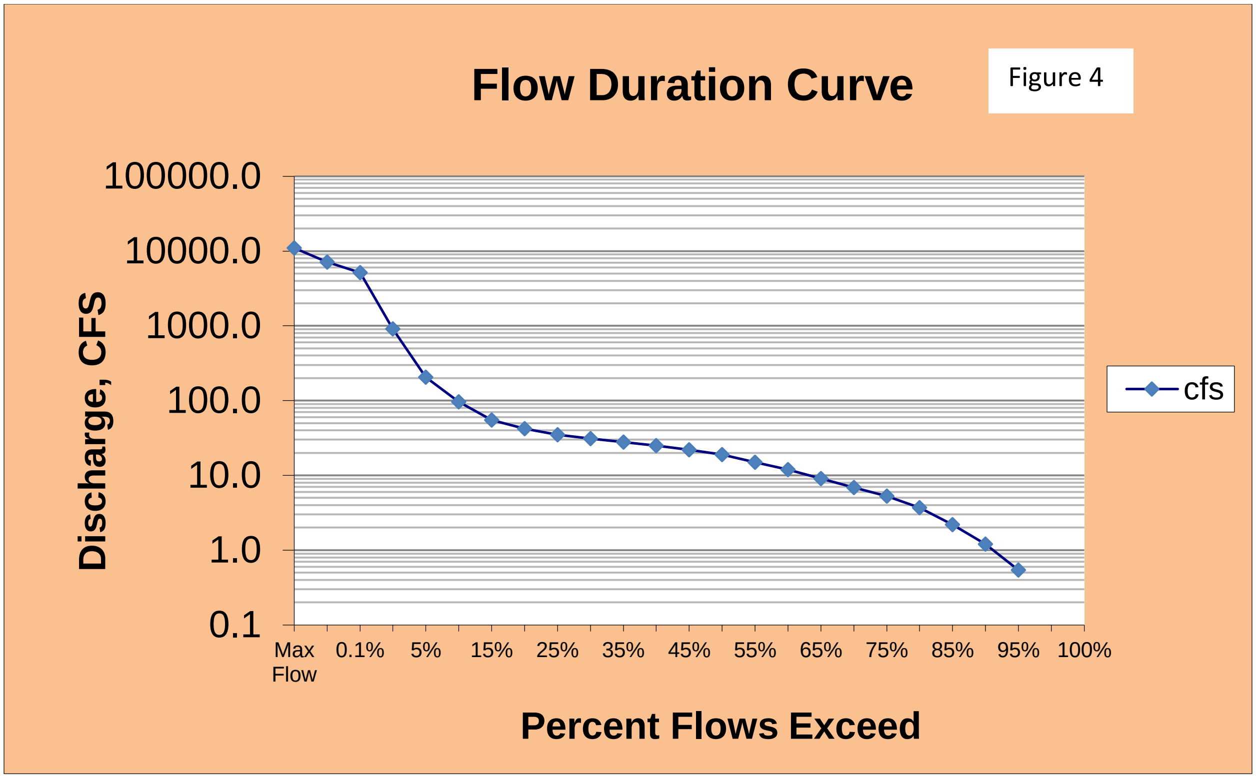
Analytical Methods

In regards to the analysis of samples collected for this project, in the initial stages of the East Verde TMDL project the analysis of water samples was handled by Xenco Laboratory in Tempe. Near the end of 2011 the analysis of water samples was shifted to TestAmerica Laboratory, also located in Tempe. When submitting samples, it was requested that the analysis of total arsenic be reported down to the detection limit. Both labs used a detection limit that was well below the DWS designated use standard of 10 µg/L. Some of the low concentrations that were reported were identified with a lab notation of E4. A result that is labeled as E4 is considered below the laboratory' reporting limit but above or at the method detection limit.

