

GEOCHEMICAL CLUES TO GROUNDWATER SOURCES OF THE
PEDERNALES RIVER, TEXAS

by

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DEDICATION

To my sousaphone, for waiting ever so patiently while I focus on one adventure at a time.

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ABSTRACT

Interactions between aquifers and rivers are recognized as important components of the hydrologic system. Central Texas rivers and aquifers are especially well connected due to karstic carbonate geology where gaining and losing streams, springs, and caves are common. The Pedernales River is an important source of water for local communities, the city of Austin, and downstream water users of the Colorado River, to which it drains. The Pedernales River Basin is surrounded by rapidly developing areas with increasing water demands, but the majority of the watershed is developed only for agriculture. Identifying critical areas for water quality and quantity protection while the land is still relatively undeveloped creates an opportunity for proactive water resource protection. The primary objectives of this study were: 1) to compare water quality and geochemistry of water from the Pedernales River, its tributaries, springs across the basin, wells screened in specific aquifers, and historic data; 2) to identify groundwater sources of the river; and 3) to assess whether or not changes in water quality have occurred in the Pedernales River between 1962 and 2015. By conducting this study during baseflow conditions, the water sources are assumed to originate exclusively from groundwater, as opposed to runoff or soil interflow. Geospatial information was evaluated for springs, surface geology, and river gains and losses. Stable isotope ratios, principal component analysis, and spatial analysis highlight the importance of groundwater contributions and human impacts to the river and indicate that evaporation is controlling the geochemical evolution of surface waters. Water quality throughout the watershed was generally good.

Hydrogen and oxygen stable isotope ratios for spring and well samples defined a regional groundwater signature, and tributary and main river samples plotted along an evaporative trend with the groundwater signature as the source. Principal component analysis identified two groups of variables which strongly represent variation in sample geochemistry: humanly impacted variables and groundwater signature variables. Spatial analysis also revealed patterns of human impacts and groundwater inputs. The groundwater source locations were combined with surface geology to identify host geologic unit, and therefore source aquifers, of groundwater in the river basin. Groundwater in the Pedernales River is derived from the Edwards-Trinity Plateau Aquifer, the Trinity Aquifer, the Marble Falls Aquifer, and the Ellenburger-San Saba Aquifer.

1. INTRODUCTION

Water is essential for life, and as demand for a limited supply increases, understanding the natural system remains a high priority. Population growth and development are occurring at a rapid rate in central Texas. For example, Austin was the third fastest growing metropolitan area in the U.S. from 2000-2013, and the population of Travis County is projected to increase from around 1 million in 2010 to 1.6 million in 2050 (CAPCOG 2016). Comprehensive information about our water resources is therefore crucial for planning and sustainable management. Rivers and aquifers provide most of the fresh water used in Texas, and the contributions of aquifers to rivers and vice versa are recognized as important components of the hydrologic system. Interactions between surface water and groundwater are gaining attention as water managers recognize the importance of managing the water system as a whole (e.g. Winter et al. 1998). Central Texas rivers and aquifers are especially well connected because the region consists of karstic carbonate geology where gaining and losing streams are common, as are springs and caves. Gaining streams gain water from springs and seeps, and losing streams lose water to aquifers via fractures, caves, sinkholes, and swallets. Understanding and quantifying groundwater and surface water interactions in the Pedernales River will aid water resource management and planning (Meadows Center 2015). Successful techniques employed during this study will also guide similar studies occurring in other central Texas rivers (Meadows Center and Wierman 2014).

Streams and rivers in karst settings have complex interactions with groundwater sources and sinks. These systems are often characterized by a high level of connectivity between surface and groundwater (Katz et al. 1997, Winter et al. 1998, Sophocleous

2002). Rivers and streams may gain water from obvious springs or from springs that are hidden under the water's surface, likewise surface water may be losing into obvious sinkholes or sinking underground without a perceptible whirlpool. Patterns in water chemistry provide evidence that can be used to determine water sources and flowpaths. For example, aquifer water reacts with the host rock, and this imparts a geochemical signature to the water. Several studies have evaluated time series and flood relationships between surface and groundwater geochemistry in karst streams (e.g. Uliana and Sharp 2001, Mahler and Massei 2007, Mahler et al. 2008, Bailly-Comte et al. 2009, Musgrove et al. 2010); however, by sampling during baseflow conditions, patterns in the water chemistry may allow linkage of surface water with aquifer sources. An important consideration is that human impacts may also affect water chemistry patterns. Hyporheic and vadose water also play important roles in the intricacies of the natural hydrochemical system, but in this study the focus was on a large-scale perspective. Three types of hydrochemical analysis were performed: major ion chemistry is a standard tool used to decipher hydrogeochemical patterns (Appelo and Postma 2005) as well as impacts of human activity (Dunne and Leopold 1978), nutrients are frequently used to evaluate human impacts, and stable isotopes are often used as naturally occurring tracers of water flowpaths. In this study, geochemical analysis of surface water and groundwater was used to evaluate water quality, examine human impacts, and understand water pathways of groundwater to the surface and vice versa. The primary objectives of this study were to:

- 1) compare water quality and geochemistry of water from the Pedernales River, its tributaries, springs across the basin, wells screened in specific aquifers, and historic data;

2) identify groundwater sources of the river; and 3) assess whether or not changes in water quality have occurred in the Pedernales River between 1962 and 2015.

Baseflow is generally defined as the sustained stream flow in the absence of surface run-off from precipitation (USGS 2016). This can also be thought of as the continued “low-flow” during dry weather conditions. Another definition of baseflow is the water flow in a river when the hydrograph has stabilized after a storm pulse (Wayland et al. 2003). River discharge during baseflow conditions should be relatively stable and originate from a relatively constant groundwater source. Fetter (2001) defines baseflow simply as “groundwater contribution to a stream”. In central Texas, baseflow sources are usually springs, and surface water samples collected during baseflow should reflect groundwater conditions of the spring source rather than runoff from precipitation.

Baseflow conditions vary depending on antecedent conditions and can be difficult to quantify. The Pedernales River is most frequently flowing at baseflow conditions, so the long-term median discharge is representative of baseflow conditions. This provided a quantitative discharge goal for the study to target baseflow sampling. Aquifers may extend beyond the boundaries of surface watersheds, so understanding the groundwater contributions is important for understanding where the water is coming from and has applications for conservation.

Previous work in the Pedernales River watershed provides a framework for understanding river flow dynamics and regional aquifer chemistry (Mount 1963, Holland and Hughes 1964, Bluntzer 1992, Barker and Ardis 1996, Barrett 1998, Strickland 2009). Spatial variations in water chemistry have been previously interpreted to be due to groundwater inputs, precipitation influence, and human impacts from the Fredericksburg

and Johnson City wastewater treatment plants. In general, concentrations of individual ions were higher upstream than down (Barrett 1998, Strickland 2009). For the current study, a synoptic water quality and chemistry study was conducted in fall of 2015 during baseflow conditions on the Pedernales River. Spatial variability in geochemistry and surface geology were evaluated in springs and surface waters in order to evaluate surface water - groundwater interactions. Results for surface waters were compared to previously published data for the river and to regional groundwater compositions to provide a regional and temporal context. Identifying the sources of water to the Pedernales River is important for managing water quantity and quality within the river, and this information will be used to provide direction and delineate priority areas for long-term conservation efforts by organizations such as The Mitchell Foundation.

2. HYDROGEOLOGIC SETTING

The Pedernales River flows across Kimble, Gillespie, Blanco, and Hays Counties in central Texas and terminates at its confluence with the Colorado River at Lake Travis in eastern Travis County (Figure 1). The Colorado River is the primary source of water for the city of Austin, a rapidly growing urban center. The Pedernales River contributes a significant amount of water to the Colorado River upstream of Austin, and is therefore an important source of water for the city and downstream users. The river is also important for rural communities and cities within the basin, including Fredericksburg, Johnson City, Stonewall, and Harper. Aquifers underlying the Pedernales River include the Trinity Aquifer, the Edwards-Trinity Plateau Aquifer, and the Ellenberger-San Saba Aquifer (TWDB 1990a and 1990b). The predominant geology outcropping in the Pedernales River Basin includes the Edwards Formation, the Glen Rose Formation, and the Hensell Formation (Barnes 1986). Geology of the river basin is predominantly limestone and dolomite and is complicated by the presence of Paleozoic and Precambrian rocks that are part of the Llano Uplift in the north-central portion of the basin. Limestone and dolomite rocks are susceptible to dissolution and the formation of karst landforms and subsurface conduits that can transmit water rapidly. Of the four aquifers in the basin, the Trinity Aquifer is known to contain caves, and the Ellenburger is described as karstic (Standen and Ruggiero 2007). Fewer caves and sinkholes are documented within the Pedernales River basin than from areas immediately to the north and south; however, the river basin contains karst springs and gaining/losing discharge characteristics typical of karst areas. Also, karst aquifers and flowing waters can utilize dissolution-enlarged fractures and

preferential flowpaths on a smaller scale than humanly accessible caves, and these small-scale karst pathways may be less obvious to an observer walking across the landscape.

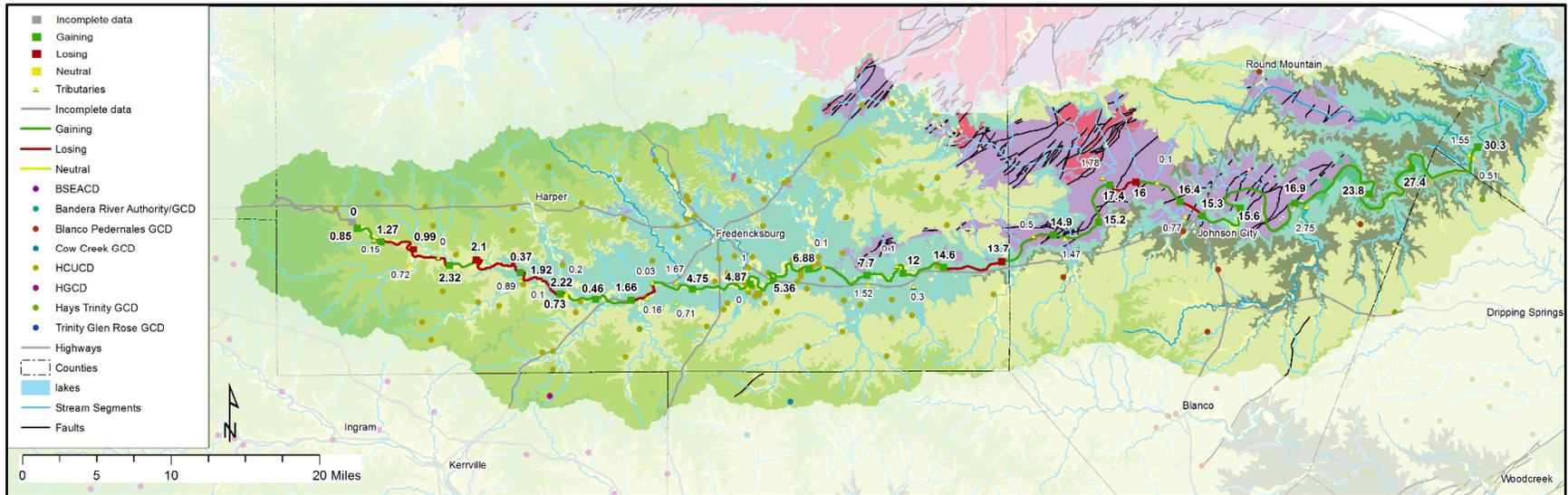


Figure 1. Location map.

Draining 1,280 square miles, the Pedernales River is overall a gaining system with spring inputs along the entire river basin; however, a 1962 basin-wide study revealed sections of loss as well as gain via discharge measurements along the river and in certain tributaries (Holland and Hughes 1964). Personnel and collaborators with the Meadows Center for Water and the Environment analyzed the 1962 data and created a map displaying gaining and losing sections of the Pedernales River (Figure 2) (Meadows Center 2015). Within Gillespie and Blanco Counties (where most of the watershed is

located) there is reasonable habitat for 63 federally-listed or state-listed threatened or endangered species or Species of Greatest Conservation Need: one salamander, 12 birds, two fish, six mammals, three reptiles, two insects, five mussels, and 32 plants (TPWD 2016).

Water use is changing as demands change in the Pedernales River Basin. The city of Fredericksburg is growing, and much of the treated wastewater that was formerly discharged into the river is now used for watering golf courses, potentially reducing discharge in the river. Water wells have been drilled for the cities of Fredericksburg and Johnson City, and their effects on groundwater contributions to the Pedernales River are unknown. The dominant land use in the Pedernales River watershed is agriculture and ranch land; however, many ranches in the central Texas Hill Country are eventually sold and subdivided, creating additional demands and impacts on water resources. Understanding from where the water in the Pedernales River comes may assist in identifying critical areas for water resource protection.



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Figure 2. Gain/loss in the Pedernales River based on USGS data from 1962 (Holland and Hughes 1964). Red areas represent losses and green areas represent gains in the river. Map reproduced from Meadows Center report (2015).

3. METHODS

Immediately prior to collection of water samples, an inventory of flowing water in the river basin was conducted. Using a geographic information system (GIS) analysis, tributary flowlines from the National Hydrography Dataset by the United States Geological Survey (USGS) were combined with roads from the Texas Department of Transportation (TxDOT) to identify 932 publicly accessible locations where roads intersected stream courses (Figure 3). During the inventory, the 932 locations throughout the river basin were visited, and presence of flowing water was recorded along with other parameters such as ease-of-access. Of the 932 locations, 117 sites had water present. The inventory occurred on 10 and 11 August 2015 during river discharge conditions that were very close to the long-term median discharge as calculated by the USGS for 1939-2015 at Johnson City (USGS 2015a). By targeting median flows, the goal of this study was to document baseflow conditions. At gauge sites in Fredericksburg, Johnson City, and Reimer's Ranch, discharge at the time of this study was within 2.8 cubic feet per second (cfs) of flow during the 1962 basin-wide study performed by the USGS (Table 1). The synoptic water sampling occurred within one month of the inventory, and no precipitation or extreme weather events occurred during the intervening time period.

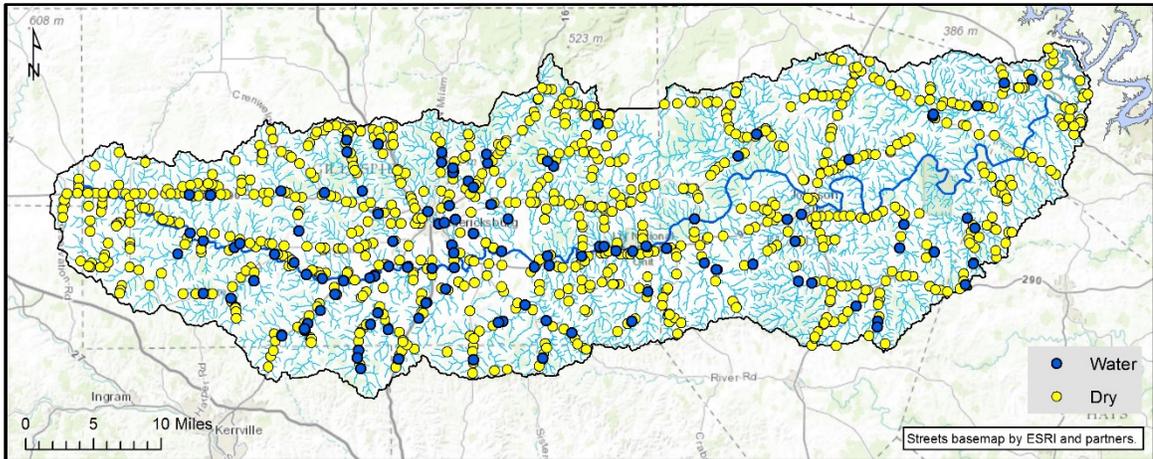


Figure 3. Inventory locations at publicly accessible water crossings.

Table 1. River flow comparison for 1962 and 2015.

1962 data from Holland and Hughes (1964). 2015 data at Fredericksburg and Johnson City from USGS 2015a and 2015b.

Pedernales River Location	May 1962 (cfs)	August 2015 (cfs)
Fredericksburg @ Hwy 87	4.8	2.0
Johnson City @ Hwy 281	15.3	18.0
Reimer's Ranch	30.3	27.8

3.1. Water Sample Collection

Synoptic water sampling events are designed to capture a “snapshot in time” of water chemistry or some other parameter. Synoptic sampling techniques are used to analyze spatial trends or differences between two or more discrete events, and they have been used for geochemistry in other studies (e.g. Grayson et al. 1997, Wayland et al. 2003). Funding was available for 100 samples, including quality assurance samples such as duplicates, so 91 sites were chosen. Private land access to springs and wells was not a priority during this project; however, access was granted to nine springs and three wells. Seventy-nine sample locations were chosen from publicly accessible locations with flowing water based on the inventory discussed above. The 79 sites were selected in an attempt to maximize the distribution of samples across the watershed (Figure 4). The sampling event occurred between 27 August and 10 September 2015, during which time no precipitation occurred.

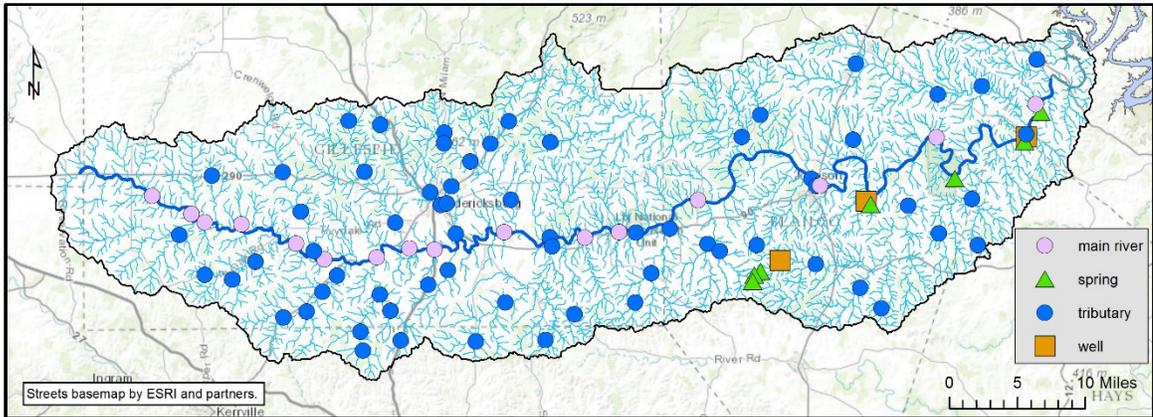


Figure 4. Water sample locations.

At each site a one liter sample was collected, field measurements were made using hand-held meters (temperature (T), pH, dissolved oxygen (DO), and specific conductance (SC)), and several qualitative water quality observations were recorded. Meters were calibrated each morning and checked at the end of the day. Qualitative observations of flow, clarity, percent algae cover, color, surface characteristics, and odor were documented. For quality assurance, duplicate samples were collected at six randomly selected sites, and two blank samples of de-ionized water were collected. Each water sample was immediately placed on ice in a cooler for transport.

3.2. Laboratory Analyses

Water samples were delivered to the lab on ice and placed in a refrigerator for less than 48 hours until processed (well below the 72 hour maximum hold time for all parameters). Samples were analyzed for major ions, nutrients, and isotopes in Dr. Benjamin Schwartz's lab at Texas State University in San Marcos, and each sample was processed and analyzed using the appropriate standard methods as noted below. After processing, which involved filtration and/or preservation, all liquid samples were refrigerated until analyzed and filters were frozen. Samples to be analyzed for isotopes, ions, and dissolved nutrients were filtered through Pall A/E (1 μ m pore) ashed filters.

Total and dissolved nutrient samples were preserved with 188 μL of 1 N H_2SO_4 and stored in 125 mL HDPE bottles. Water samples for analysis of liquid water stable isotopes (oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$)) and major ions were filtered and stored in 60 mL HDPE bottles. Filtered samples for dissolved organic carbon (DOC) analysis were stored in 40 mL glass vials. The Pall A/E (1 μm pore) ashed filters were stored in aluminum foil for total suspended sediments (TSS) and nonvolatile suspended sediments (NVSS) analysis. Particulate phosphorus (PP) was filtered onto large GF/F filters, folded, and stored in glass vials. Particulate carbon (PC) and particulate nitrogen (PN) were filtered onto small GF/F filters and stored in aluminum foil.