Data Analysis

126 samples were collected at 27 sites throughout the watershed. Review of the total arsenic data collected at the sites located on the East Verde River indicated that any exceedances of the DWS designated use standard occurred at site VREVR002.62. Of the 13 samples collected at VREVR002.62, only two were lower than 10 µg/L. The highest result analyzed from the samples was 59.1 µg/L. This result also corresponds with the lowest gauged discharge of 2.7 cfs. Conversely, the lowest total arsenic value of 3.1 µg/L was recorded on the sample visit with the highest measured discharge of 370 cfs. A basic statistical analysis indicates a median value of 26.1 µg/L, and an average value of 28.9 µg/L. Analysis of the flow data collected at the site indicates a median flow value of 13.4 cfs. None of the 109 samples collected at the other sample sites produced a result greater than or equal to 10 µg/L, except for a site located at the mouth of Pine Creek in the wilderness area (VRPIE000.29), which did have a single exceedance on August 15, 2007 of 13 µg/L. The associated flow for the site was estimated at 0.01 cfs, with field notes stating that the creek was "barely flowing". Sixty three of the 109 samples, or approximately 58%, were reported as non-detect. Of the 46 samples that did produce results, the highest values were from the auto-sampler located at VREVR023.39. Six samples collected on July 26, 2013 had an average value of 4.4 µg/L. The discharge rate during the remote sampling was calculated from the level logger data to be approximately 30 cfs. Results for the other 40 sample events ranged from 0.52 µg/L at VRPIE016.49 to 4.0 µg/L at VRAMG000.76.

Analysis of the flow data from the USGS gauge station located at VREVR002.62 helps to demonstrate the flow patterns of the reach, and also helps illustrate the loading of arsenic in kilograms per day (based on the sample results and discharge for that day). The gauge currently has 51 years' worth of flow data, although only the data which the USGS has approved can be accessed. The USGS uses this data to compile a number of variables, one of which is the average daily flow, typically expressed in cubic feet per second. Figure 4 shows the flow duration data for the gauge station in chart form, representing about 50 years' worth of average daily flow information. The chart illustrates the data on a logarithmic scale so that it is easier to represent. However, zero values cannot be plotted correctly on log charts. This explains why the discharge is not represented after the 95% Flows Exceed on the horizontal axis. At that point it begins to enter into the flows that were recorded as zero cfs. The peak average daily flow was 11,000 cfs. The data shows that about 95% of the time the flows are 0.5 cfs or greater.



By using the flow duration data from the USGS gauge and the arsenic sample data collected by USGS personnel, load duration curves can be created. The load duration curve in Figure 5 shows only the data that was collected by the USGS personnel from December of 2009 to March of 2011. The total arsenic sampling results have been converted to kilograms per day to illustrate the amount of loading occurring at that particular point in time in relation to the gauged flow. The solid lines indicate the loading of total arsenic along the flow duration curves for the FBC and DWS designated use standards. These lines indicate the loading that is necessary to meet the two uses, but not exceed them. Simply stated, any total arsenic data point that lies below, or directly on top of the solid line is meeting the standard. Data points that plot above the lines are exceedances of the arsenic standard for that particular designated use.