Liquid water stable isotopes were analyzed using a Picarro L2130-I Cavity Ringdown Spectrometer Isotope Analyzer (Picarro, Inc., Santa Clara, CA, USA). Major ions (fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})) were analyzed with Dionex ICS 1600 Liquid Ion Chromatographs (Thermo Fischer Scientific, Walther, MA, USA). Total phosphorus (TP), soluble reactive phosphorus (SRP), and PP concentrations were determined utilizing the ascorbic acid method 4500-P E (Standard Methods 2005). Total nitrogen (TN) was quantified using second-derivative spectroscopy on a Varian 50S UV/VIS Spectrophotometer, method 4500-NO₃ C (Standard Methods 2005). Ammonium (NH_4) was measured using methods modified from Wetzel and Likens (2000) and method 4500-NH₃ F (Standard Methods 2005). DOC was measured using a Total Organic Carbon Analyzer, TOC-Vcsh, ASI-V, Shimadzu and method 5310 B-2000 (Standard Methods 2005). PC and PN were analyzed using a NC Elemental Analyzer, FlashEA 1112 Series, CE Elantech, Inc., Thermo Finnigan Corporation. TSS and NVSS

are determined by weighing the dried (at 50°C) and muffled (550°C) Pall A/E filters and taking into account volume of water filtered, from methods 2540 D and E (Standard Methods 2005). A typical set of Pedernales water samples during laboratory analysis is displayed in Figure 5.



Figure 5. Typical set up of water samples during laboratory analysis.

For quality assurance and quality checks, a calibration and linear regression was done on all laboratory instrumentation at each run to account for instrumentation drift on the day of analyses. An R^2 of 0.98 or better was achieved in every calibration. In addition to the field duplicates, additional pseudoreplicates were created from randomized

samples for the major ion and isotope analyses. All duplicates and pseudoreplicates were within an acceptable range, with one exception. The acceptable range is defined as: both values must be within two standard deviations of each other. The one exception to acceptable results was sample number 940 and its duplicate, which were out of range for calcium and ammonium; this was likely due to an unknown source of contamination in the sample bottle. These two samples were analyzed multiple times to confirm that the issue was not related to instrumentation or methods. All other ions and assorted parameters were within acceptable ranges for sample number 940. All blank sample results were as anticipated with no values found above detection limits.

3.3. Spatial Analysis

Spatial analysis and maps were created using ArcGIS (version 10.3.1, copyright 1999-2015 Esri Inc.). GIS data were obtained from the USGS and the Texas Natural Resources Information System (TNRIS) as shapefiles in geographic datum NAD83. Field and lab data for the sample locations were stored in a geodatabase, and all data were projected as UTM 14N NAD83. Tributaries to the Pedernales River were grouped into subwatersheds as defined by the USGS Watershed Boundary Dataset and were used to group and spatially interpret the geochemistry results. These subwatersheds are defined for general analysis of cause and effect relationships in stream networks (USGS 2015c), such as this analysis. Data were separated into four categories: main river channel, tributaries, springs, and wells. Tributary data were averaged by subwatershed to evaluate inputs along the main river. River miles were calculated for sample sites and downstream intersections of the subwatersheds with the river based on the TNRIS major river

segment for the Pedernales. Surface geology at sample sites was determined based on the Geologic Atlas of Texas digitized by the USGS (TNRIS 2015).

For visual evaluation of chemistry trends in the river and tributary subwatersheds, maps were created to illustrate variation of each constituent. The mean value for each subwatershed was displayed using graduated colors with 5 classes defined by the quantile method: darkest color represents the highest chemical concentration and the lightest color represents the lowest, while subwatersheds without any samples (and therefore without any data) are shown in white. The subwatershed mean value is also labeled for specificity. Each tributary sample location is displayed using graduated symbols with five classes defined by the natural breaks method: largest circles representing highest concentrations and smallest circles representing lowest concentrations. Displaying locations and analyte concentrations in this way helps to illustrate heterogeneity among samples within each subwatershed. The main river channel samples are labeled with the chemical concentration at that point for comparison with the subwatersheds. City locations are also overlain for reference.

Spatial patterns in stable isotope data were evaluated with respect to surface geology and the position of sampling sites in the watershed. Because the relationship between oxygen and hydrogen stable isotopes varies linearly, oxygen isotope values were arbitrarily chosen to display the isotopic gradient. $\delta^{18}\text{O}$ values are displayed using graduated colors with five classes defined by equal intervals and the blue to red color gradient: blue sites have the lowest values (least enriched) and red sites have the highest values (most enriched).

3.4. Geochemistry Analysis

Stable isotopes are measured as the ratio of heavy isotopes to light isotopes in the sample to the ratio of these isotopes in a standard; so a ratio of ratios. Evaporation and precipitation affect whether the hydrogen and oxygen isotopes are heavier or lighter (Fetter 2001). The cumulative effect of evaporation and precipitation results in strong continental trends, seasonal variation at a given location, and high variability of rain or snow during an individual precipitation event. The Global Meteoric Water Line is an equation that describes the relationship between hydrogen and oxygen isotopes (Craig 1961). A straight line trending away from the GMWL toward more enriched isotopic values, but with a lower slope than the GMWL, indicates evaporative loss (SAHRA 2005). In groundwater systems with temperatures less than 50°C, oxygen and hydrogen isotopes are nonreactive and can be used as naturally occurring tracers (Freeze and Cherry 1979). Groundwater isotope values depend on the source of the water and often represent an average of annual precipitation in a given location.

A piper diagram is a form of trilinear diagram that is commonly used in water chemistry studies (Piper 1944, Fetter 2001). Analytic results are plotted as a percentage of the total of each cation, anion, or pair. Patterns in dominant ions allow classification of hydrochemical facies, which are groundwaters that differ in chemical composition. Bicarbonate for this analysis was calculated via charge balance.

3.5. Statistics Analysis

Principal Component Analysis (PCA) is a multivariate statistical method used to reduce complexity and look for patterns in data by highlighting variables that account for the greatest variance out of a larger number of original variables (Wold et al. 1987,

Jolliffe 2002). PCA has been successfully applied to geochemical water quality studies in other areas with complex groundwater - surface water interactions (e.g. Melloul and Collin 1992, Fournier et al. 2007, Cloutier et al. 2008, Menció and Mas-Pla 2008, Moore et al. 2009). For this study, PCA was applied to the water chemistry results of 25 variables for 86 water samples using the “princomp” function in the program R (version 3.2.3, copyright 2015 by the R Foundation for Statistical Computing). Variables included major ions (F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}), stable isotopes (δ^2H and $\delta^{18}O$), SC, TSS, NVSS, T, nutrients (TN, NH_4 , PN, TP, SRP, PP, PC, DOC), time of collection, and presence or absence of odor. Only 86 out of the original 91 samples were used in this analysis because wells samples were excluded along with two major outliers (site 951 collected downstream of the Johnson City wastewater treatment plant and site 960 with an abnormally high concentration of particulate matter). The 86 water samples included all spring, tributary, and river samples, except for the two major outliers. Normalizing the data with a z-transformation did not affect the analysis results, so the original unaltered data were used.

Each principal component (PC) is defined by the variables with the strongest loadings. PC loadings represent the strength and direction of the correlation between each variable and the respective PC. Since PCs are perpendicular to each other, they can be represented as axes in Cartesian coordinate space to explore the relationship among data points or variables. For example, PC1 can be plotted on an x-axis and PC2 on a y-axis. Direct relationships appear as positive loadings and inverse relationships as negative loadings. The strongest loadings reflect the variables with the greatest influence on the PC. The greatest portion of the variance is accounted for by the first PC, and the

subsequent PCs account for progressively less variance. Component scores are calculated for each sample variable measurement on each PC and can be plotted to examine trends. Patterns emerge when samples' component scores show similar variable loadings as a result of the influence of similar processes. Likewise, samples with differing scores are likely influenced by more variable processes.

3.6. Historic Data Compilation

Historic data were compiled from several sources for comparison with the current study. A baseflow water quality and gain-loss study was performed by the USGS in 1962 and provides a baseline for temporal comparison (Holland and Hughes 1964). River discharge data was obtained from the USGS gages at Fredericksburg and Johnson City, river gauging at Reimer's Ranch, and gauging by Paul Tybor and other staff members of the Hill Country Underground Water Conservation District (HCUWCD). Geochemical data for wells were downloaded from Texas Water Development Board (TWDB).

4. RESULTS

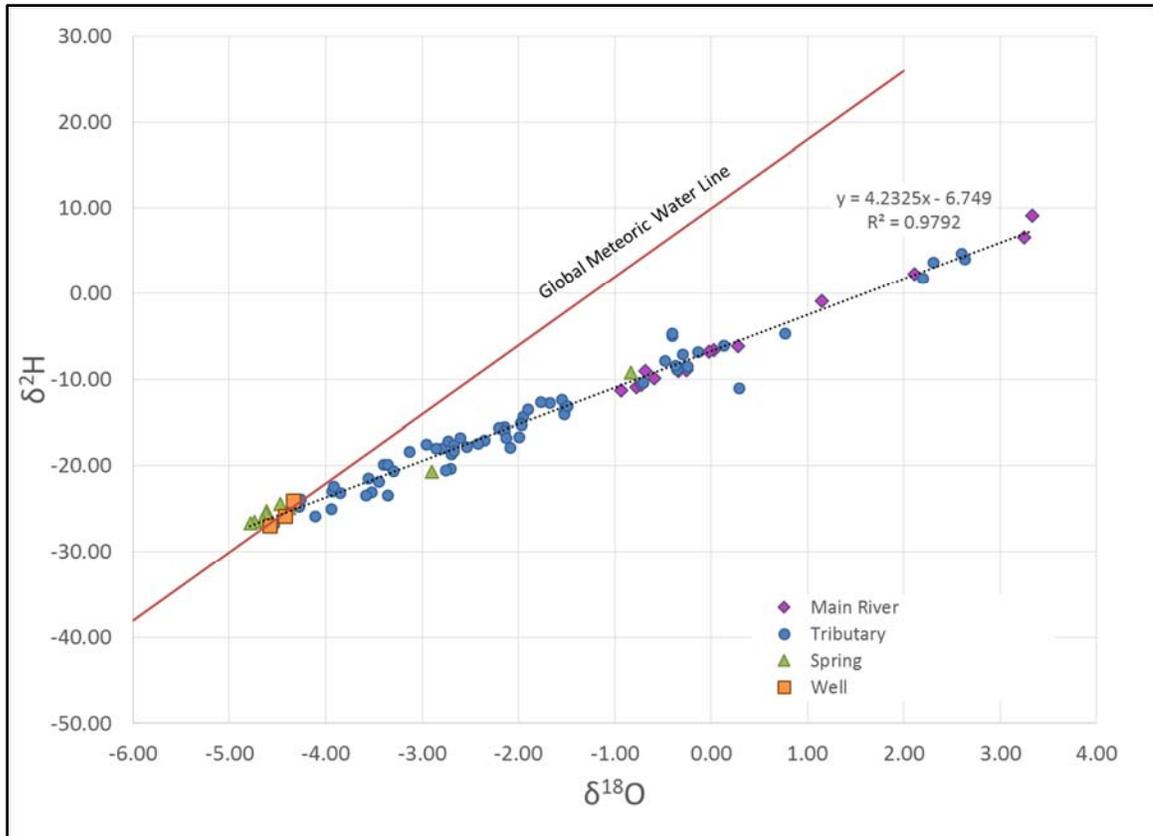
All field data and observations are included in Table 4 in the Appendix.

Chemistry results for all water sample sites are included in Table 5 in the Appendix. Two samples stood out as outliers in the data: sample 951 was elevated in dissolved constituents and was located immediately downstream of the Johnson City wastewater treatment plant, and sample 960 was elevated in particulate constituents both visually and analytically and was collected from a manmade concrete trough retaining sediment and organic detritus at a spring orifice. All ion and nutrient concentrations met EPA (2015) drinking water limits, but at 16 sites TDS was above the 500 mg/L limit based on SC measurements and conversion ($TDS = 0.64[SC]$).

4.1. Hydrogen & Oxygen Stable Isotopes

Stable isotope values ranged from -4.79 to 3.33 $\delta^{18}O$ and -26.66 to 9.10 δ^2H . Data plot along a linear trend of $\delta^2H = 4.217 (\delta^{18}O) - 6.7737$ with $R^2 = 0.9795$ (Figure 6), which is a clearly evaporitic trend deviating from the GMWL ($\delta^2H = 8 [\delta^{18}O] + 10$). Springs and well samples are tightly clustered with isotopic ratios that represent a single isotopic groundwater signature and fall on the GMWL. Main river channel samples are more enriched, and tributary samples fall along a gradient between groundwater samples and samples enriched due to evaporative loss. The gradient from less enriched to more enriched is highlighted in the map of results for $\delta^{18}O$ which are displayed with graduated colors and overlain with surface geology in Figure 7. Two springs have isotopically enriched values, likely due to the water originating from shallow subsurface flow rather than a true groundwater source. To substantiate this observation, at least a portion of the water discharging from Pedernales Falls Spring (site 956) has been dye traced from four

miles upstream in the riverbed (Brune 1981), and site 953 appears to be shallow subsurface bypass flow of surface water as a result of a private dam immediately upstream. As a result of enriched values and a suspicion that these springs do not represent pure groundwater, those two samples are treated as surface water samples for further analyses.



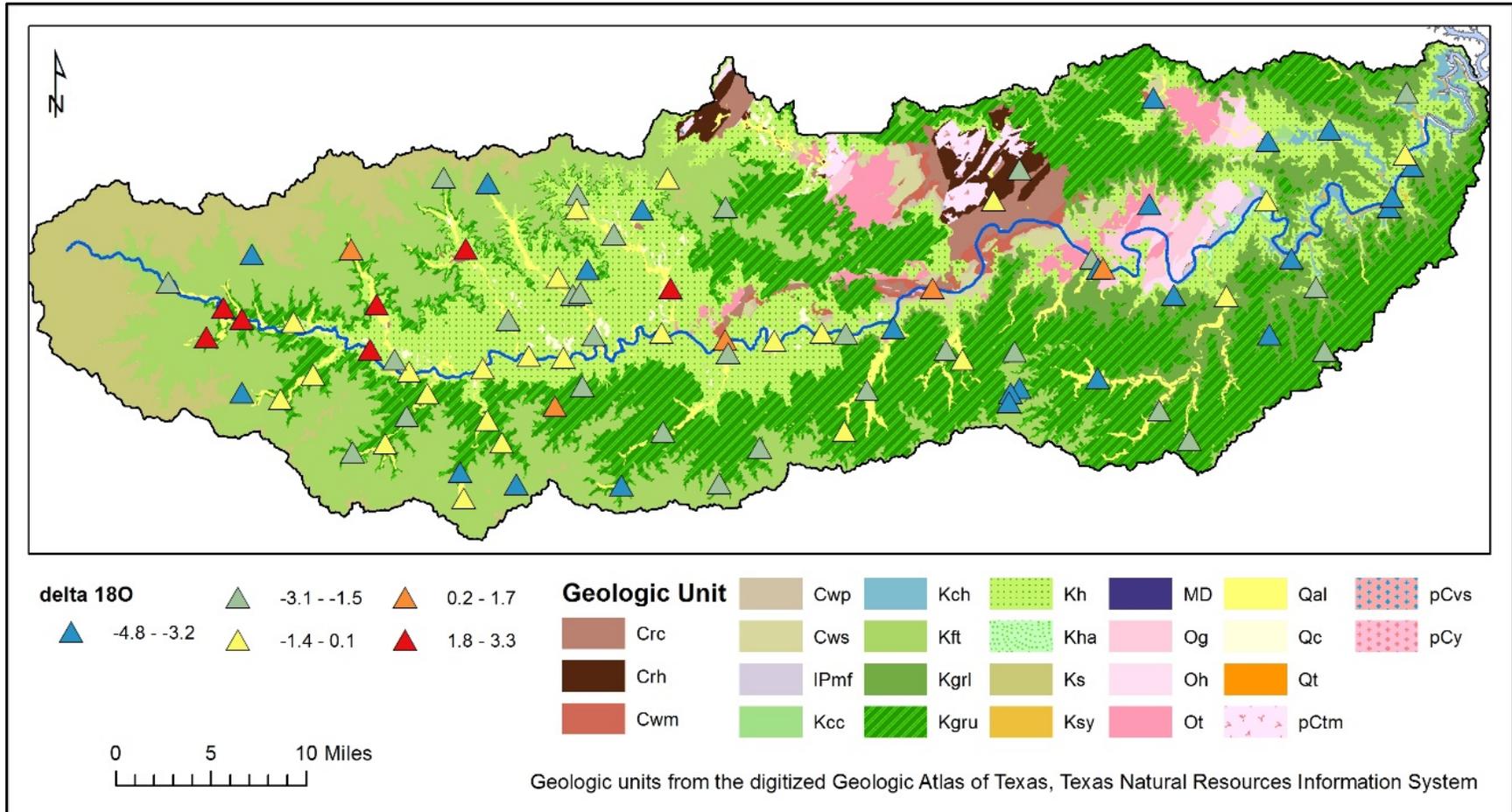


Figure 7. Stable isotope $\delta^{18}O$ gradient overlain with map of surface geology.

4.2. Major Ions and Piper Diagram

Geochemistry, nutrient, and sediment data are listed in the Appendix, and major ion results are summarized in Table 2. Concentration maps for each major ion are displayed along with a corresponding graph of concentration by river mile in Figure 8 through Figure 25. Conductivity and particulate phosphorus are included in Table 2 and Figure 26 through Figure 29 because they are of interest due to the PCA results (discussed below). Across the river basin, several patterns emerge: Cl^- , Na^+ , K^+ , and NO_3^- are all highest near Johnson City; F^- and Mg^{2+} are highest near Fredericksburg; SO_4^{2-} and Ca^{2+} are highest in between Stonewall and Johnson City; and Br^- is highest south of Fredericksburg. Cl^- in both the river and tributaries is generally higher in the western portion of the river basin and lower in the east, and is generally higher in the river than it is in the tributaries. F^- in the river basin is generally lower to the east and west and higher in the middle. SO_4^{2-} and NO_3^- are generally higher to the west, and Br^- is slightly higher. Na^+ is generally lower to the east within the river basin. K^+ and Mg^{2+} are generally higher in the central part of the river basin. Ca^{2+} in the river is variable in the west and relatively constant in the central and eastern portion of the river basin. Ca^{2+} in the tributary samples is generally higher in the east.

Table 2. Major ion summary table with minimum (min), mean, and maximum (max) values for n (number of samples) in parts per million (ppm) for ions, micrograms per liter ($\mu\text{g/L}$) for PP, and microsiemens (μS) for SC, as indicated.