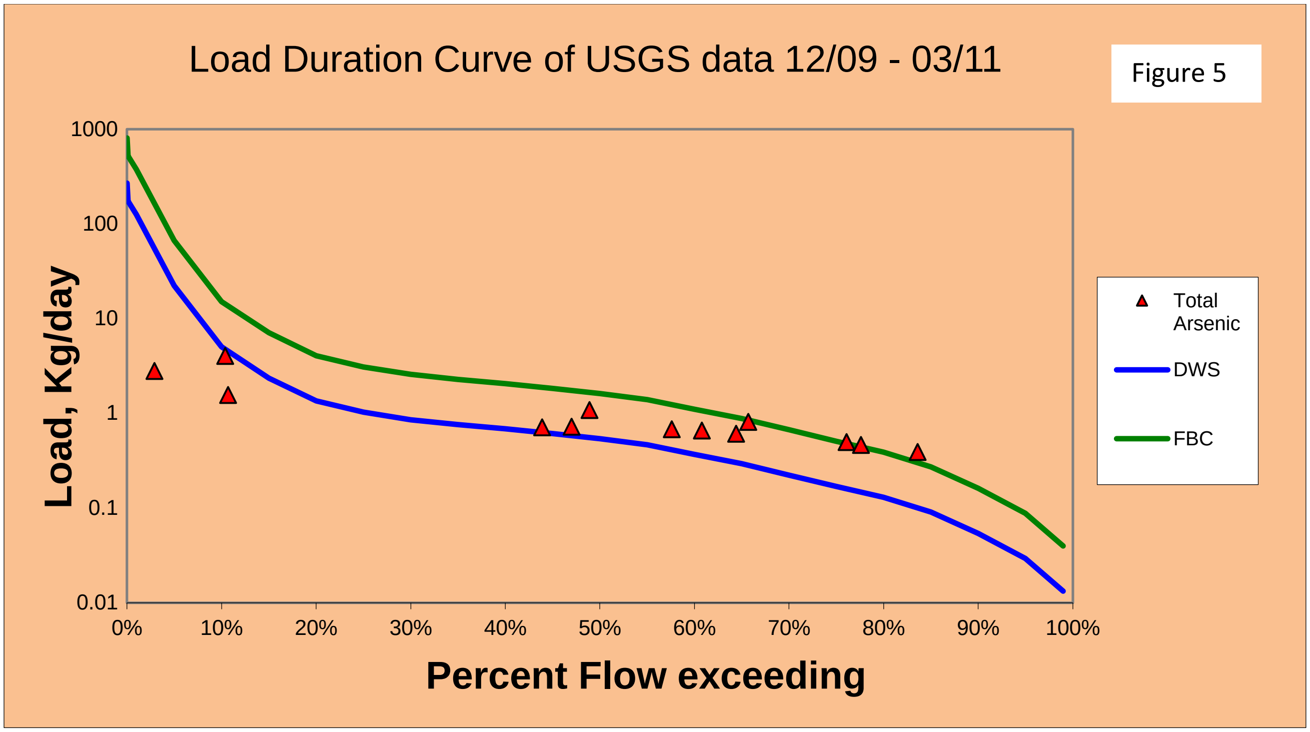
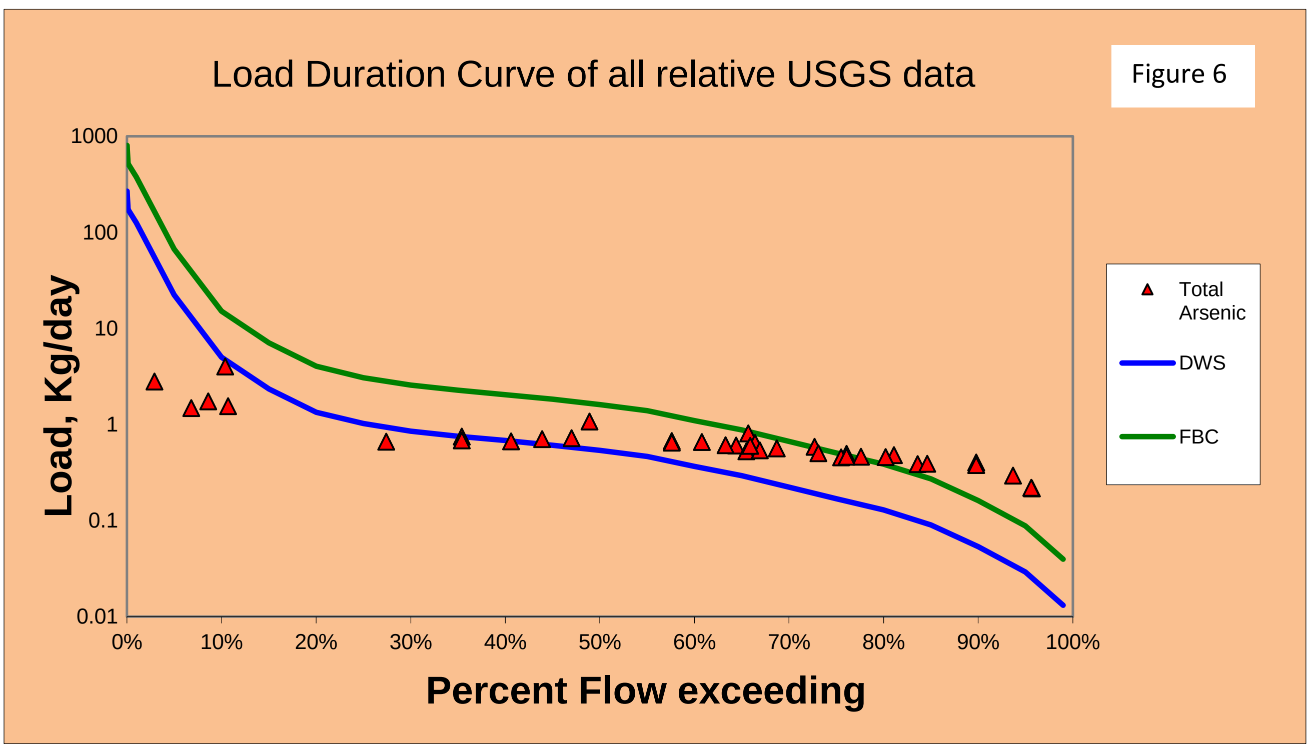


Figure 6 illustrates the same loading curves for the DWS and FBC designated uses, but with all the significant total arsenic sample results that have been collected by the USGS from January of 1998 to March of 2011. All sample results were reviewed and any questionable or suspicious looking results were discarded. Also, any sample visits that reported a discharge of 0 cfs were discarded.