Constituent	River Values (n=16)			Tributary Values (n=72)			Subwatershed Mean Values (n=23)		
	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
Cl ⁻ (ppm)	29.2	55.5	80.0	6.3	33.4	113.2	7.0	32.0	71.2
F ⁻ (ppm)	1.4	1.8	2.3	1.1	2.0	4.6	1.3	2.0	3.5
SO ₄ ²⁻ (ppm)	13.8	25.0	40.3	2.1	28.0	268.7	3.1	27.5	100.2
NO ₃ ⁻ -N (ppm)	0.0	0.1	0.8	0.0	0.4	9.2	0.0	0.3	2.4
Br ⁻ (ppm)	0.3	0.4	1.3	0.0	0.2	0.7	0.0	0.2	0.6
Na ⁺ (ppm)	17.4	35.7	52.2	4.4	20.6	95.0	4.4	20.1	53.6
K ⁺ (ppm)	1.8	3.7	5.3	0.7	2.8	13.6	1.5	2.8	7.7
Mg ²⁺ (ppm)	16.2	34.1	43.2	14.1	34.6	81.3	15.9	32.4	57.3
Ca ²⁺ (ppm)	20.9	42.1	72.1	22.8	57.8	129.1	27.9	58.2	89.1
SC (μS)	390	632	758	370	652	1223	373	639	937
PP ($\mu\text{g/L}$)	3.5	17.0	57.2	0.0	33.0	1540.6	0.0	32.9	516.0

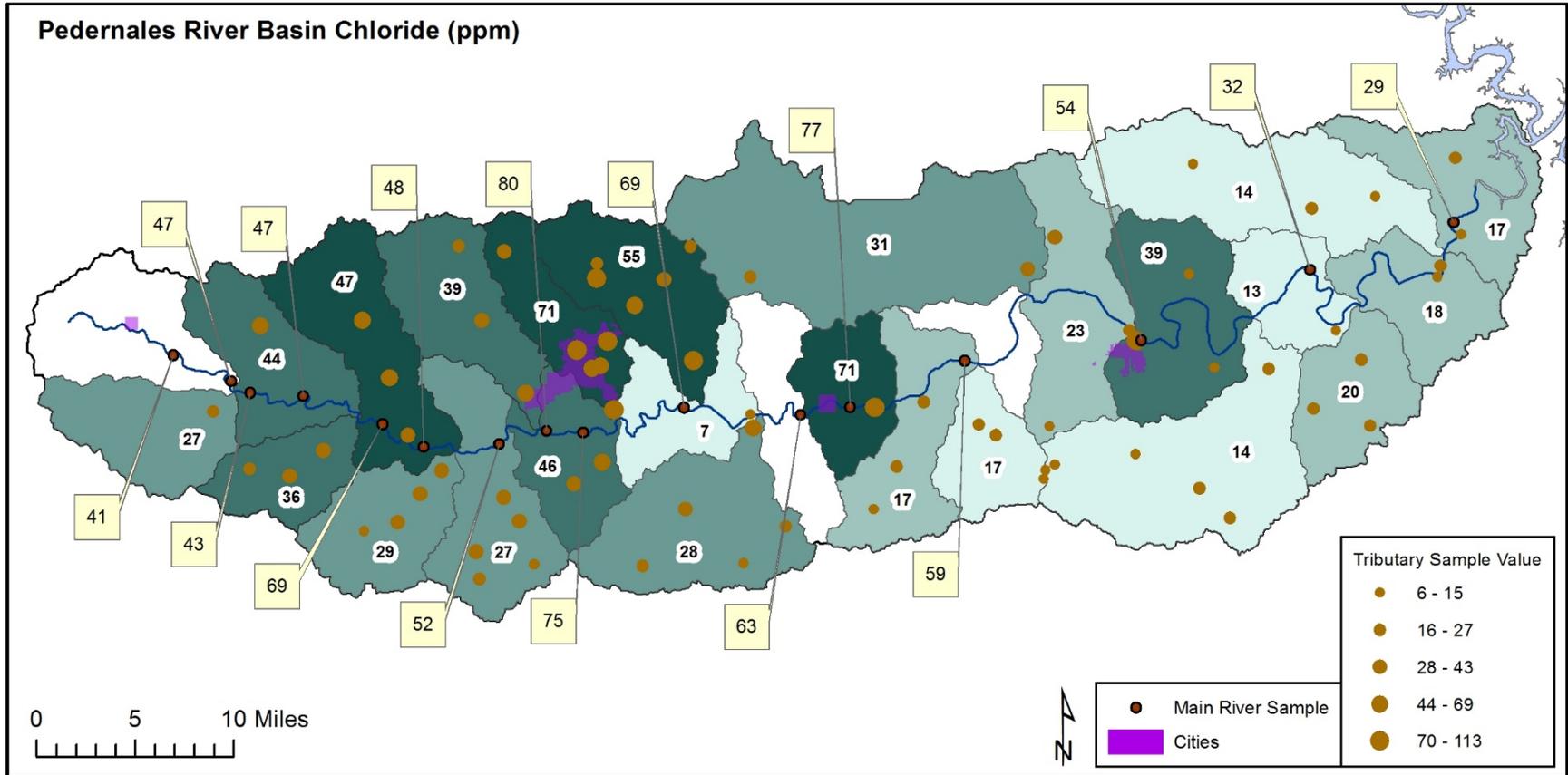


Figure 8. Chloride ion concentration map (ppm).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

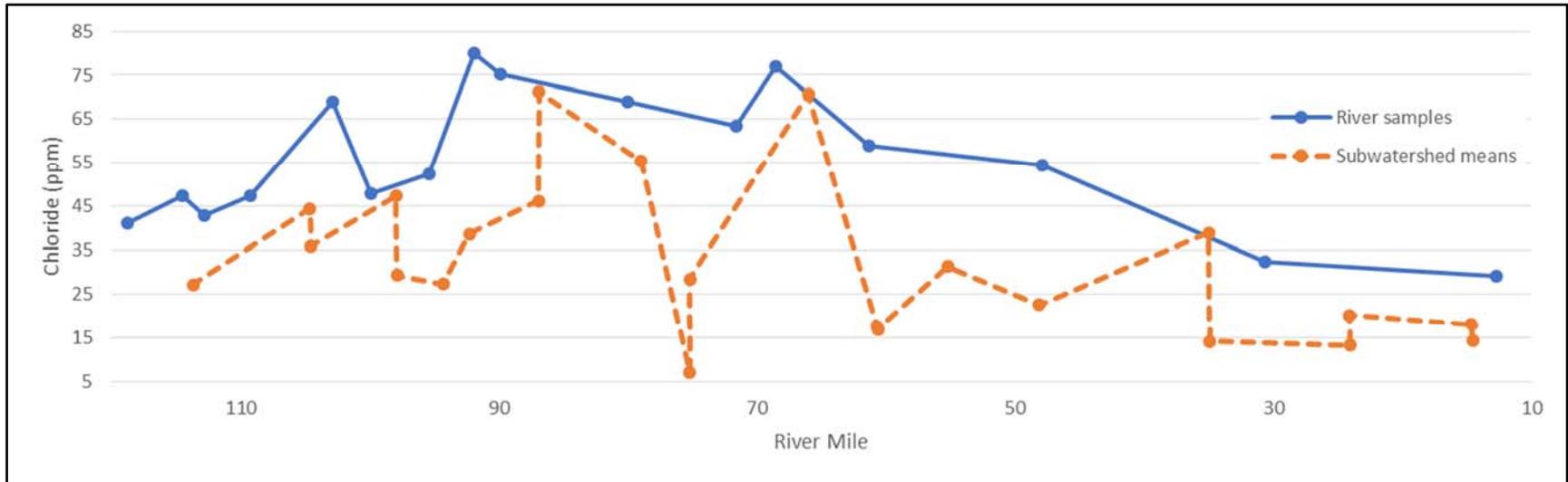


Figure 9. Chloride ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

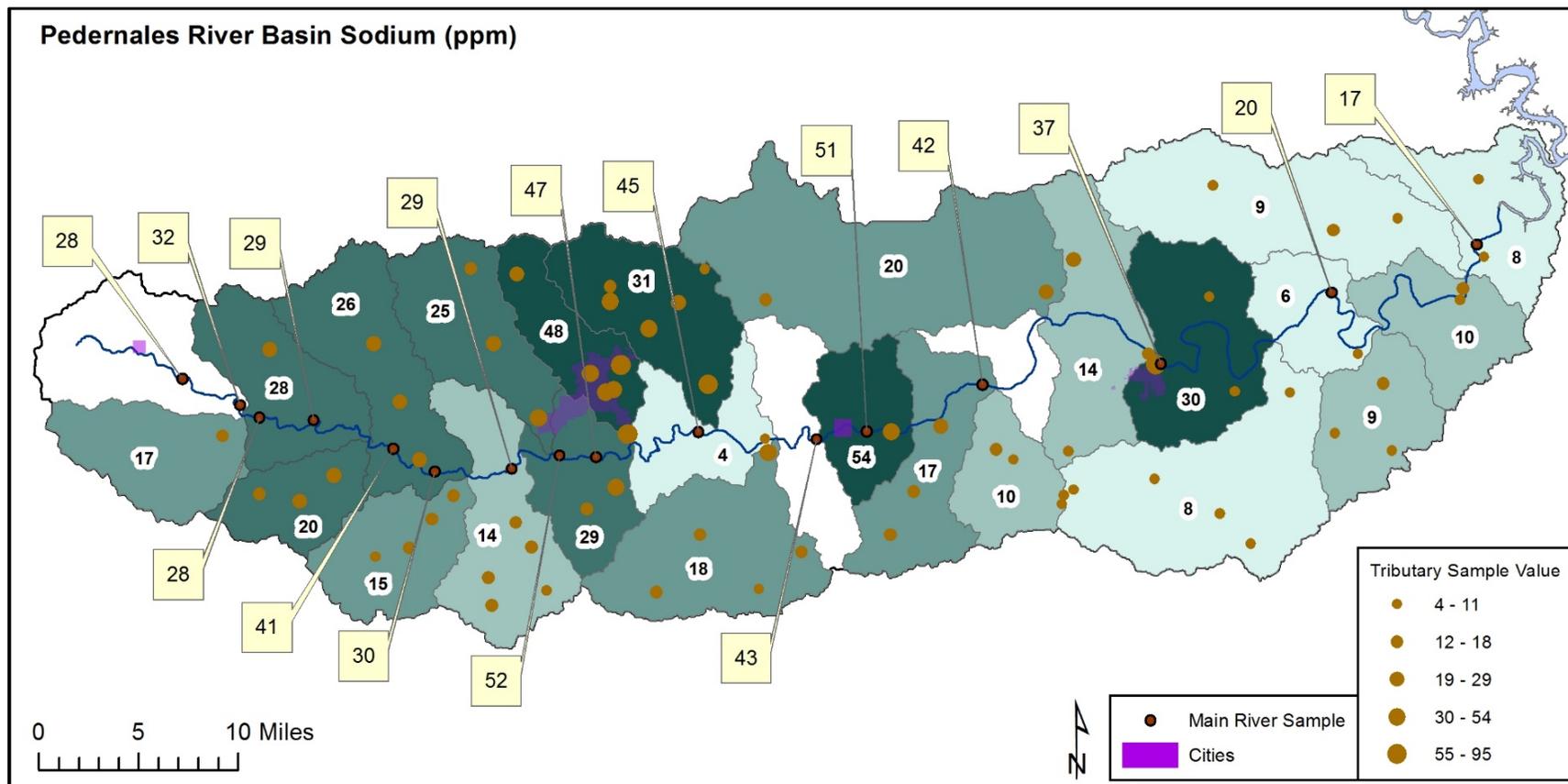


Figure 10. Sodium ion concentration map (ppm).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

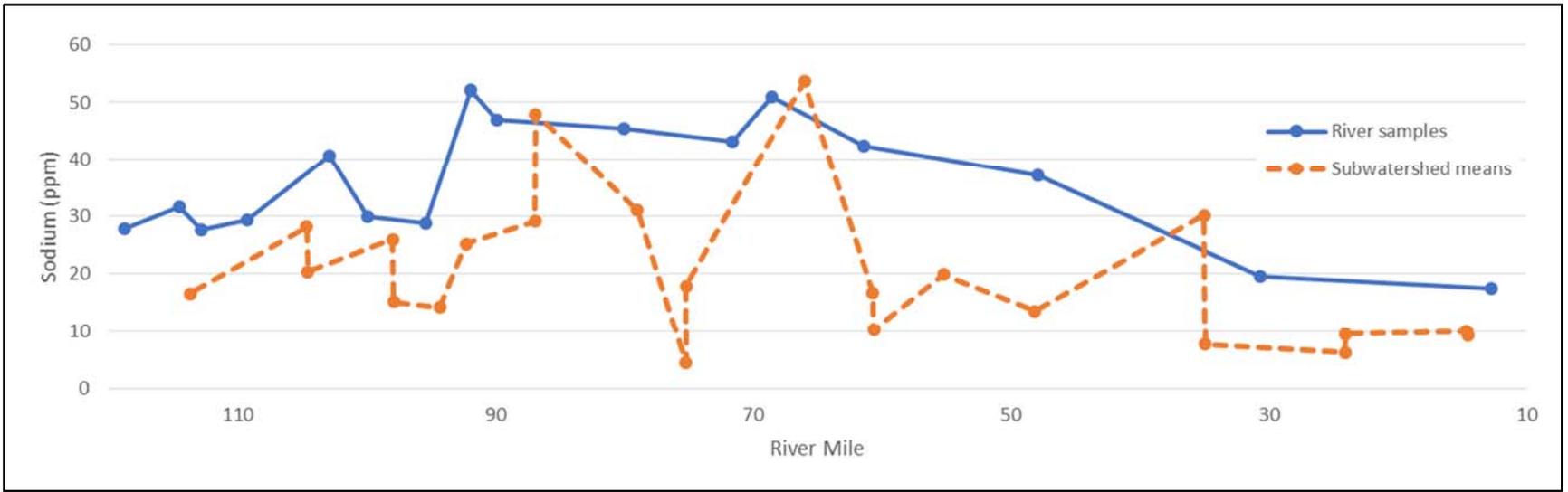


Figure 11. Sodium ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

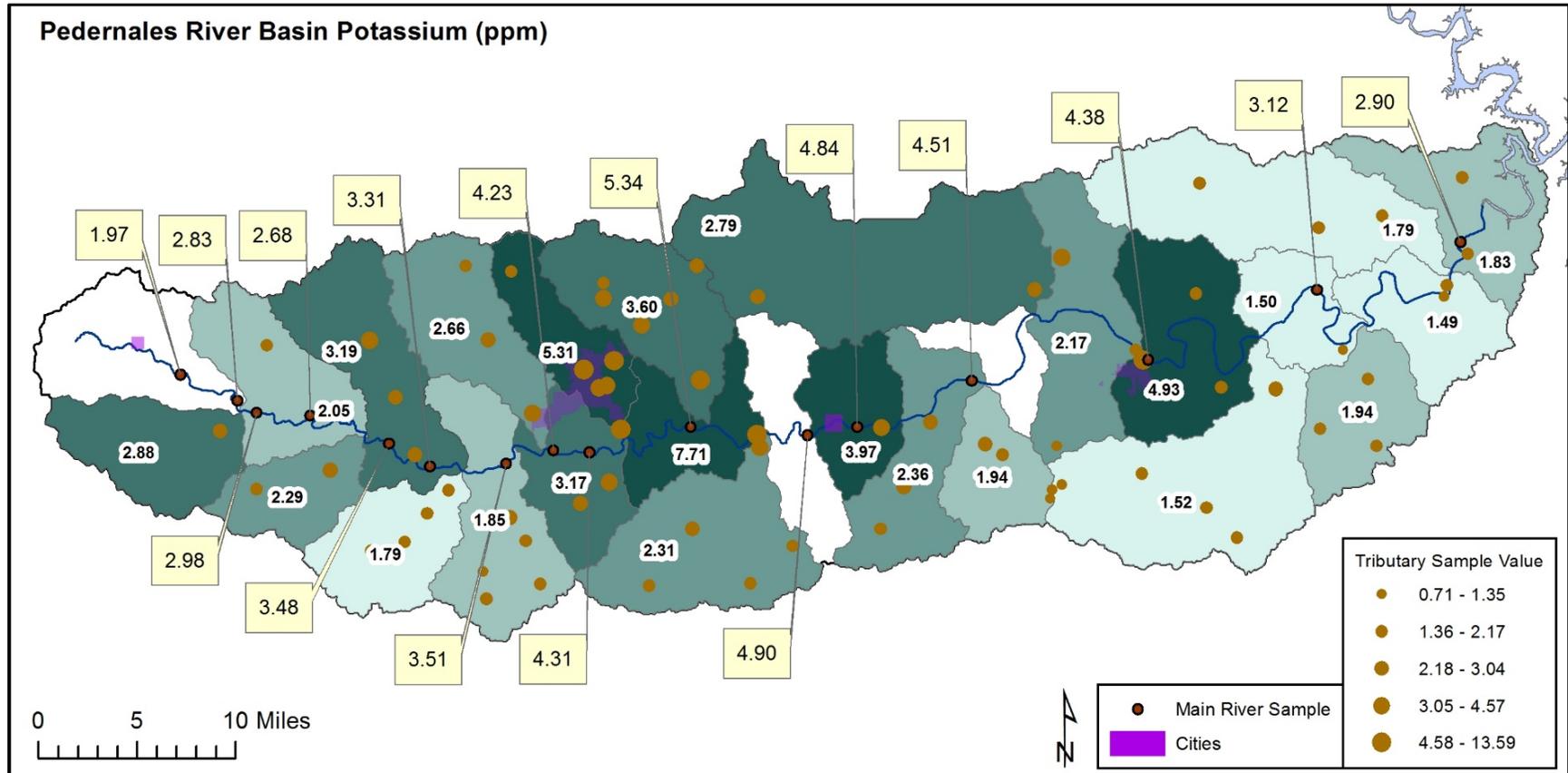


Figure 12. Potassium ion concentration map (ppm).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

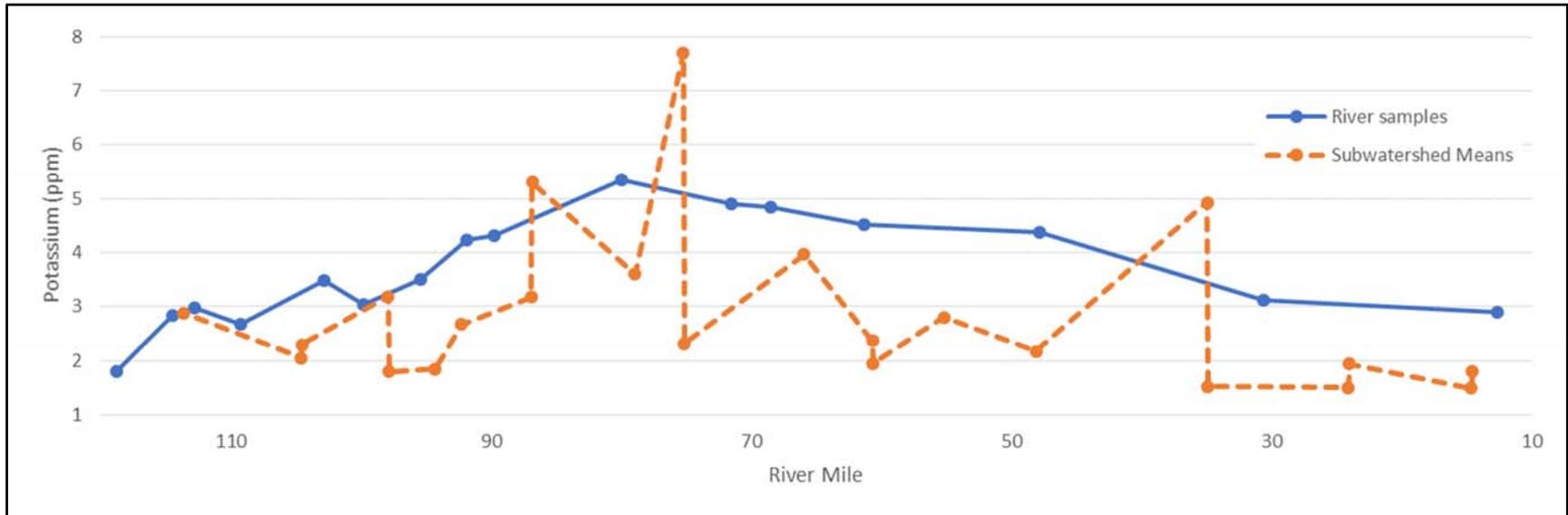


Figure 13. Potassium ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

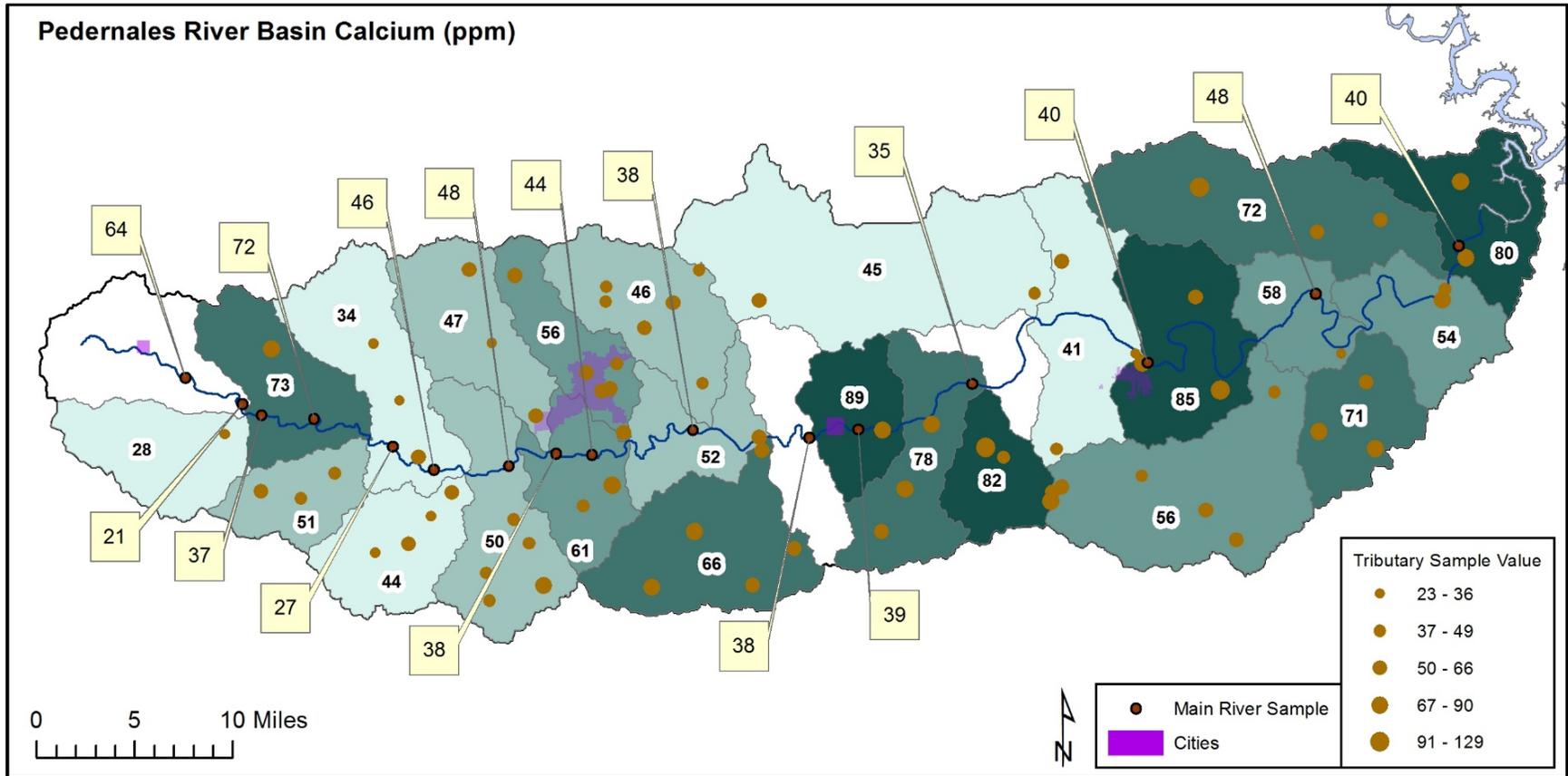


Figure 14. Calcium ion concentration map (ppm).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