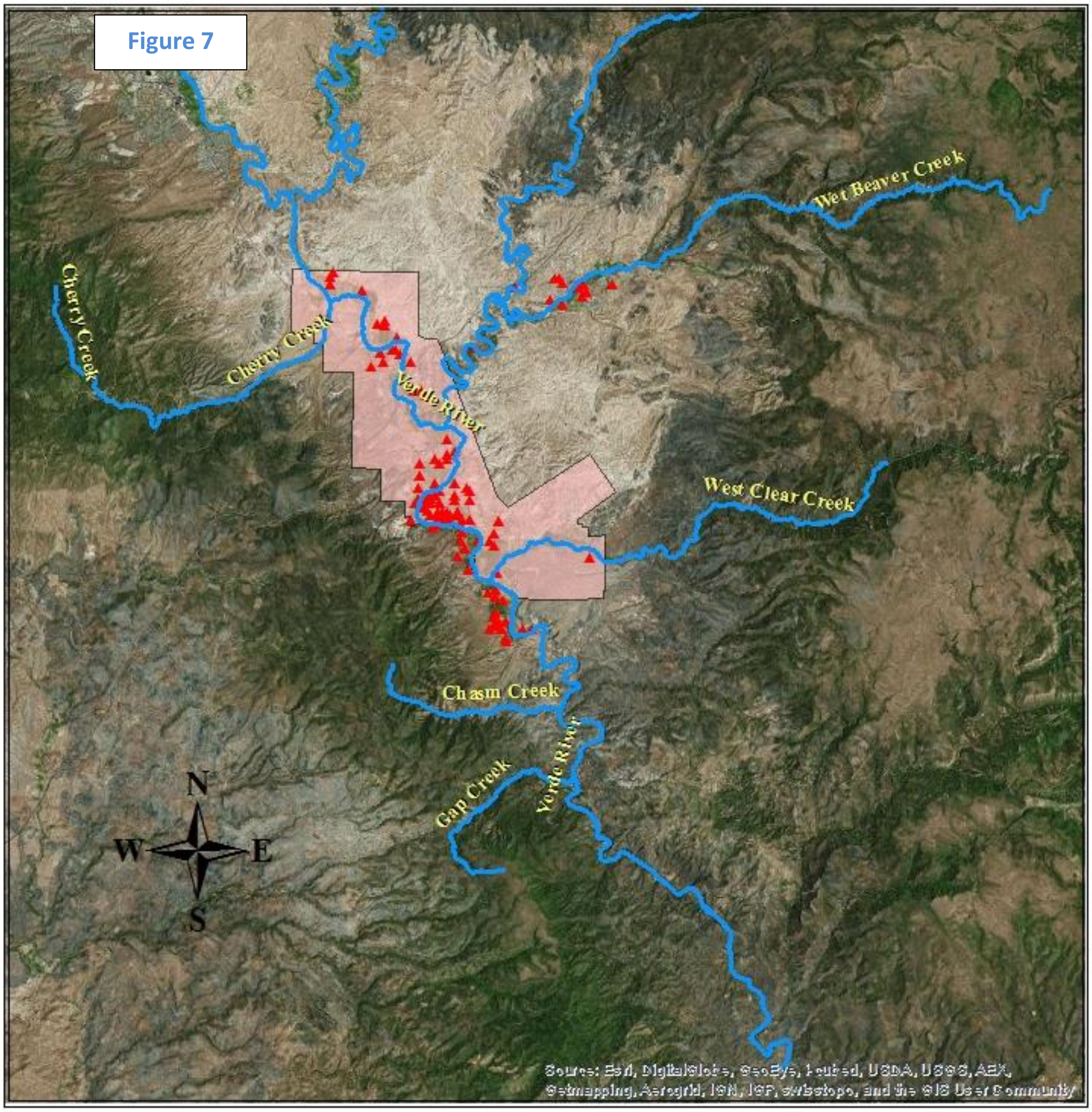


The results of the Load Duration Curves strongly suggest groundwater influence at the USGS gauge site. By utilizing available groundwater data, the data from VREVR002.62, and the data from all other sample points above VREVR002.62 along the main stem of the East Verde, it is possible to analyze statistically the possible relationship between groundwater and surface water.