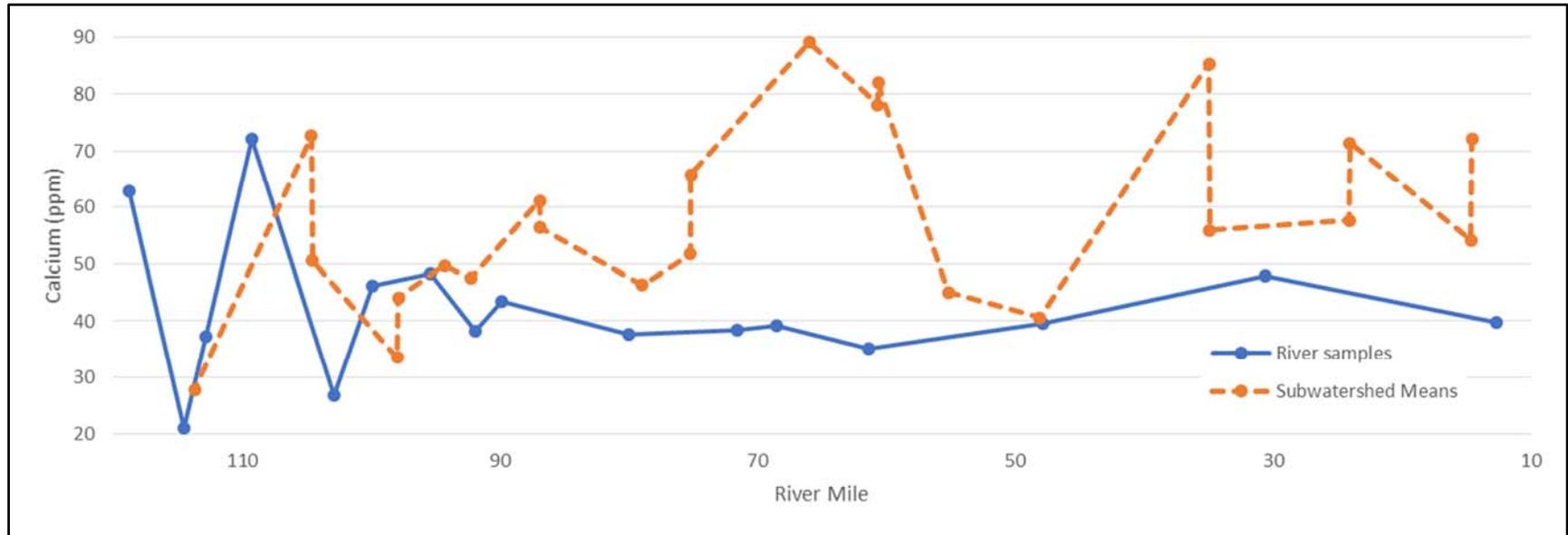


Figure 15. Calcium ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

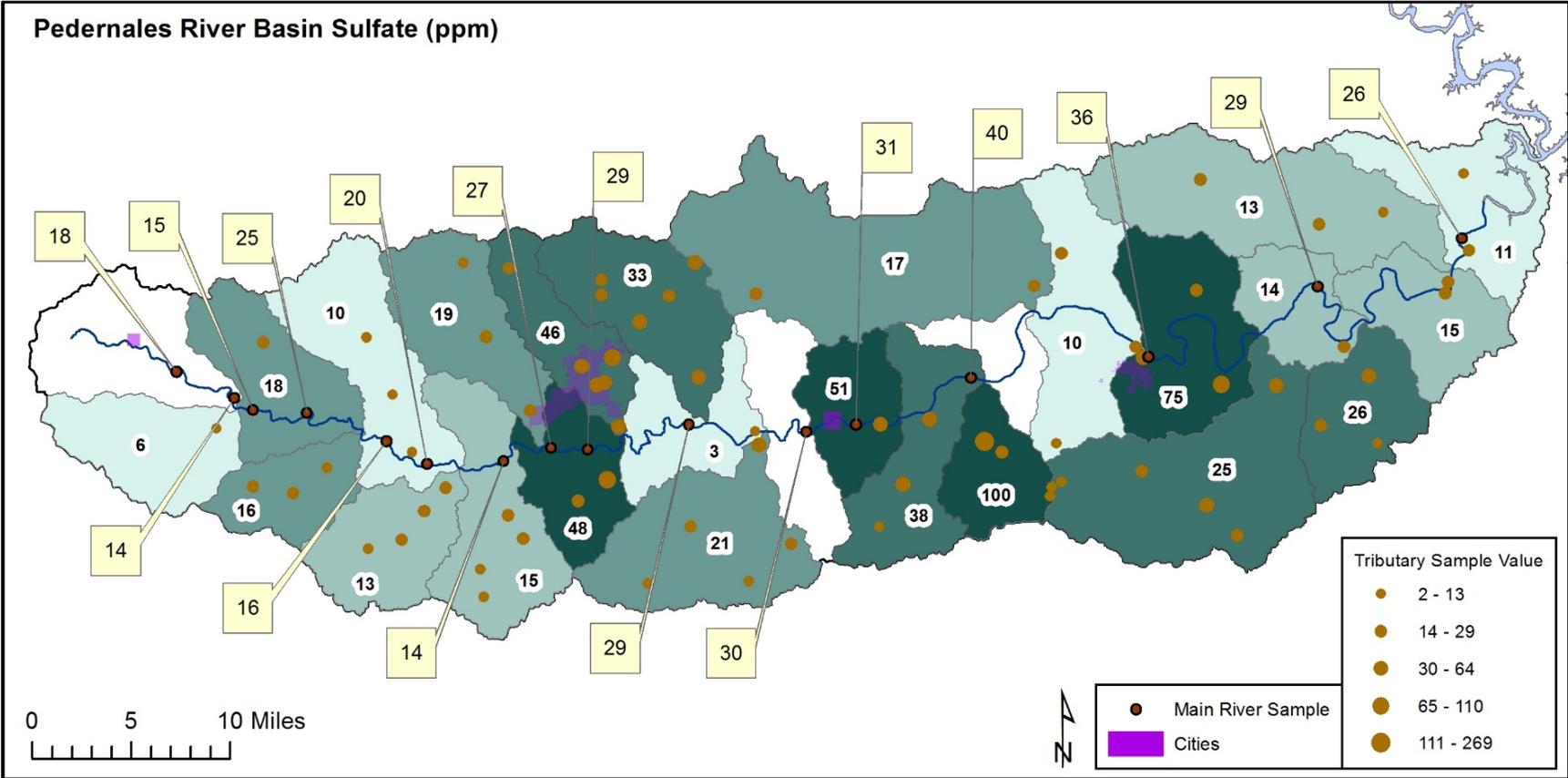


Figure 16. Sulfate ion concentration map (ppm). Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

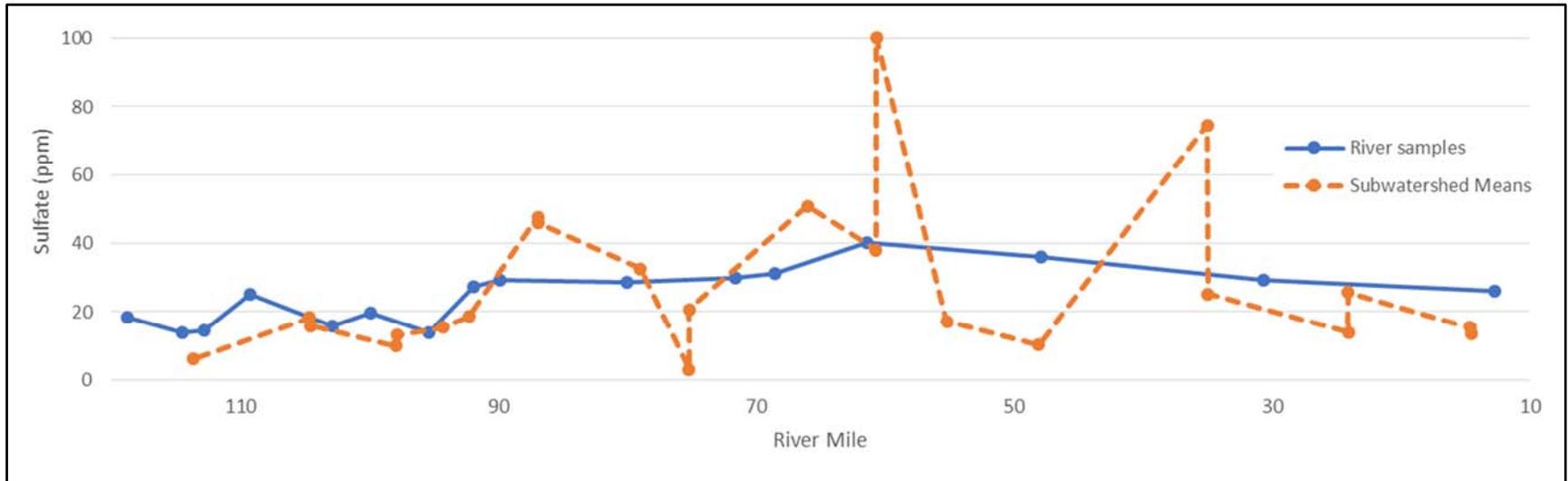


Figure 17. Sulfate ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

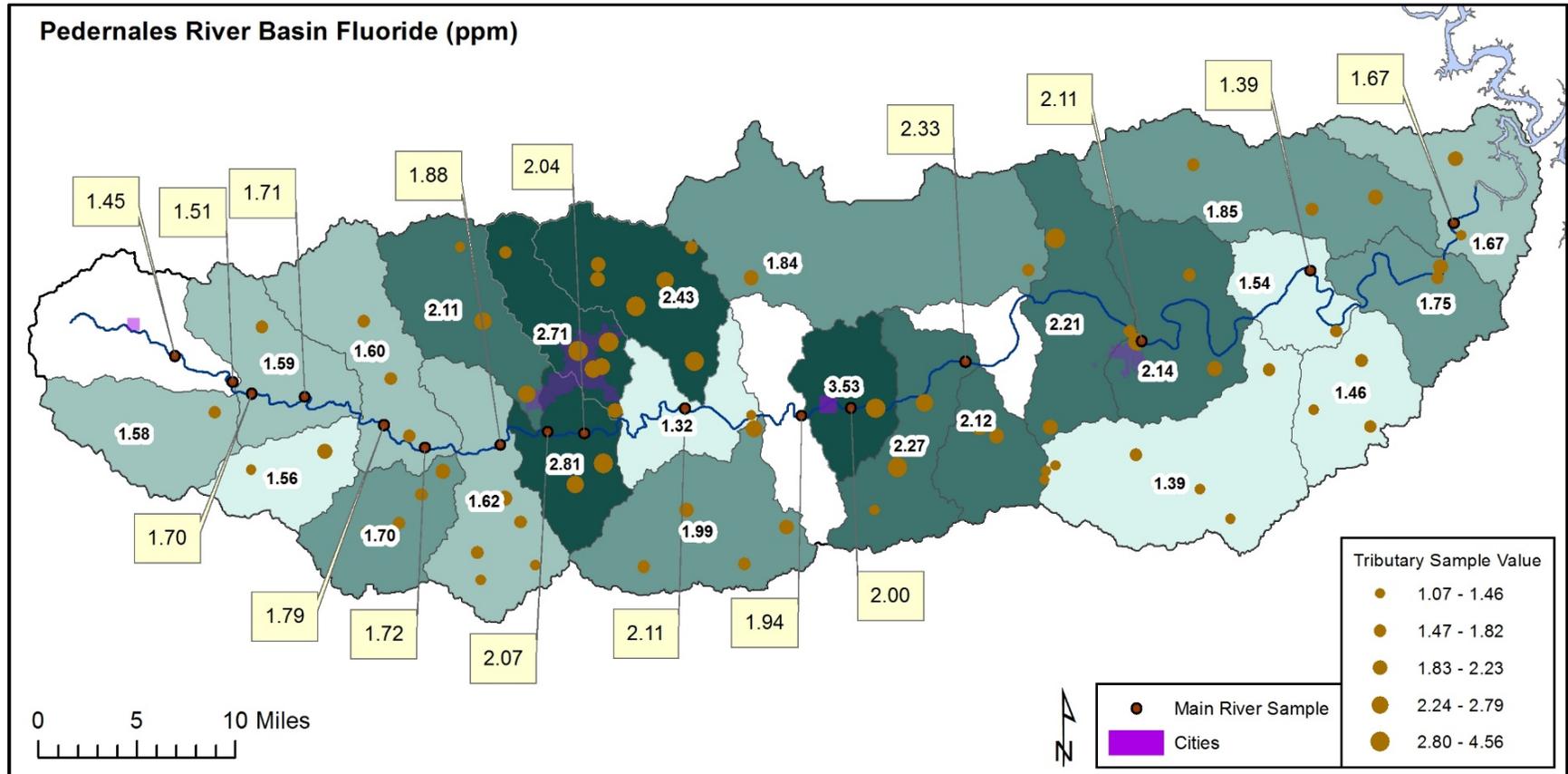


Figure 18. Fluoride ion concentration map (ppm). Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

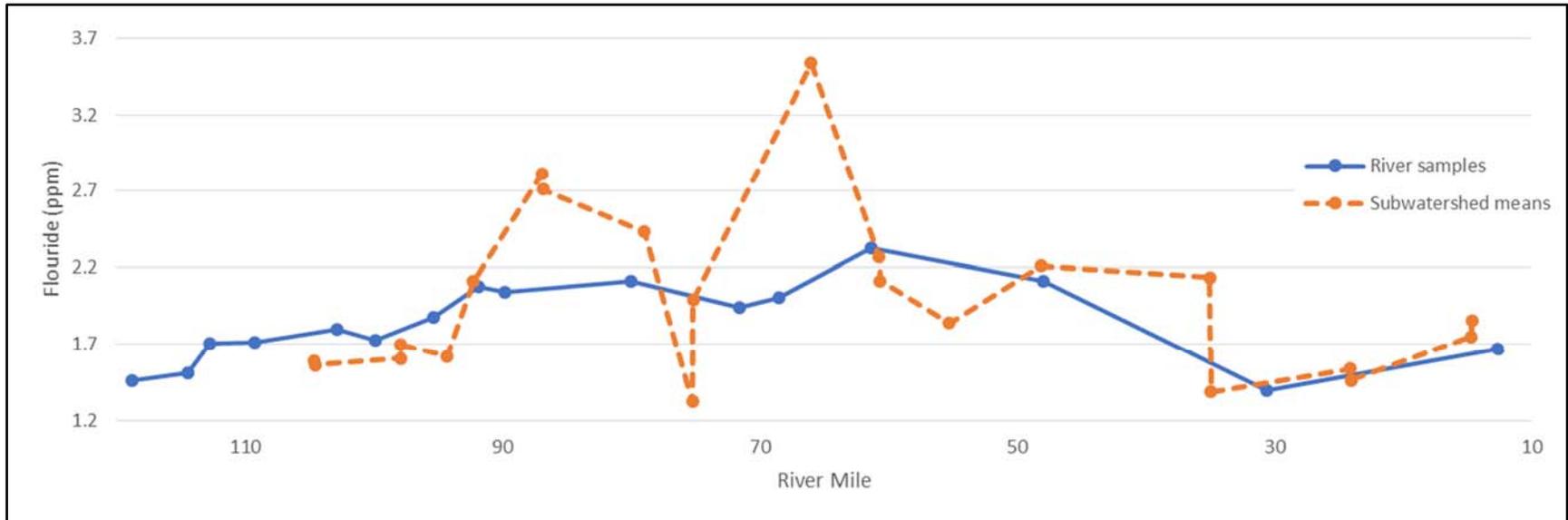


Figure 19. Fluoride ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

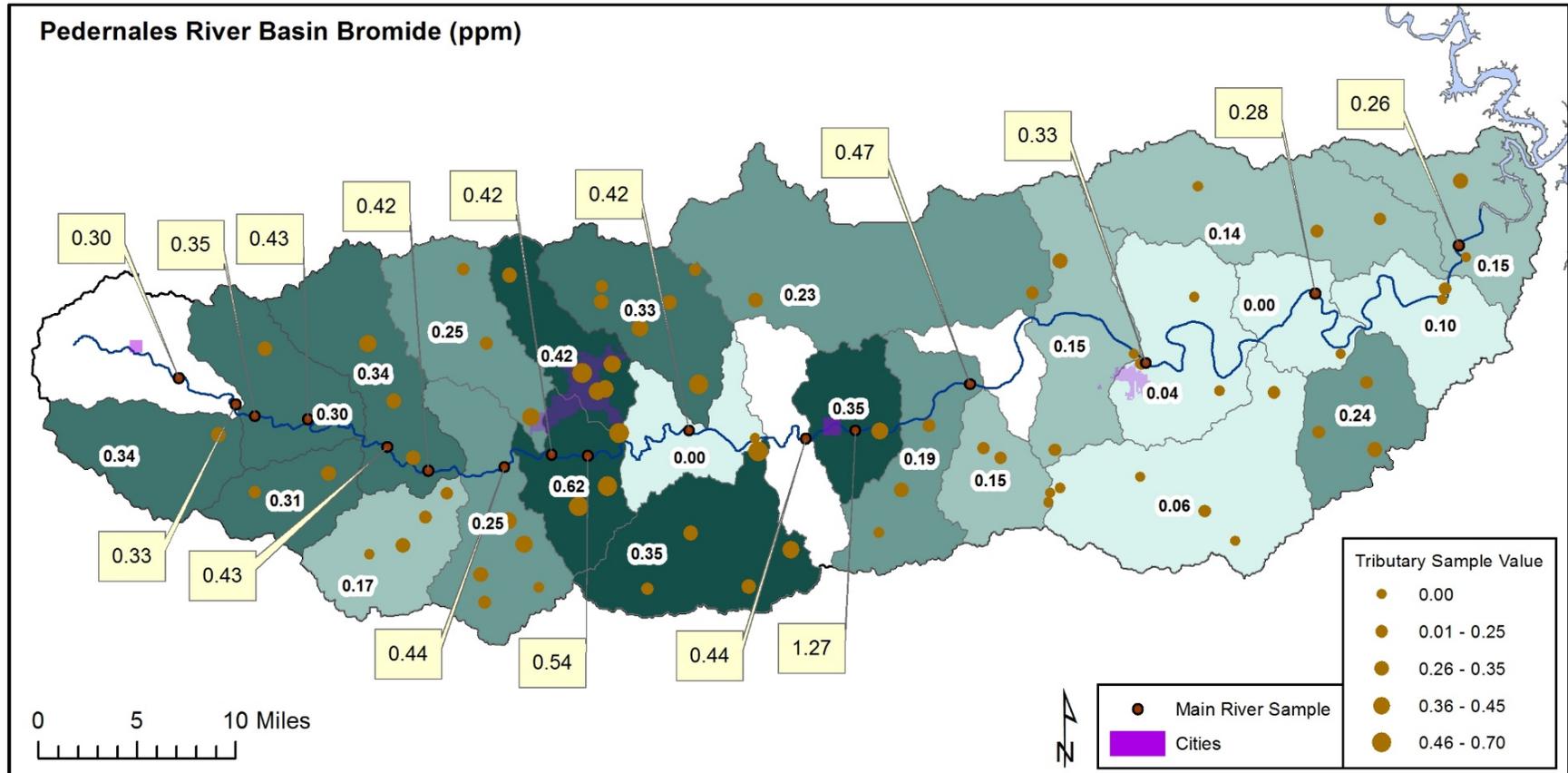


Figure 20. Bromide ion concentration map (ppm).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

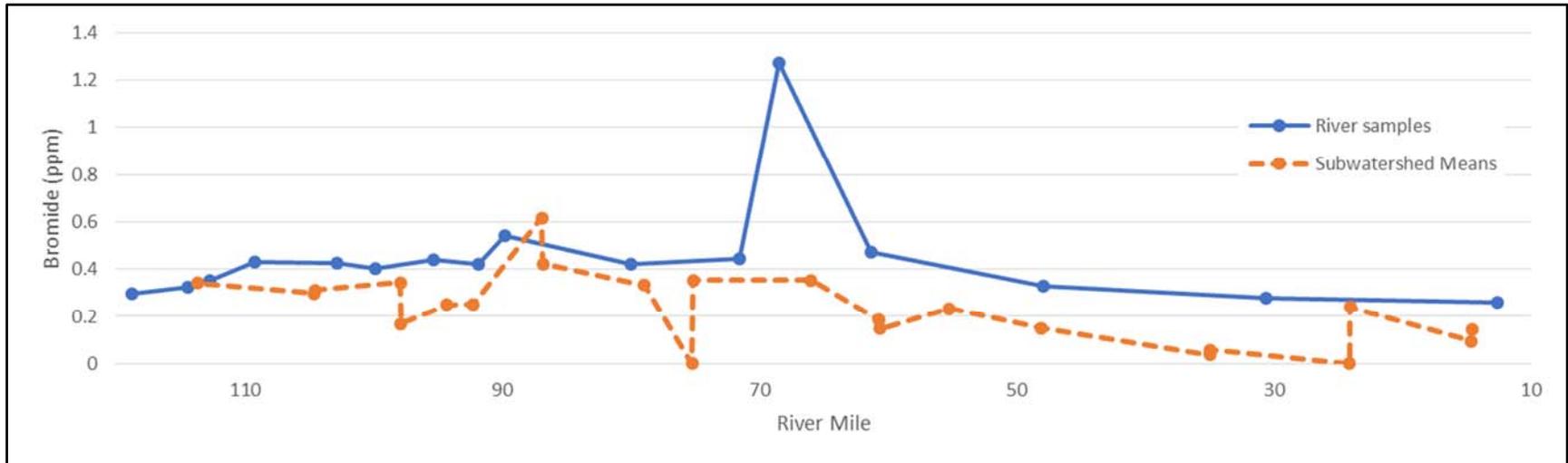


Figure 21. Bromide ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

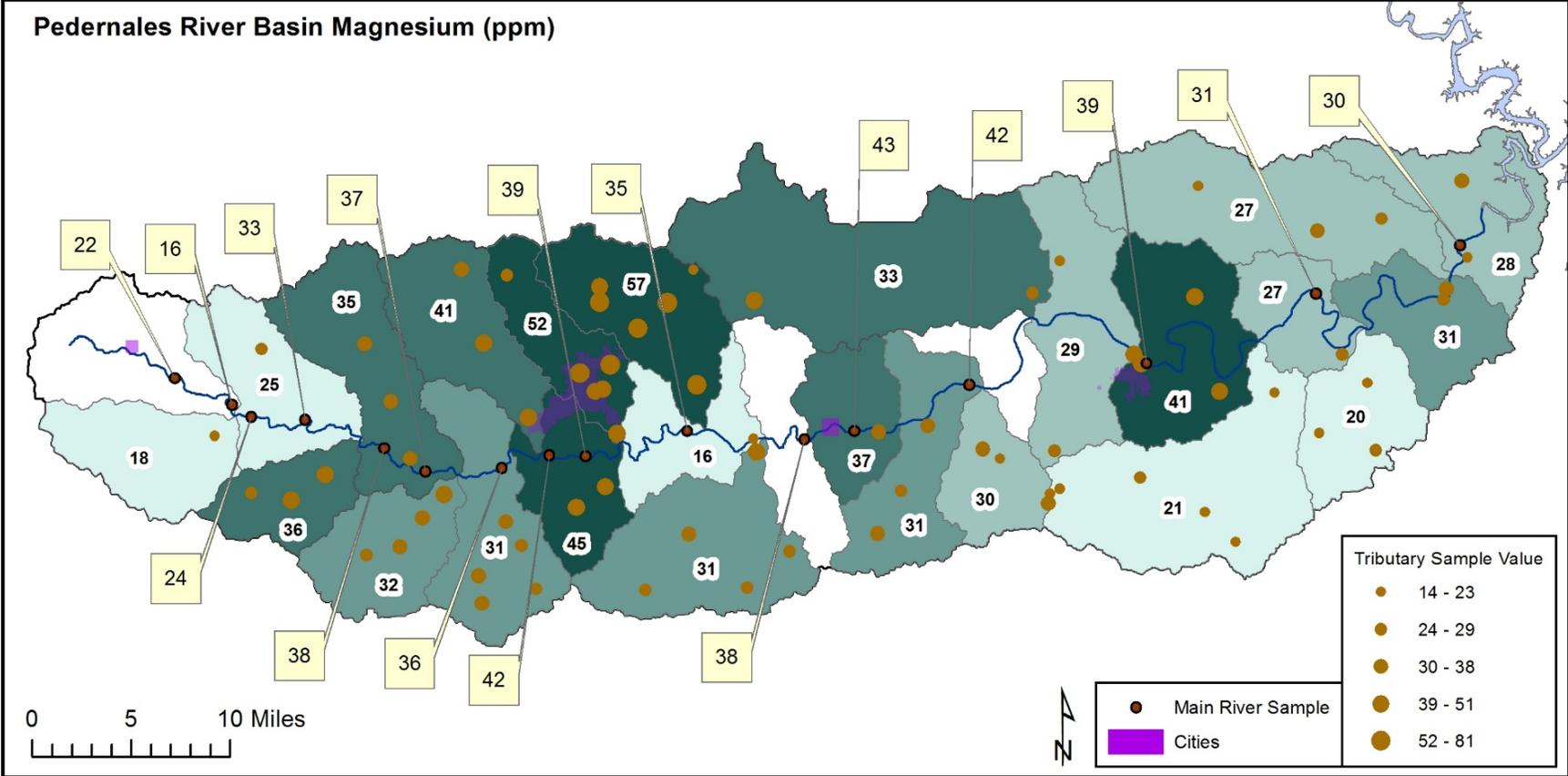


Figure 22. Magnesium ion concentration map (ppm). Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

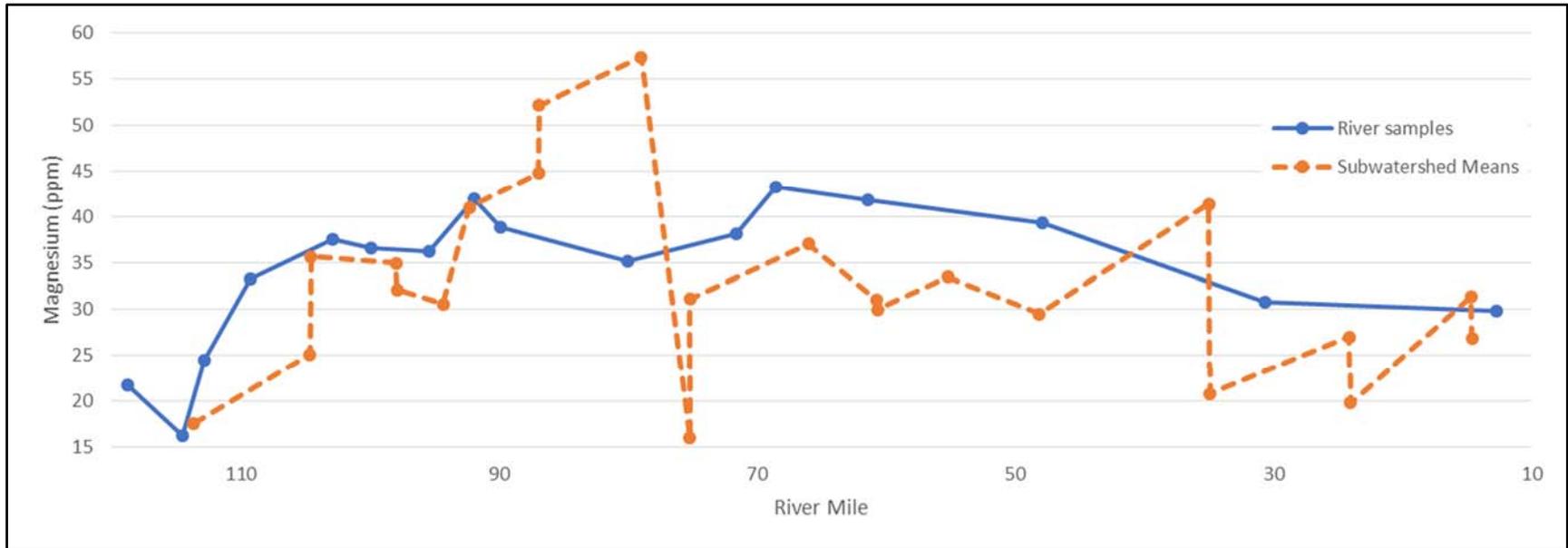


Figure 23. Magnesium ion concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

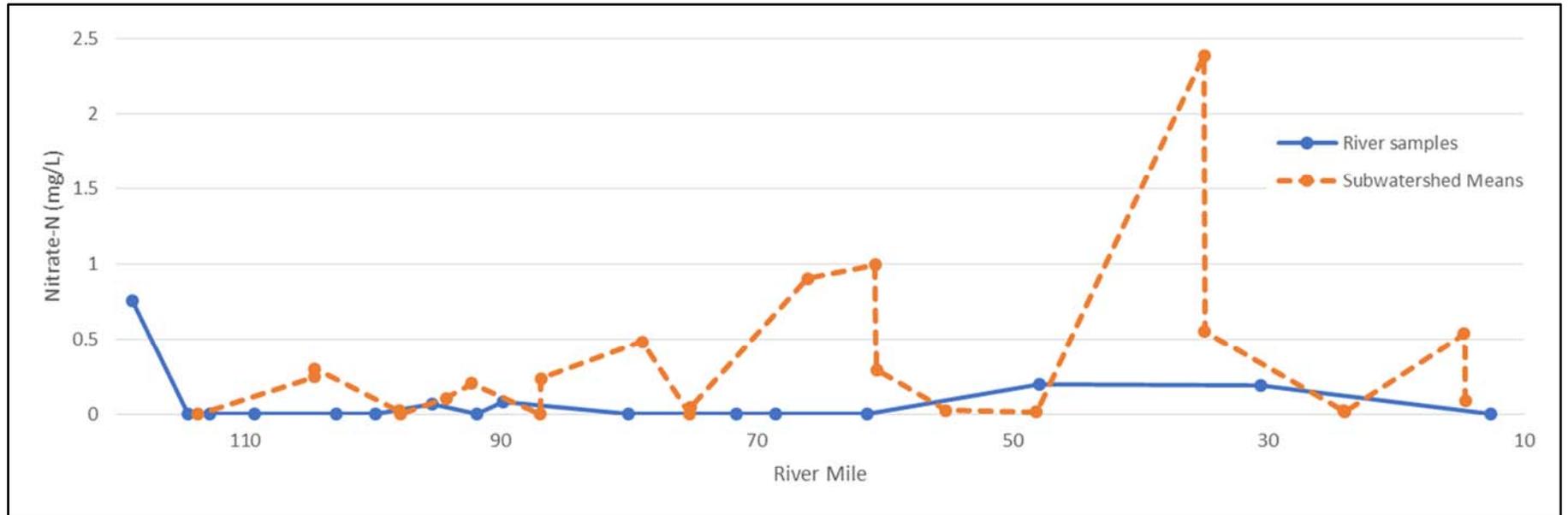


Figure 25. Nitrate-N concentration for river samples versus means for subwatersheds.
River mile for subwatersheds is calculated at the most downstream intersection with the river.

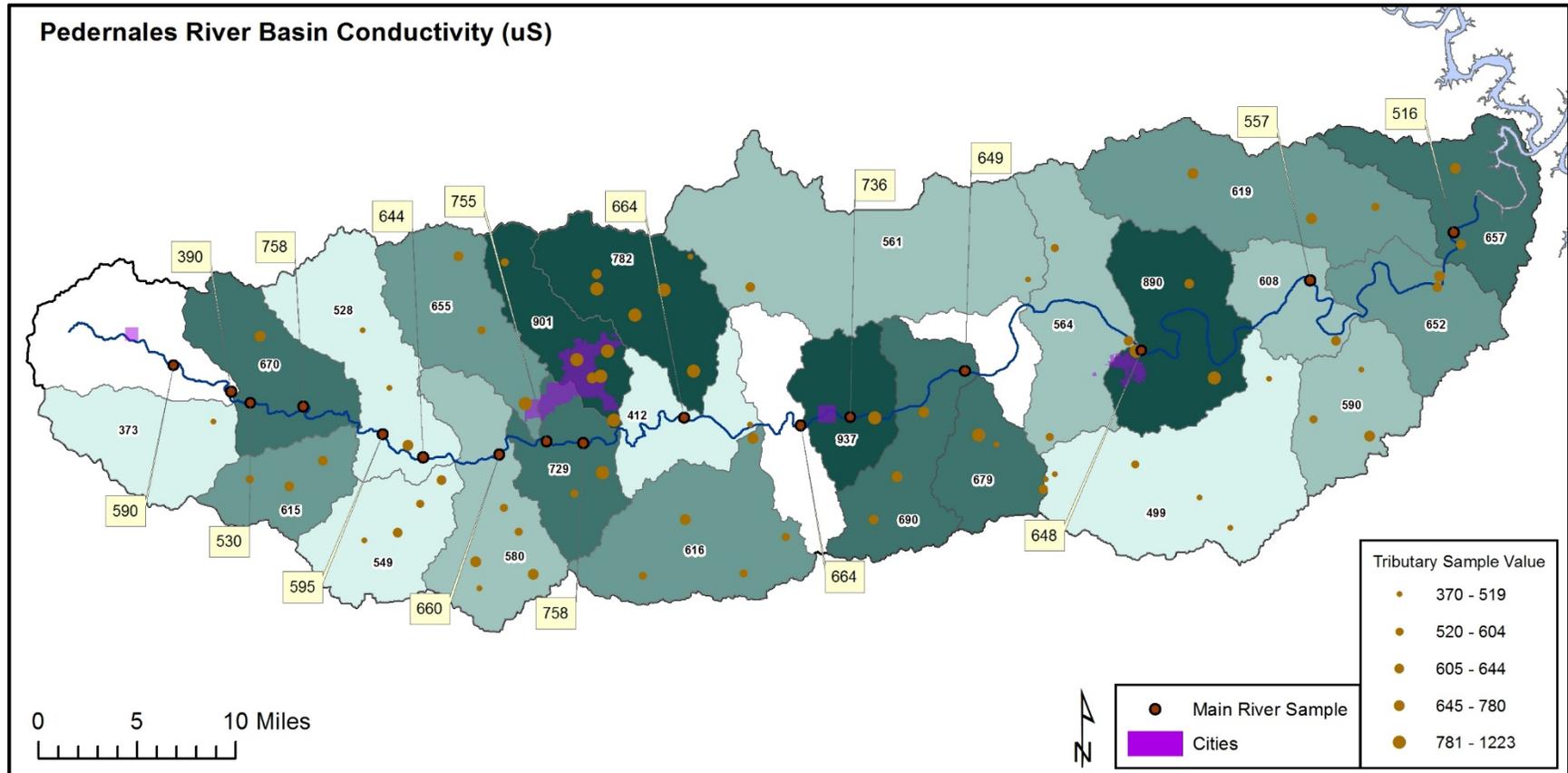


Figure 26. Conductivity map (μS).

Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

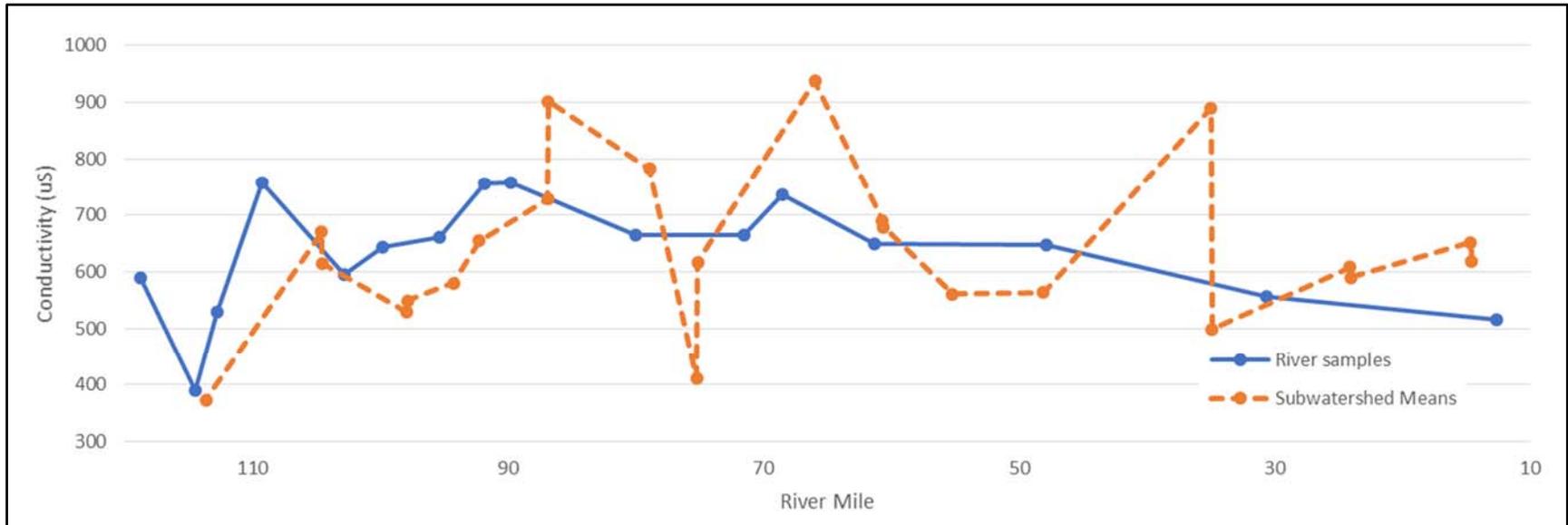


Figure 27. Conductivity for river samples versus means for subwatersheds.
River mile for subwatersheds is calculated at the most downstream intersection with the river.