There are two statistical approaches that can be used, the two sample t-test and the Kruskal-Wallis test. A t-test is a statistical examination of the means of two separate populations of data. The test statistic in the t-test is referred to as the t-statistic. A t-test examines the t-statistic, t-distribution, and degrees of freedom to determine a probability, or p value that can be utilized to conclude whether the differences in the population means is actually significant, or if it is instead due to random chance. In a two sample t-test, two sample means are compared to determine whether they come from the same population, meaning that there is essentially no difference between the two population means. The test can also be used to analyze the data using either a pooled variance or separate variance method.

An ADEQ groundwater database query for total arsenic levels of wells located in A-T13N R4E & R5E and A-T14N R4E & R5E produced 156 sample results from 138 wells. These wells are located in and around the city of Camp Verde, approximately 2.5 river miles upstream of the confluence of the East Verde River and the Verde River. As was noted in the section regarding the geology of the area, these wells all overlie the Verde Formation. Two other populations of total arsenic data were also created, all data from VREVR002.62 (39 sample results) and all total arsenic data from any existing sample sites on the main stem of the East Verde River above VREVR002.62 (31 sample results). The locations of the wells that provided the groundwater arsenic data can be found in Figure 7.

Figure 7



Verde Valley Well Locations

Verde Valley Streams

Wells with As data

Camp Verde boundaries

Utilizing the statistical software package Systat 12.0 to run the two sample t-test on the three groups of data produced the following results:

GROUP	N	MEAN	STD DEVIATION
VREVR002.62	39	46.282	50.989
EVR OTHER SITES	31	2.394	1.276

Separate Variance:

Difference in Means	43.889
95.00% Confidence Interval	27.354 to 60.423
T	5.373
df (degrees of freedom)	38.060
p-value	0.000
Bonferroni Adjusted p-value	0.000
Dunn-Sidak Adjusted p-value	0.000

Pooled Variance:

Difference in Means	43.889
95.00% Confidence Interval	25.582 to 62.195
T	4.784
df (degrees of freedom)	68.000
p-value	0.000
Bonferroni Adjusted p-value	0.000
Dunn-Sidak Adjusted p-value	0.000

The results show a great degree of difference in the means of the two data sets, and the p-values indicate a significant difference between the means of the two sample populations suggesting the source water is different for VREVR002.62 versus all the other East Verde River sites. The next test was run on all the other East Verde River sites except VREVR0002.62 and the queried well data.

GROUP	N	MEAN	STD DEVIATION
EVR OTHER SITES	31	2.394	1.276
WELL DATA	156	50.410	44.990

Separate Variance:

Difference in Means	-48.017
95.00% Confidence Interval	-55.146 to -40.887
T	-13.303

df (degrees of freedom)	156.245
p-value	0.000
Bonferroni Adjusted p-value	0.000
Dunn-Sidak Adjusted p-value	0.000

Pooled Variance:

Difference in Means	-48.017
95.00% Confidence Interval	-63.994 to -32.039
T	-5.929
df (degrees of freedom)	185.000
p-value	0.000
Bonferroni Adjusted p-value	0.000
Dunn-Sidak Adjusted p-value	0.000

Again the results show a great degree of difference in the means of the two data sets, and the p-values also indicate a significant difference between the means of the two sample populations suggesting the source water is different for groundwater versus all the other East Verde River sites except VREVR002.62. The last test is run on those data sets that are suspected of being related to each other, the queried well data and the data from VREVR002.62.

GROUP	N	MEAN	STD DEVIATION
VREVR002.62	39	46.282	50.989
WELL DATA	156	50.410	44.990

Separate Variance:

Difference in Means	-4.128
95.00% Confidence Interval	-22.022 to 13.765
T	-0.463
df (degrees of freedom)	53.733
p-value	0.646
Bonferroni Adjusted p-value	0.646
Dunn-Sidak Adjusted p-value	0.646

Pooled Variance:

Difference in Means	-4.128
95.00% Confidence Interval	-20.453 to 12.197
T	-0.499
df (degrees of freedom)	193.000

p-value	0.619
Bonferroni Adjusted p-value	0.619
Dunn-Sidak Adjusted p-value	0.619

In this test run the degree of difference in the means of the two data sets is much smaller than the two previous test results, and the results indicate that the groundwater sample sites and surface water site VREVR002.62 are likely being influenced by the same source.