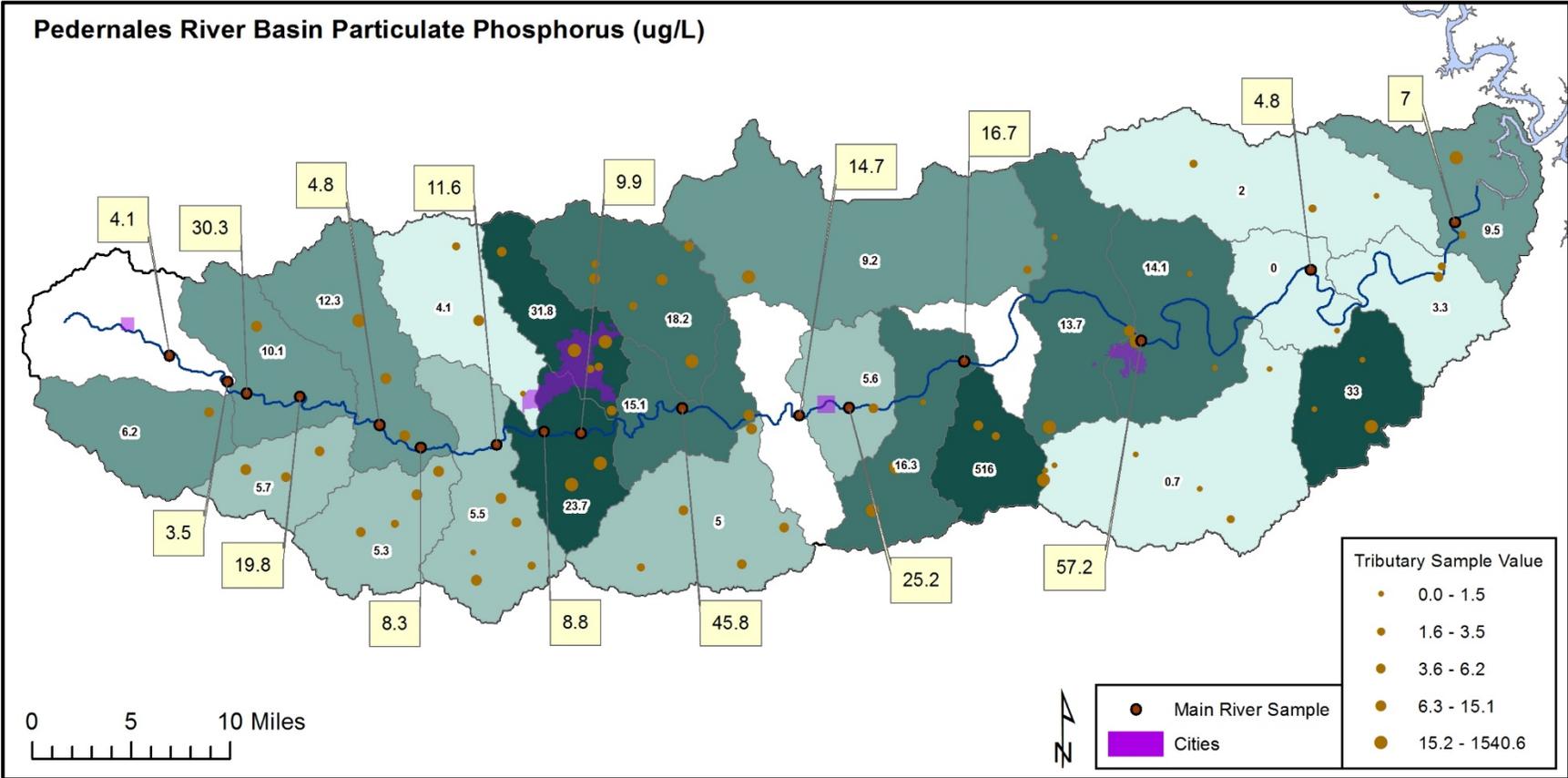


Figure 28. Particulate phosphorus concentration map ($\mu\text{g/L}$). Darker colored subwatersheds represent higher concentrations and lighter colors represent lower concentrations. White subwatersheds had no data. Numbers in yellow box labels represent river sample values, and numbers with white backgrounds are the mean for each subwatershed.

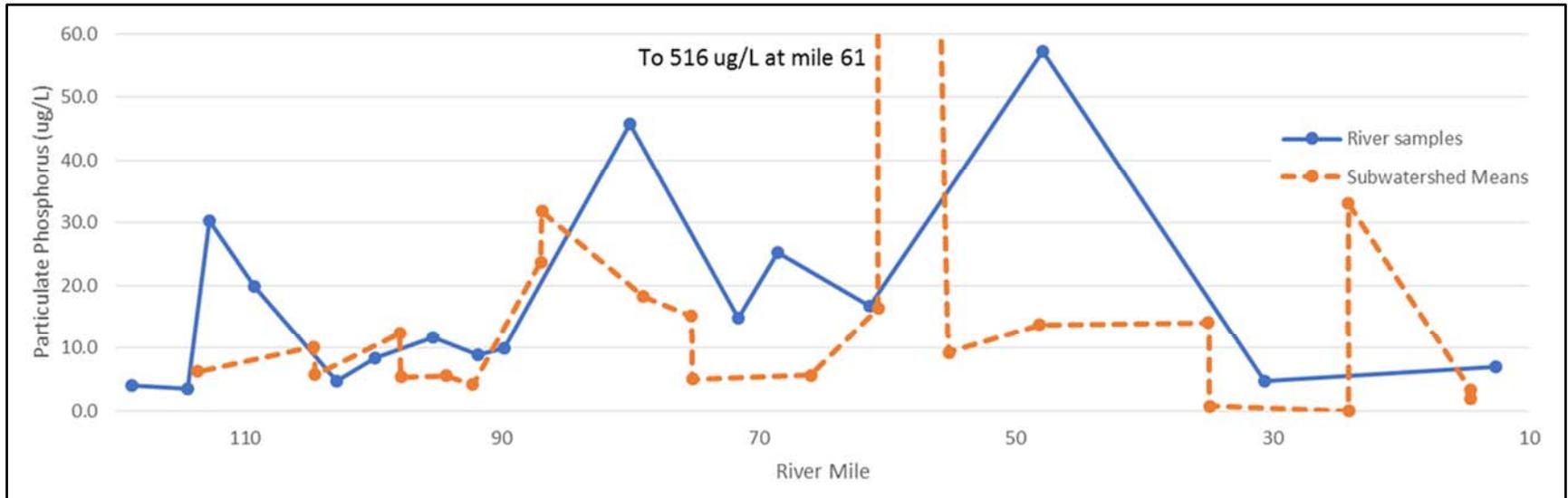


Figure 29. Particulate phosphorus concentration for river samples versus means for subwatersheds. River mile for subwatersheds is calculated at the most downstream intersection with the river.

The geochemistry of all water samples fall within the regional groundwater signature based on a piper diagram using TWDB well chemistry data (Figure 30). The spring samples are very similar to each other except for one which is elevated in sulfate (Figure 31). Two of the well samples are very different from most of the other samples, one in the Ellenburger Aquifer and one in the Lower Glen Rose Aquifer, and seem to be closer to end-member chemistry for the respective aquifers. This difference in water chemistry is likely a result of the wells pulling water from a deeper level than most springs in the basin. For anions, the samples are all bicarbonate type waters except for two Lower Glen Rose samples (one well and one tributary) which are sulfate type. For cations, waters range between calcium type, magnesium type, and mixed. This reflects the effects of dissolution of the regional limestone and dolomitic host rock on groundwater geochemistry. The only exception is the Ellenburger Aquifer well which is sodium/potassium type.

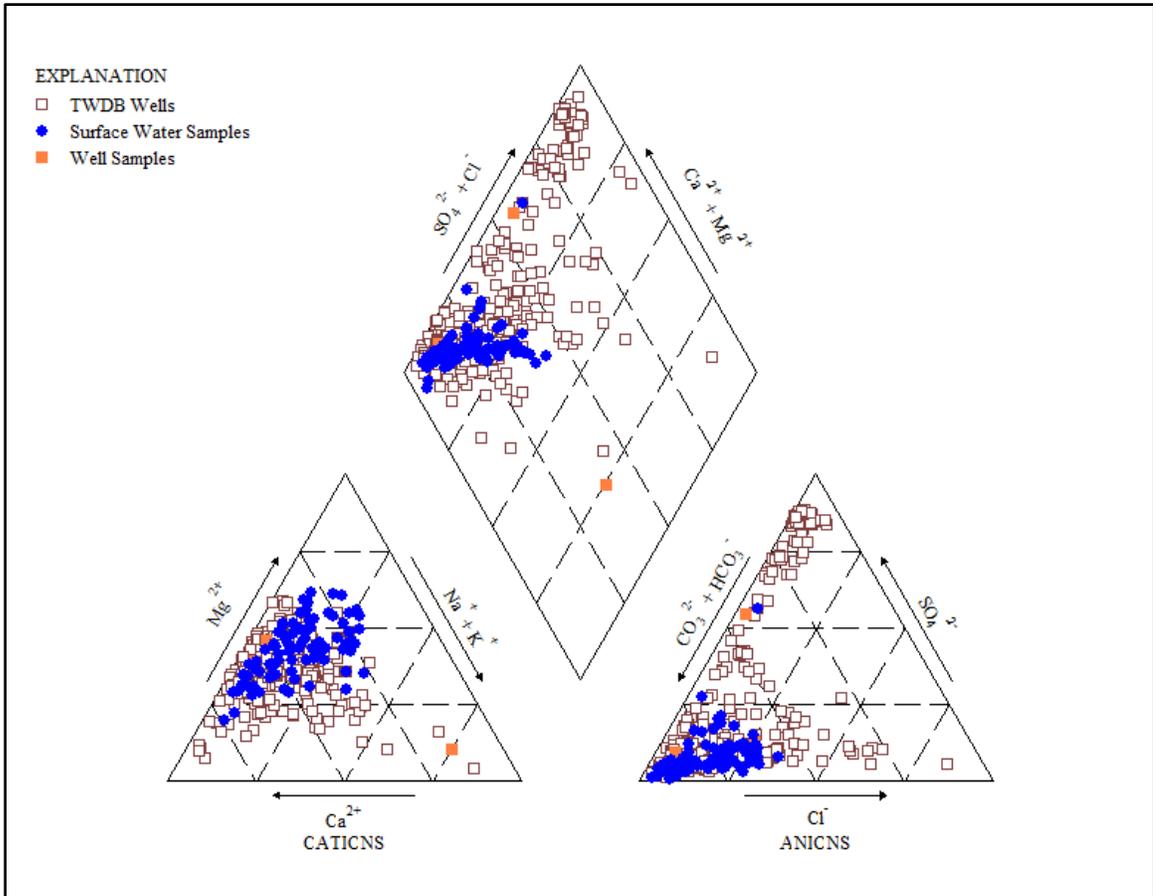


Figure 30. Piper diagram of synoptic water sample chemistry with TWDB well chemistry.

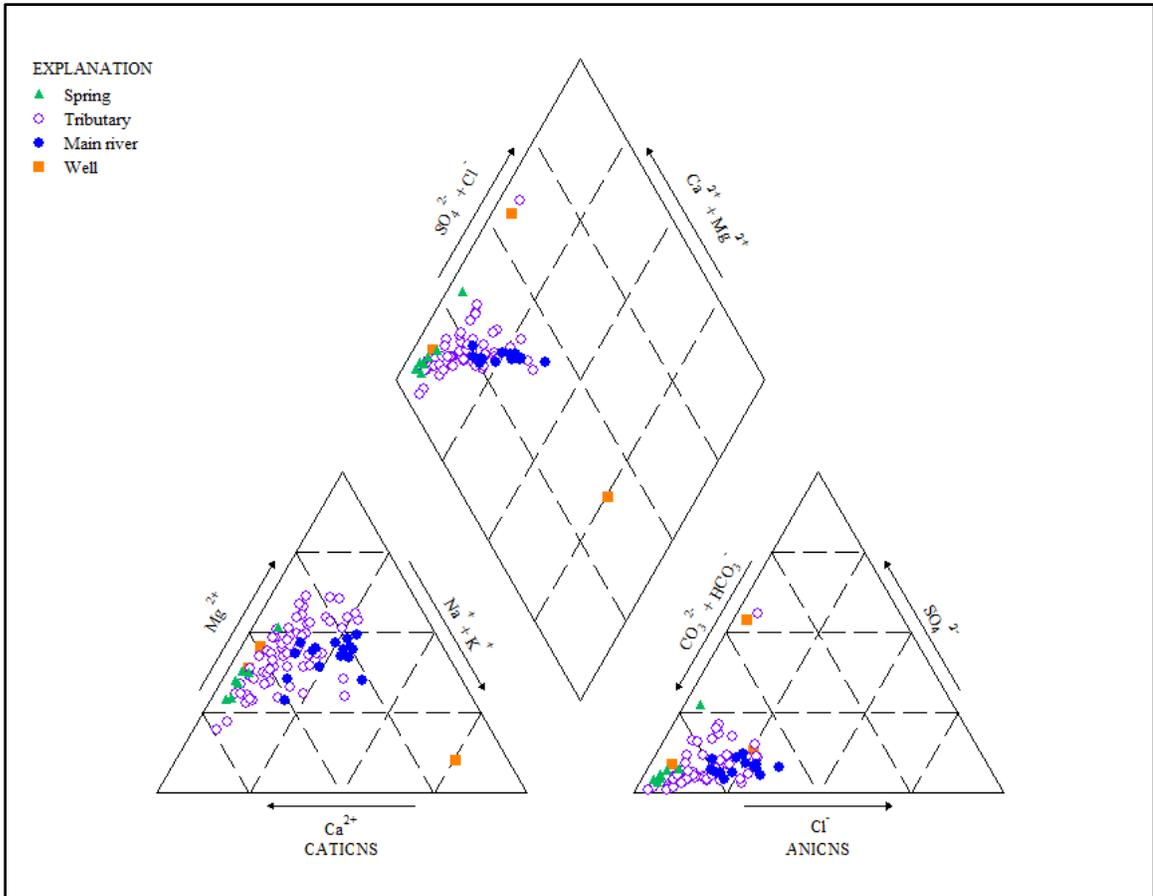


Figure 31. Piper diagram of synoptic sample chemistry.

4.3. Principal Component Analysis

Principal Component Analysis was applied to summarize the relative influence of components on the composition of the water. The first two principal components accounted for 44.3% of the variation among sites, or 28% and 17% respectively (Table 3). Principal component loadings are displayed graphically in Figure 32. The cut-off for strong loading of variables was arbitrarily set at $> |0.28|$ because that value captured several of the strongest variables on each component. Principal component 1 (PC1) shows strong negative loading with regard to Cl^- , Na^+ , K^+ , and PP. Principal component 2 (PC2) shows strong loading of enriched stable isotope ratios and high temperatures

grouped towards the negative with SC and Ca²⁺ grouped towards the positive. An inverse relationship exists between T and Ca²⁺ concentration.

Table 3. PCA variable loadings.
Loadings greater than |0.28| are in bold.

Variables	Loadings:	
	PC1	PC2
Fluoride (F ⁻)	-0.253	0.249
Chloride (Cl ⁻)	-0.304	0.078
Bromide (Br ⁻)	-0.255	-0.004
Nitrate (NO ₃ ⁻)	0.030	0.229
Sulfate (SO ₄ ²⁻)	-0.090	0.265
Sodium (Na ⁺)	-0.304	0.110
Potassium (K ⁺)	-0.307	0.049
Magnesium (Mg ²⁺)	-0.269	0.182
Calcium (Ca ²⁺)	0.072	0.315
Oxygen isotope ratio (δ ¹⁸ O)	-0.201	-0.329
Hydrogen isotope ratio (δ ² H)	-0.205	-0.320
Total Suspended Solids (TSS)	-0.184	-0.175
Non-volatile Suspended Solids (NVSS)	-0.143	-0.198
Total Nitrogen (TN)	-0.141	0.129
Total Phosphorus (TP)	-0.162	0.029
Conductivity (SC)	-0.232	0.356
Particulate Nitrogen (PN)	-0.219	-0.155
Particulate Carbon (PC)	-0.189	-0.174
Dissolved Organic Carbon (DOC)	-0.248	-0.141
Ammonium (NH ₄)	-0.153	0.229
Particulate Phosphorus (PP)	-0.282	-0.055
Soluble Reactive Phosphorus (SRP)	-0.126	0.076
Time of collection (time)	-0.046	0.041
Temperature (T)	-0.063	-0.313
Odor	-0.008	-0.054
% Variance	28	17

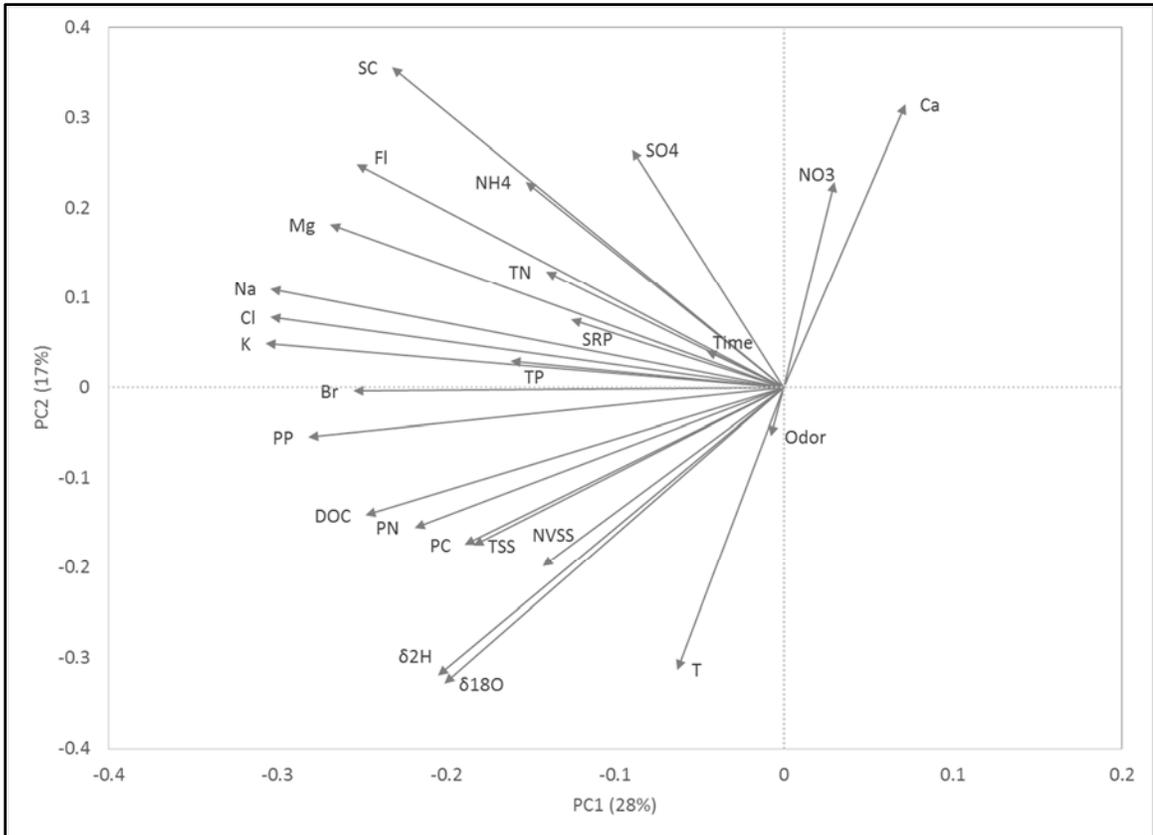


Figure 32. Graph of PCA loadings of each variable.
 Length and direction of lines correlate with loadings from Table 3.

A component score is calculated for each sample by multiplying the PC loadings by the normalized values and adding all variables together.

$$\begin{aligned} \text{For example: PC1 score} = & -0.253(\text{F}^-) - 0.304(\text{Cl}^-) - 0.255(\text{Br}^-) + 0.030(\text{NO}_3^-) - \\ & 0.090(\text{SO}_4^{2-}) - 0.304(\text{Na}^+) - 0.307(\text{K}^+) - 0.269(\text{Mg}^{2+}) + 0.072(\text{Ca}^{2+}) - 0.201(\delta^{18}\text{O}) - \\ & 0.205(\delta^2\text{H}) - 0.184(\text{TSS}) - 0.143(\text{NVSS}) - 0.141(\text{TN}) - 0.162(\text{TP}) - 0.232(\text{SC}) - \\ & 0.219(\text{PN}) - 0.189(\text{PC}) - 0.248(\text{DOC}) - 0.153(\text{NH}_4) - 0.282(\text{PP}) - 0.126(\text{SRP}) - \\ & 0.046(\text{time}) - 0.063(\text{T}) - 0.008(\text{odor}) \end{aligned}$$

The relative influence of each loading on the water sample is reflected by these values. In a plot of the component scores for PC1 and PC2 (Figure 33), the spring samples plot close together, and the tributary and river samples show more variation. The variance in one spring sample, which plots higher on the PC2 axis, is a result of high sulfate.

Tributary samples spread out in three directions away from the spring (groundwater) signature, and river samples in two directions. All springs plot high on the PC1 axis and thus have low values of K, Cl, Na, and PP compared to the tributary and river samples. The tributary and river samples are pulled in the negative direction on PC2 by high $\delta^{18}\text{O}$, $\delta^2\text{H}$, and T and in the positive direction by high SC and Ca. All river samples are influenced by evaporitic enrichment in stable isotopes, but some tributary samples appear to be more strongly influenced by chemistry than evaporitic enrichment.

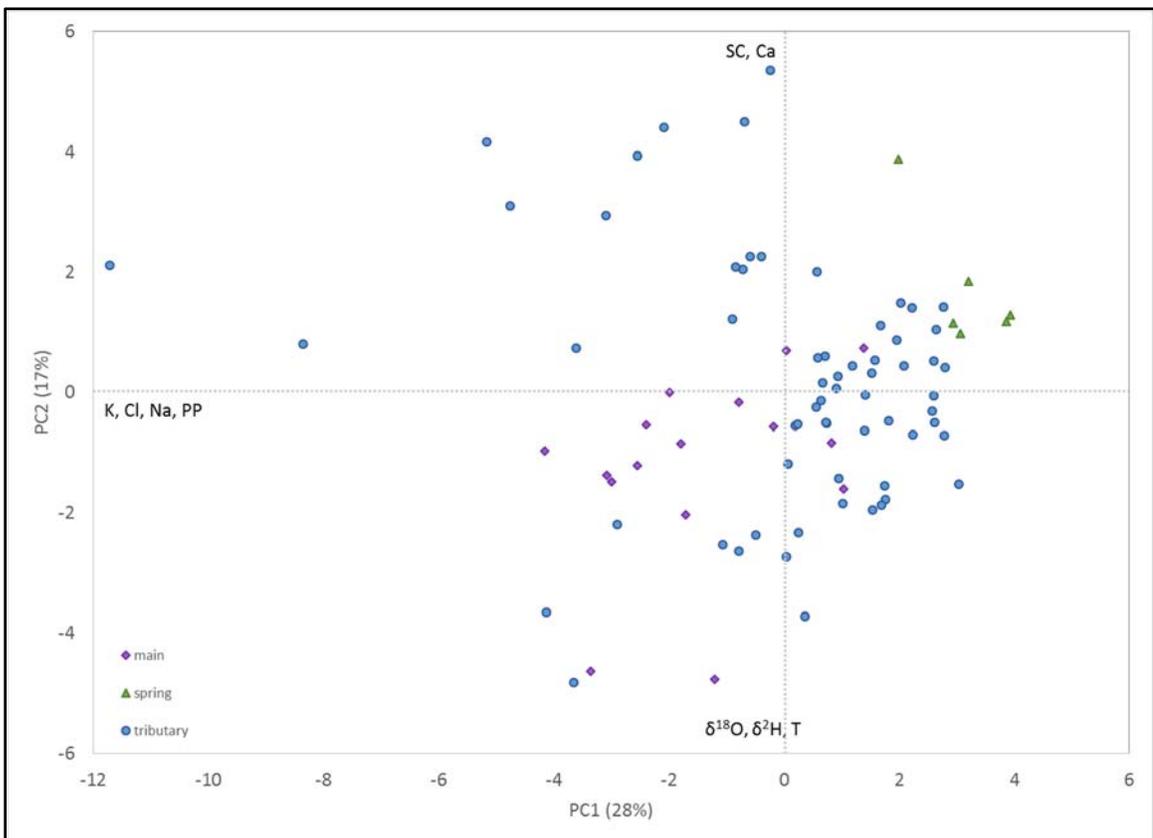


Figure 33. PCA component score graph.

By combining the PCA component score plot with the isotopic enrichment gradient, a distinct trend is apparent (Figure 34). Using less enriched samples as a proxy for groundwater, some variation in groundwater chemistry is evident, but the overall driver of chemical evolution appears to be evaporation.

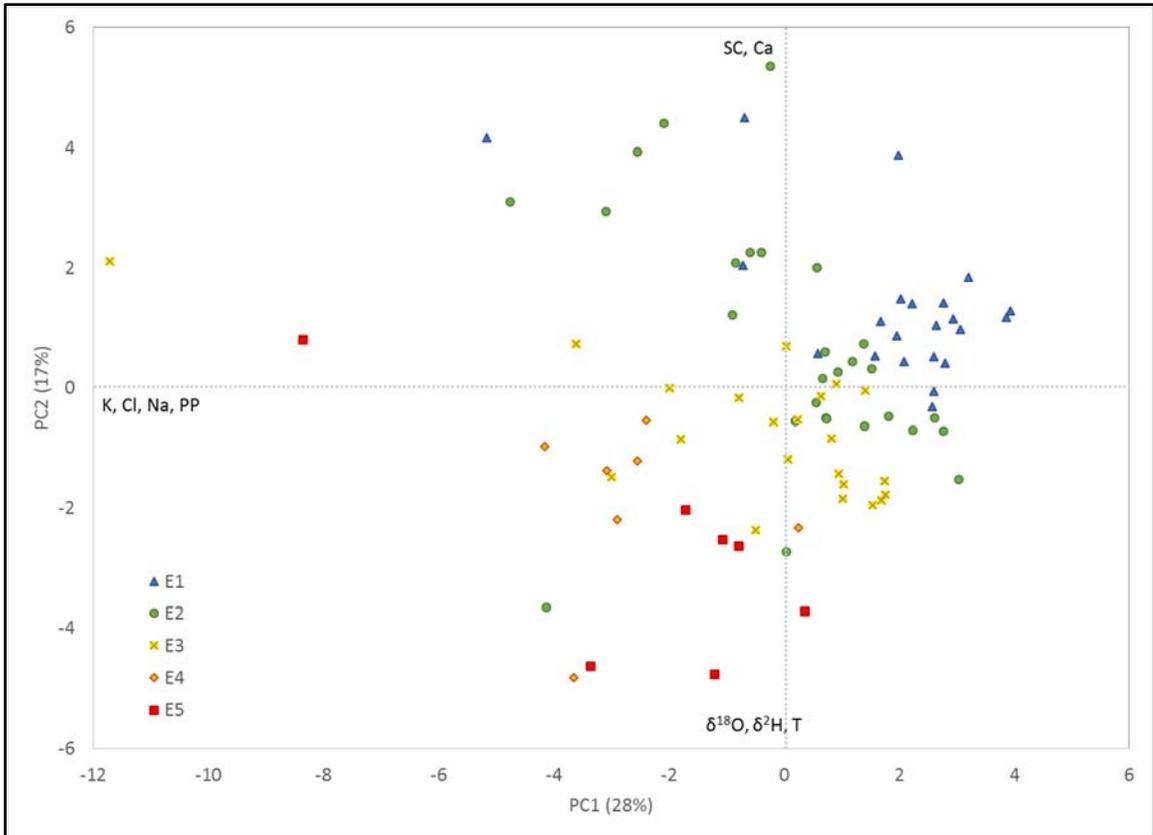


Figure 34. PCA component scores graphed by isotopic enrichment gradient.

4.4. Historic Data Comparison

A baseflow water quality study was performed in the Pedernales river basin in 1962 (Holland and Hughes 1964). The river chemistry from 1962 is compared with the river chemistry from the 2015 synoptic sampling by river mile in Figure 35 through Figure 41. Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} concentrations were generally similar during the recent and historic sampling events, though some heterogeneity occurs in the headwaters due to sampling locations. One pattern that emerged was ion concentrations just downstream of Fredericksburg were higher in 1962 than during the recent sampling. Downstream of Johnson City, Ca^{2+} and NO_3^- were slightly higher in 2015 than in 1962, while Mg^{2+} and SO_4^{2-} were very similar. Cl^- and Na^+ were similar in the headwaters and then higher in all 1962 samples downstream of Fredericksburg. F^- was higher in the 2015

samples than in the 1962 samples, though this may be due to a difference in methodologies as detection technology improves. NO_3^- was much higher in the near-headwater sample from 1962, and was highest in Baron's creek (not shown on river graph), higher than any sample from 2015.

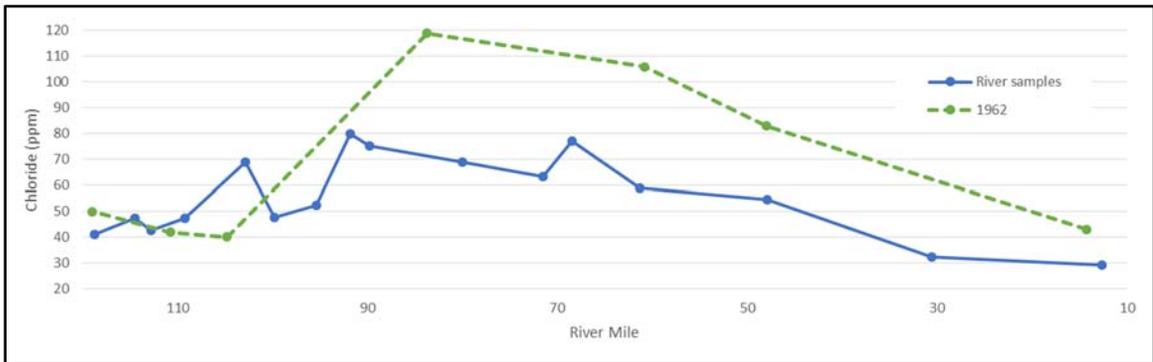


Figure 35. Chloride by river mile in 2015 and 1962.

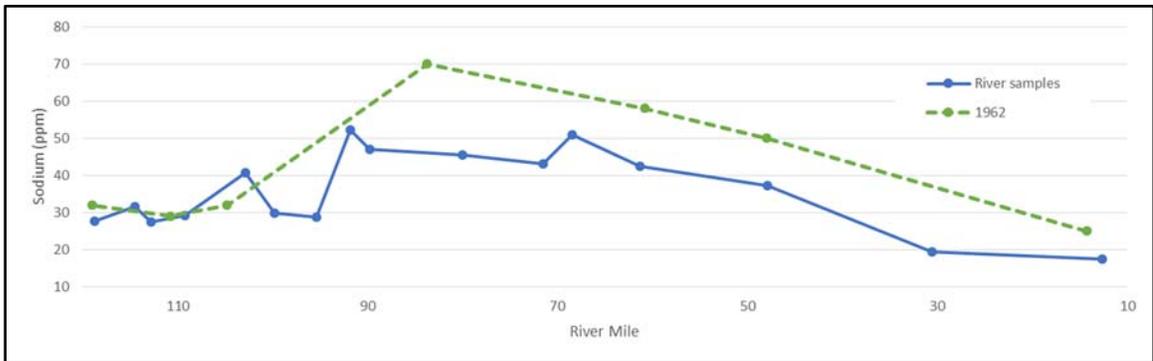


Figure 36. Sodium by river mile in 2015 and 1962.

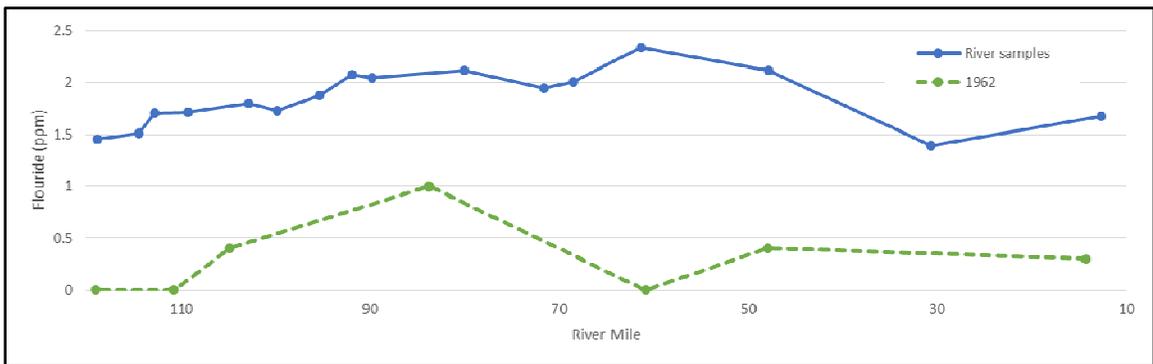


Figure 37. Fluoride by river mile in 2015 and 1962.

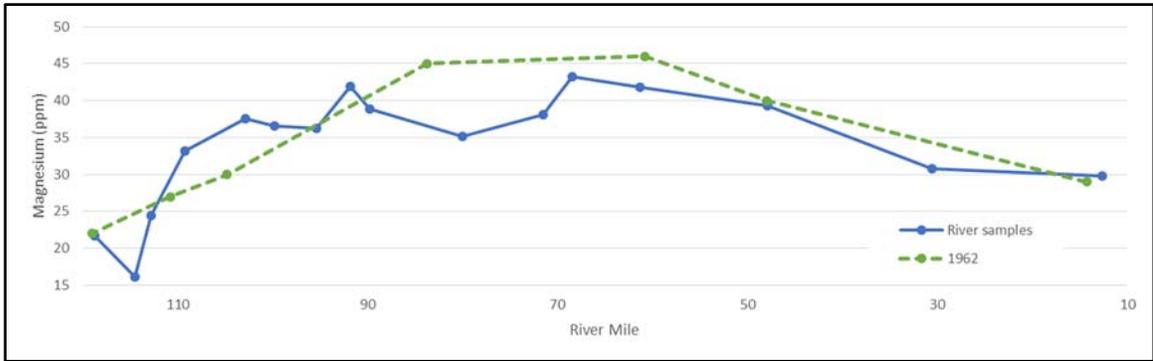


Figure 38. Magnesium by river mile in 2015 and 1962.

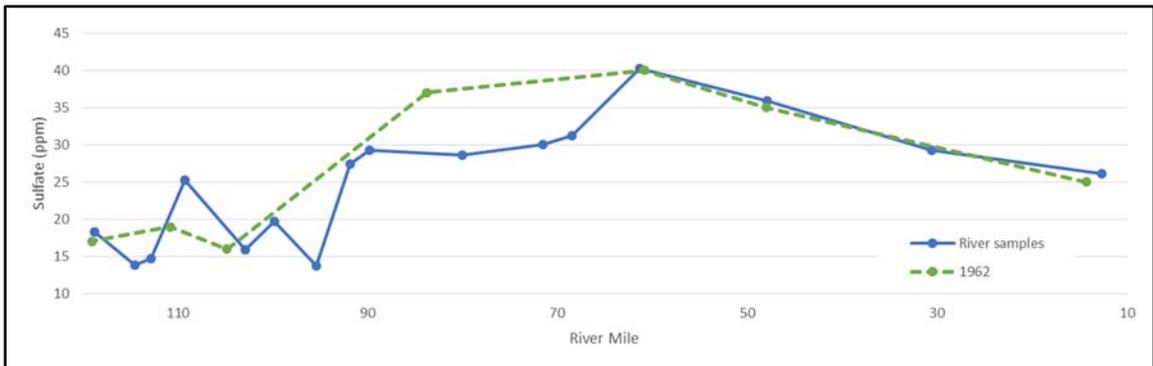


Figure 39. Sulfate by river mile in 2015 and 1962.

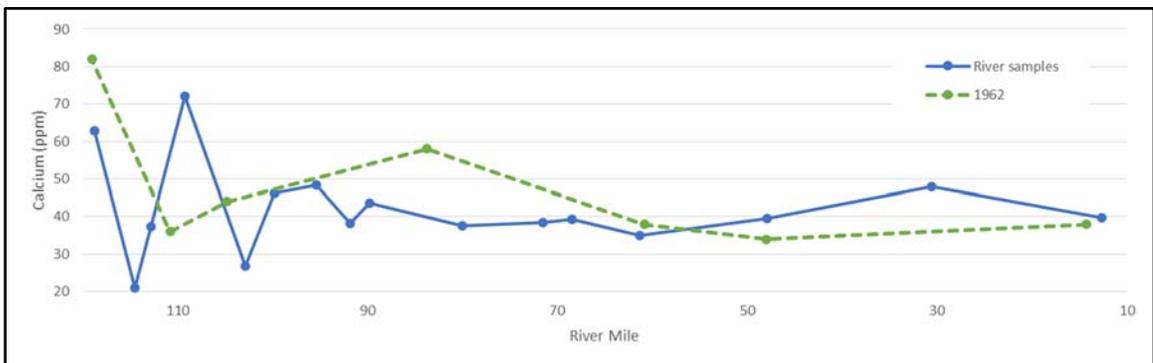


Figure 40. Calcium by river mile in 2015 and 1962.

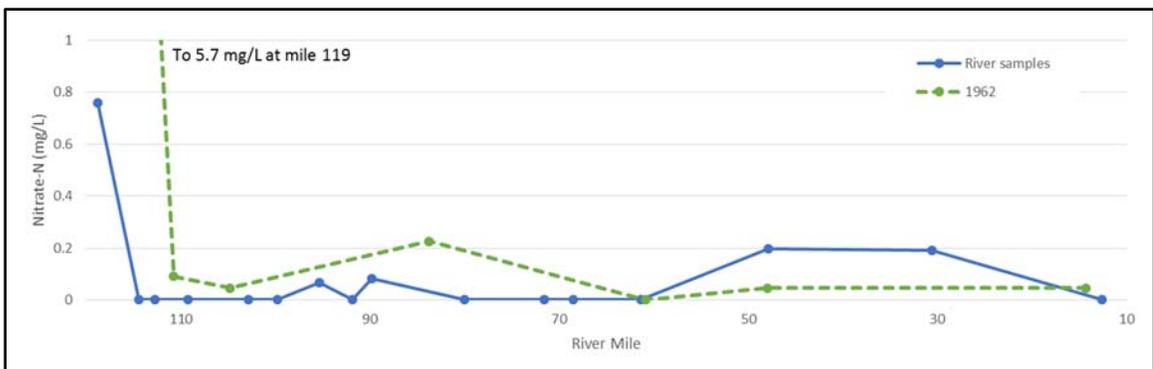


Figure 41. Nitrate-N by river mile in 2015 and 1962.

Comparison of 17 years (1998-2014) of river and tributary flow volume discharge data from the USGS Pedernales River gage at Fredericksburg and HCUWCD gauging events at Live Oak Creek and Barons Creek revealed linear relationships between each creek and the river (Figure 42 and Figure 43). For Live Oak Creek, the relationship has an R^2 of 0.76 and is defined by the equation: Live Oak cfs = $0.1175(\text{Pedernales cfs at Fredericksburg}) + 1.1529$. For Barons Creek the relationship has an R^2 of 0.73 and is defined by the equation: Barons cfs = $0.0864(\text{Pedernales cfs at Fredericksburg}) + 1.4838$. These relationships imply that these two creeks often continue flowing after the flow in the river has reduced to zero. By combining these relationships with the flow in the Pedernales River at Fredericksburg during the synoptic sampling (1.0 cfs), flow was estimated in the two creeks. At Live Oak Creek the flow was approximately 1.27 cfs, and at Barons Creek the flow was approximately 1.57 cfs. Live Oak Creek discharges to the river upstream of the USGS gage in Fredericksburg, and Barons Creek discharges into the river downstream of the USGS gage. In the discharge data from 1962, the flow was 1.67 cfs at Live Oak Creek and 1.0 cfs at Barons Creek when the flow was 4.75 cfs in the Pedernales River (Holland and Hughes 1964). The prediction based on the relationship above would have been 1.71 cfs at Live Oak Creek and 1.89 cfs at Barons Creek. The flow at Live Oak Creek was very close to the predicted value, but the flow at Barons Creek was less than predicted. This indicates that the relationship is a reasonable predictor for flow in Live Oak Creek but may be overestimating flow in Barons Creek. Barons Creek may fluctuate beyond naturally occurring levels due to some treated wastewater discharge to the creek. Live Oak Creek does not have a manmade discharge point affecting flow in the creek. Due to the similarities between flow measured in Live

Oak Creek during the 1962 study and flow predicted during the 2015 study, tributary flow contributions in 2015 may be comparable to those measured in 1962.

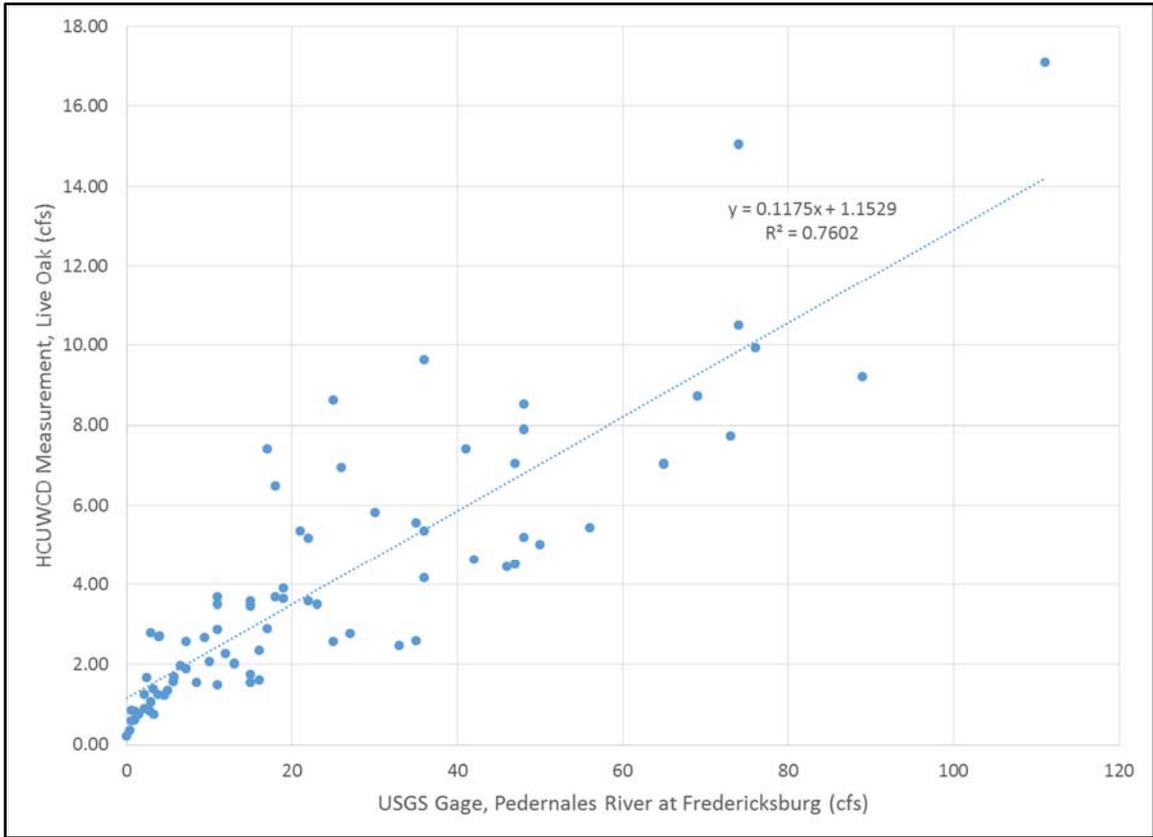


Figure 42. Relationship between flow in Live Oak Creek and Pedernales River.