The Kruskal-Wallis is a non-parametric test for one-way analysis of variance that is used to determine if three or more samples originate from the same distribution. It is essentially an approach that assigns ranks to the data points, basically replacing the data points themselves. It is similar to the Mann-Whitney U test, but it is applicable to more than two sample groups. The null hypothesis (or default assumption) is that there is no difference in variance between the two sets of data being tested. The individual running the test can choose the confidence limit that fits the application. In this case we have opted to use a 95% confidence interval, so essentially a probability value of ≤ 0.05 dictates that the null hypothesis is rejected and the alternate hypothesis (that there is a difference) is accepted. As with the two sample t-test, the data is run in pairs of groups. Utilizing the same Systat software used to run the two sample t-tests produced the following results:

GROUP	N	RANK SUM
VREVR002.62	39	1974.500
EVR OTHER SITES	31	511.000

Mann-Whitney U Test Statistic	1194.000
p-value	0.000
Chi-square Approximation	48.685
df (degrees of freedom)	1

A probability value of 0.000 shows a very strong certainty that the null hypothesis should be rejected and there is a difference between the two sets of data.

GROUP	N	RANK SUM
EVR OTHER SITES	31	519.500
WELL DATA	156	17058.500

Mann-Whitney U Test Statistic	23.500
p-value	0.000
Chi-square Approximation	75.724
df (degrees of freedom)	1

A probability value of 0.000 shows a very strong certainty that the null hypothesis should be rejected and there is a difference between the two sets of data.

GROUP	N	RANK SUM
VREVR002.62	39	3414.500
WELL DATA	156	15695.500

Mann-Whitney U Test Statistic	2634.500
p-value	0.196

Chi-square Approximation	1.672
df (degrees of freedom)	1

In this comparison of data sets a probability value of 0.196 indicates that the null hypothesis should be accepted and there is no difference between the sample populations.

Data Interpretation

The work performed by the personnel of the TMDL Unit has shown that the conditions which caused the listing of the reach as impaired for total arsenic still exist. The original listing of reach 15060203-022C was driven by the total arsenic data collected by the USGS at sampling site VREVR002.62. Historical data from both ADEQ and USGS confirmed that other sites located upstream within the East Verde watershed were not impacted by total arsenic. The most current data collected once again by ADEQ and the USGS during the East Verde TMDL project confirms the findings of the historical data. The median value of the more current total arsenic data from site VREVR002.62 is just slightly less (22.9 µg/L) than the median for the historical data (24 µg/L). This suggests that current arsenic levels at site VREVR002.62 are similar to what was documented by the USGS personnel in the period from December 1990 to April of 2005. Even though both periods showed differing concentrations mainly based on the associated flow rates, the median values of the two data sets are very close.

The fact that the impaired listing is being driven by the sample results at VREVR002.62 indicates that the exceedance of the total arsenic standard is either the cause of impacts that are occurring upstream, or it reflects natural background conditions that are typically found at the site. The next upstream sample site, VREVR016.28, is located about 0.4 miles above the boundary of the Mazatzal Wilderness Area (Figures 2 & 3). The available total arsenic data for this site indicates that it is typically quite lower, with a median arsenic value of 2.0 µg/L. Sample site VREVR034.80 is a long term site with a fairly robust data set that is located upstream of the city of Payson. It is located at about mid-reach on the main stem of the East Verde River and upstream of reach 15060203-022C. It has a median total arsenic value of 1.8 µg/L, just slightly less than VREVR016.28. In terms of arsenic loading, VREVR002.62 is contributing 0.79 Kg/day of total arsenic (based on median value of flow data and median value of both current and historic total arsenic data), while VREVR016.28 is contributing 0.024 Kg/day and VREVR034.80 is contributing .018 Kg/day. This indicates that if the higher total arsenic levels are anthropogenic in nature, the source, or sources, should be located somewhere between VREVR002.62 and VREVR016.28. Documented anthropogenic sources of arsenic are mining, wood preservation, agriculture (arsenic based pesticides), coal fired plants, and waste streams from the glass and electronics industry. The only permitted activity occurring within the Mazatzal Wilderness Area is the agricultural use of the rangeland for cattle grazing. The remoteness of the lower reaches and the extremely rugged terrain make any other activities besides grazing and recreational use extremely difficult. Early reconnaissance activity within the watershed turned up no evidence of any of the cited anthropogenic sources of arsenic occurring along the main stem of the East Verde River or its tributaries. Field work and site visits that took place mainly on a seasonal basis for several years of work confirmed the absence of human based activities that could be a source of elevated total arsenic levels.

The lack of identifiable anthropogenic sources within the watershed suggests that the levels at VREVR002.62 are a product of groundwater influence from elevated concentrations of naturally occurring arsenic. The natural high levels of arsenic in the groundwater of the Verde Valley sub-basin have been well documented over the years. The Arizona Department of Water Resources has compiled data regarding groundwater hydrology of the wells and springs located in the Verde River Basin. This data indicates that as of March, 2014, there were over 400 well or spring sites with parameter concentrations that either equal or exceed drinking water standards. The drinking water standard for total arsenic in groundwater is also 10 µg/L. Total arsenic was the parameter most frequently equaled or exceeded. Surface water sample sites along the upper to mid Verde River have also produced high levels of both total and dissolved arsenic over the years due to the influence of groundwater in the area. It is reasonable to assume that groundwater may also be affecting the arsenic levels in the lower reaches of the East Verde River. As Figure 5 and Figure 6 illustrate, the total arsenic loading sample points for both examples show a relatively flat distribution compared to the flow duration curves for the FBC and DWS designated uses. This indicates that the total arsenic mass loading levels at VREVR002.62 are steady throughout the hydrograph, which is consistent with parameter levels being influenced by additions from groundwater and not by inputs from storm water.

The statistical work-up performed on the three groups of water quality data helped to show whether the relationship illustrated in the Load Duration Curves could be proven analytically. Results from both the two sample t-test and the Kruskal-Wallis implies no statistically significant difference in the means of the arsenic data from sample site VREVR002.62 and the arsenic data from the groundwater wells. This indicates a high degree of certainty that arsenic levels in both sample populations are being influenced by a common source, in this case the Verde Formation. When comparing all other East Verde sites to both sample site VREVR002.62 and the groundwater wells sample data, the statistical data indicates that there is a significant difference in both comparisons. This implies that arsenic levels in the other East Verde sites are not being influenced by the same source that is affecting surface water site VREVR002.62 and the groundwater wells.

Conclusion

The purposes of this delisting report are to put on the record the findings of the recent TMDL monitoring results and to present the rationale for the delisting of impairment of total arsenic. As previously stated, the exceedances of the DWS designated use are occurring only at VREVR002.62. This site is the lowest downstream site that was sampled on the East Verde River. It is located at a point in the watershed where influences from the Verde Valley groundwater sub-basin are typically seen. There is no data that exists for the approximately 13.5 miles of the reach above this site due to the access restrictions associated with the site. This fact prevents the interpretation of just how far upstream arsenic from groundwater influence extends, but the data has shown that the next active upstream sampling site outside of the wilderness area has had zero exceedances for total arsenic. Interpretation of the arsenic loading at VREVR002.62 and statistical analysis of the arsenic data sets provide even more strength to the argument that total arsenic levels at the site are being influenced by groundwater.

The methods used in this project had very low detection limits and consideration of the water quality representations made by the entire body of data, and the addition of higher quality data collected more intensively during this TMDL project leads one to the conclusion that Reach 15060203-022C (East Verde River – American Gulch to the Verde River) does not warrant its continued presence on Arizona's 303(d) list for total arsenic water quality violations. In evaluating a surface water for delisting, ADEQ in accordance with Arizona Administrative Code R18-11-605(E).2.a "shall remove a pollutant from a surface water or segment from the 303(d) List based on one or more of the following criteria". The pertinent and applicable criteria subsequently listed (R18-11-605(E).2.a.vi.) states:

> *"Pollutant loadings from naturally occurring conditions alone are sufficient to cause a violation of applicable water quality standards."*

The more recent and scientifically credible data for Reach 15060203-022B of the East Verde River shows that the listing does not meet the criteria for continued listing under the applicable numeric water quality standard for total arsenic when considered under a weight of evidence approach. An informed recommendation is hereby made to officially remove the reach from the Arizona 303(d) list.

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