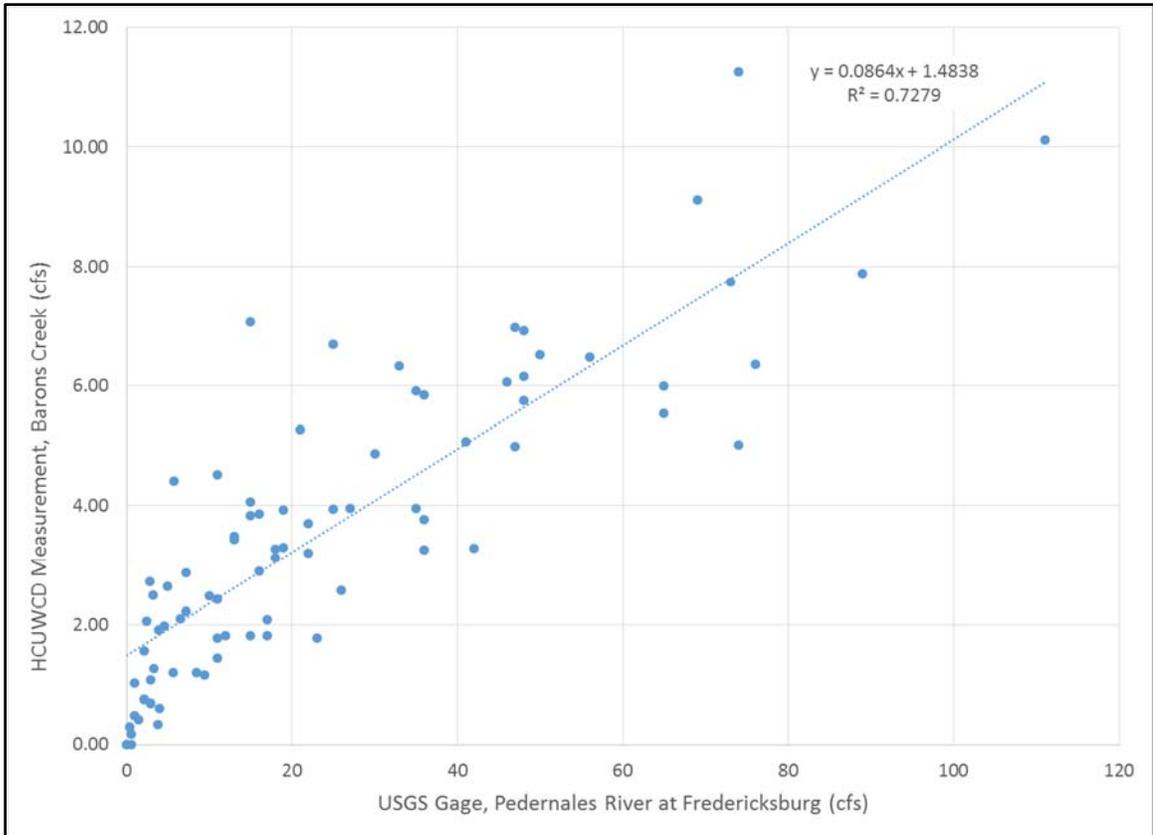


Figure 43. Relationship between flow in Barons Creek and Pedernales River.

Overall, discharge in the Pedernales River at Fredericksburg has been declining based on data collected by the HCUWCD (since 1996) and the USGS (since 1980) (Figure 44 and Figure 45). The flows in Live Oak Creek and Barons Creek have both been declining since the HCUWCD started collecting data in 1995 (Figure 46). In contrast with river flow near Fredericksburg, the discharge at the USGS gage in Johnson City has shown an increasing trend since 1940 (Figure 47).

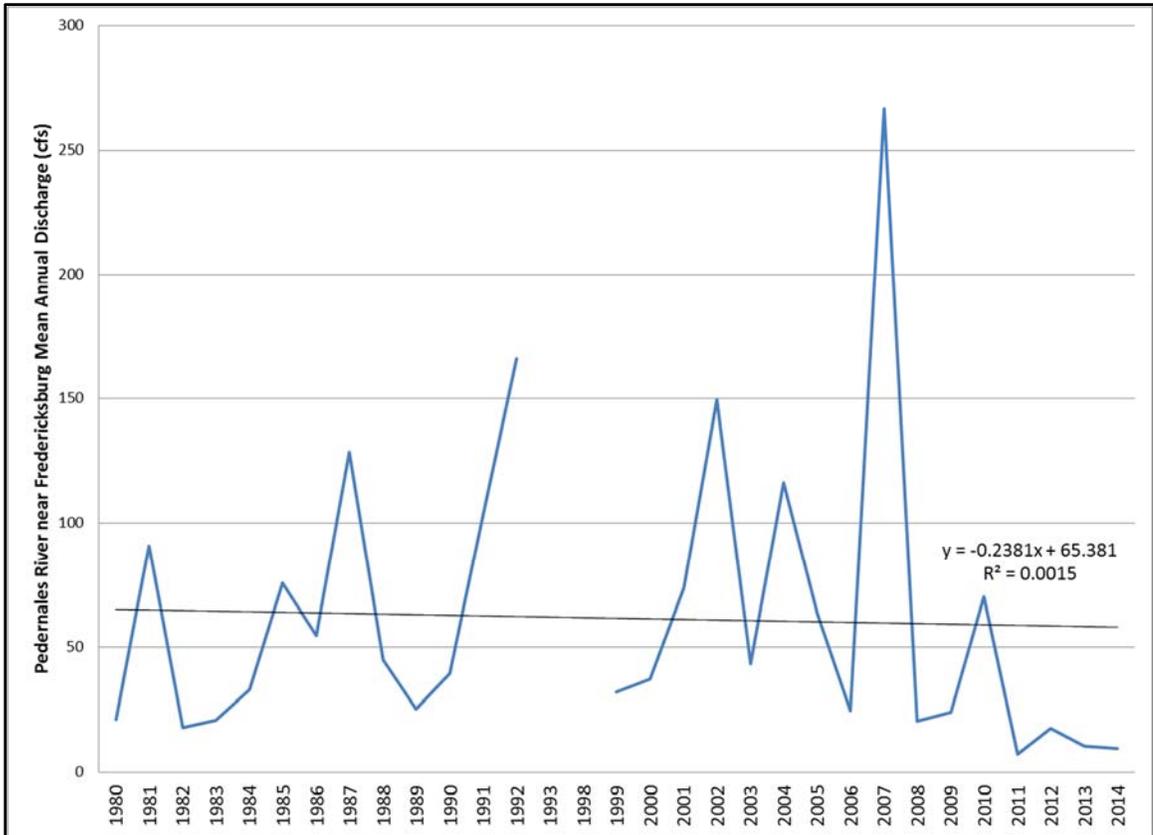


Figure 44. Mean annual flow trend at the USGS gage, Pedernales River near Fredericksburg.

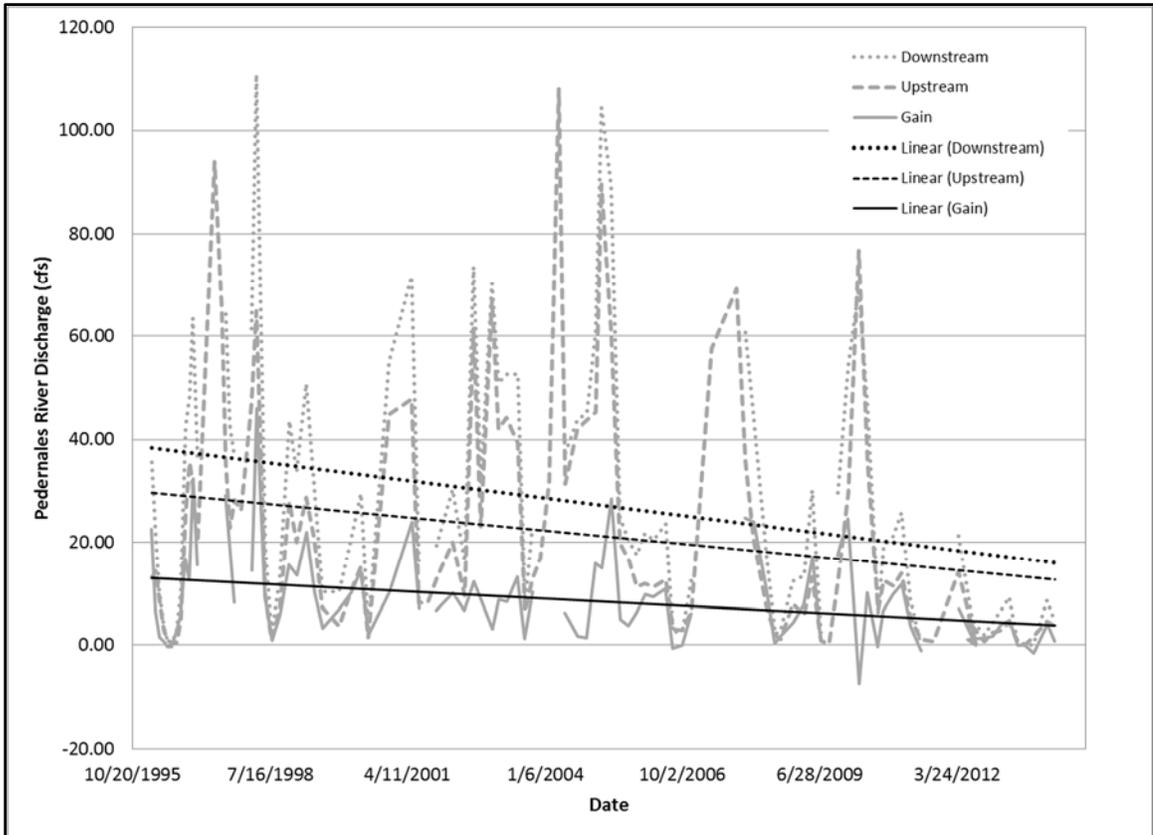


Figure 45. Flow trend at HCUWCD gauging sites upstream and downstream of Fredericksburg and trend in river gains over time.

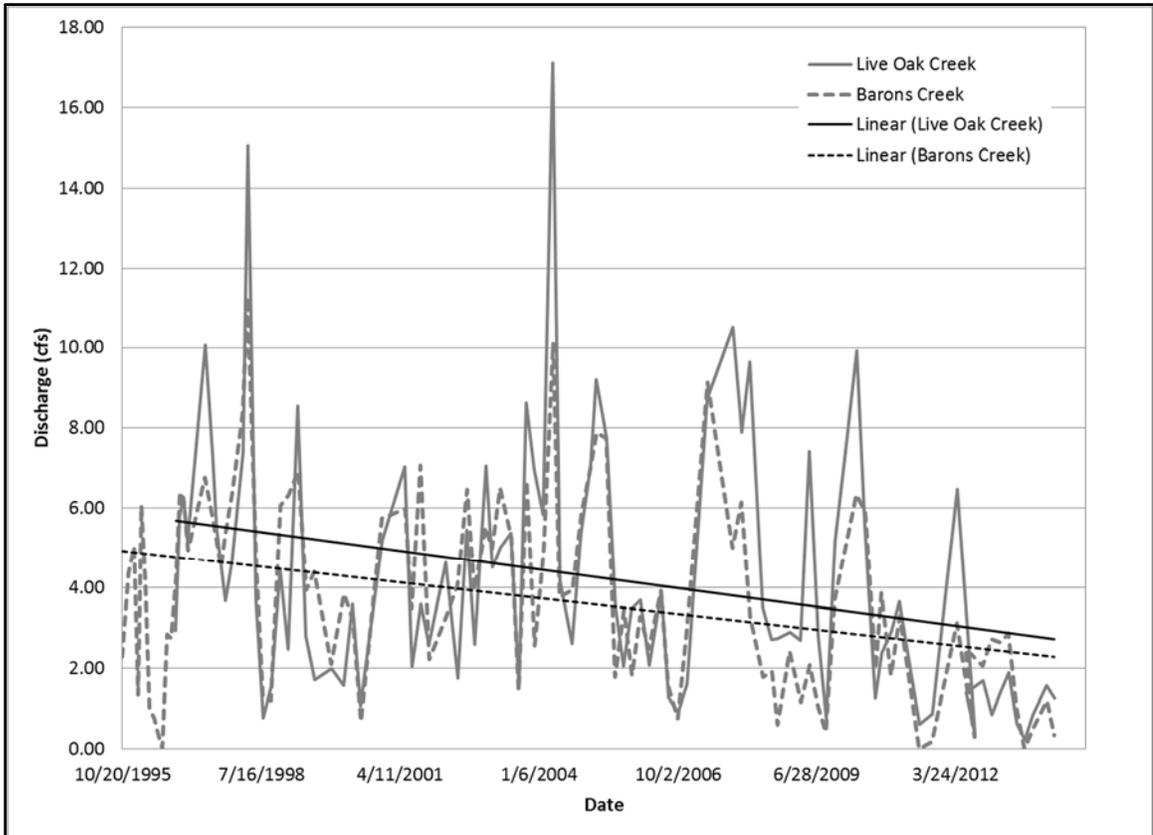


Figure 46. Trends in flow at HCUWCD gauging sites on Live Oak Creek and Barons Creek.

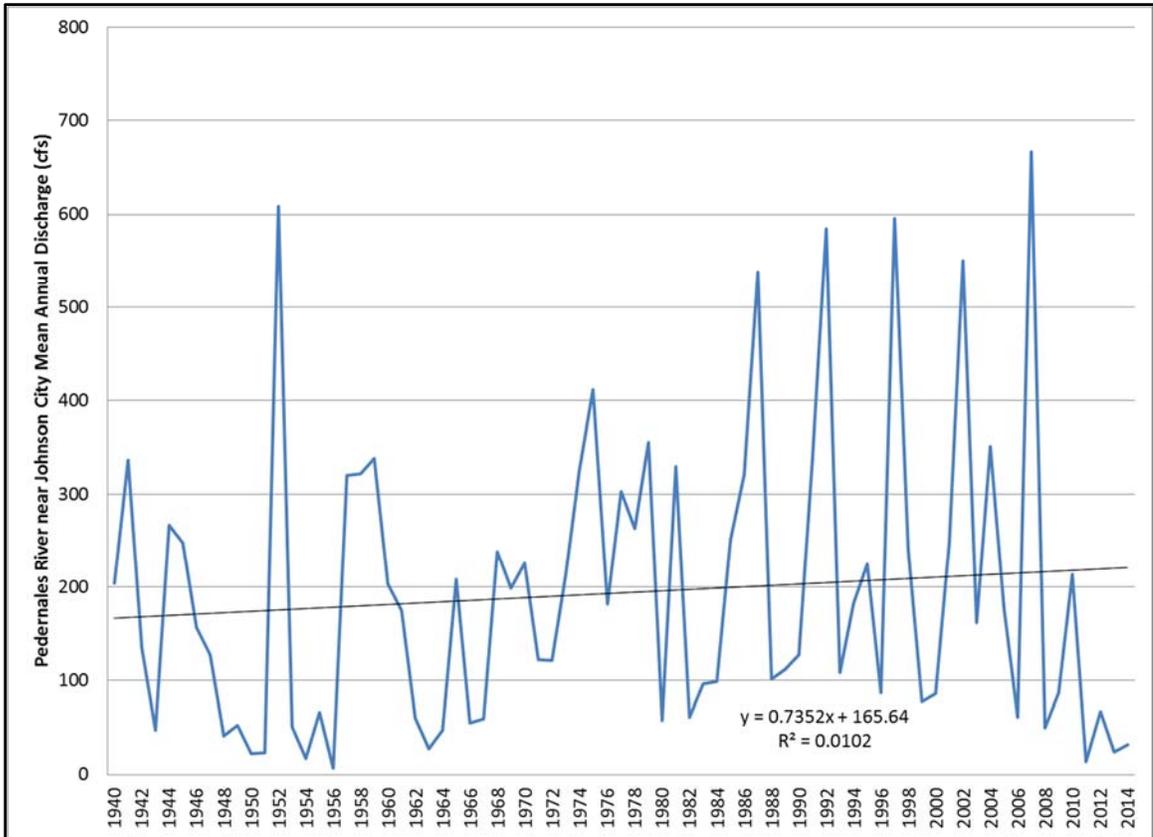


Figure 47. Mean annual flow trend at the USGS gage, Pedernales River near Johnson City.

Well chemistry from the TWDB database was analyzed in a piper diagram (Figure 48) and a box and whisker plot (Figure 49) for comparison with water chemistry from the synoptic sampling.

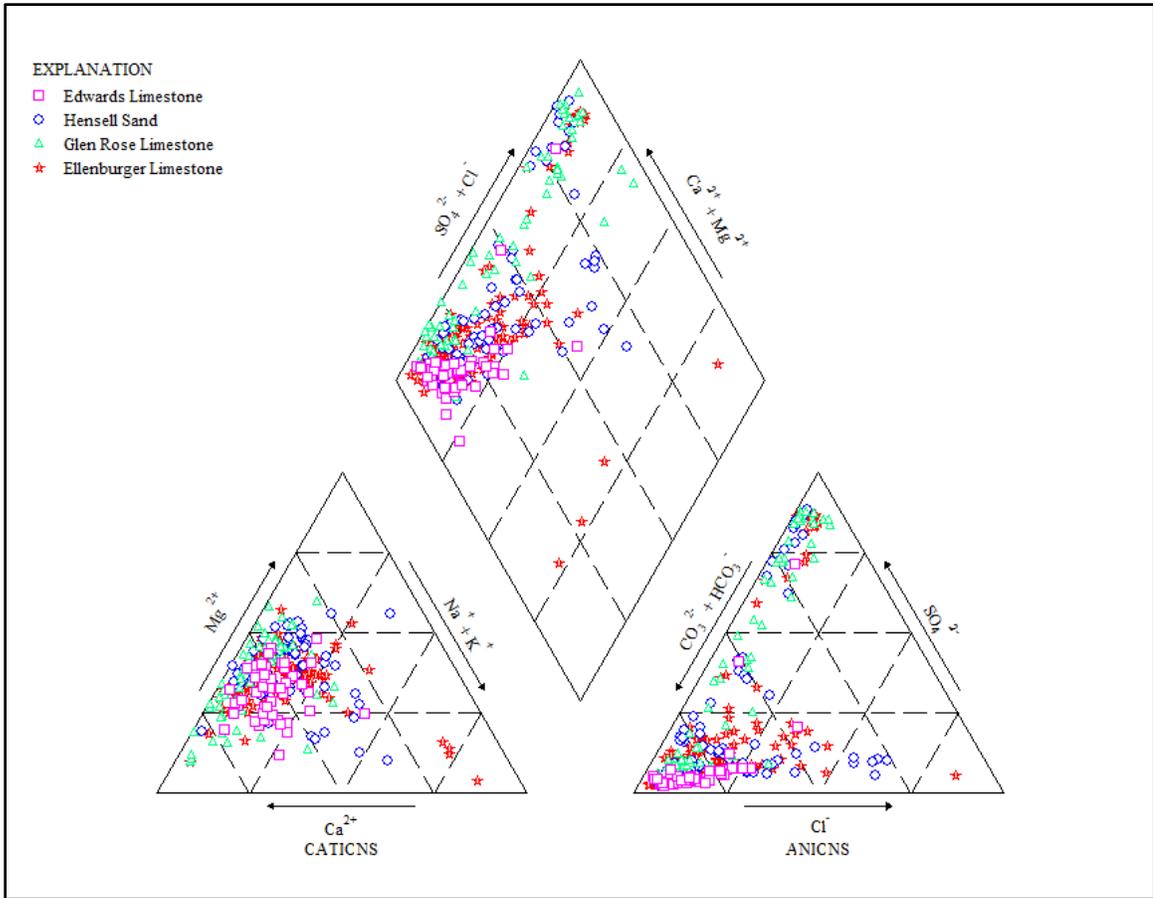


Figure 48. Piper diagram of well chemistry from TWDB database.

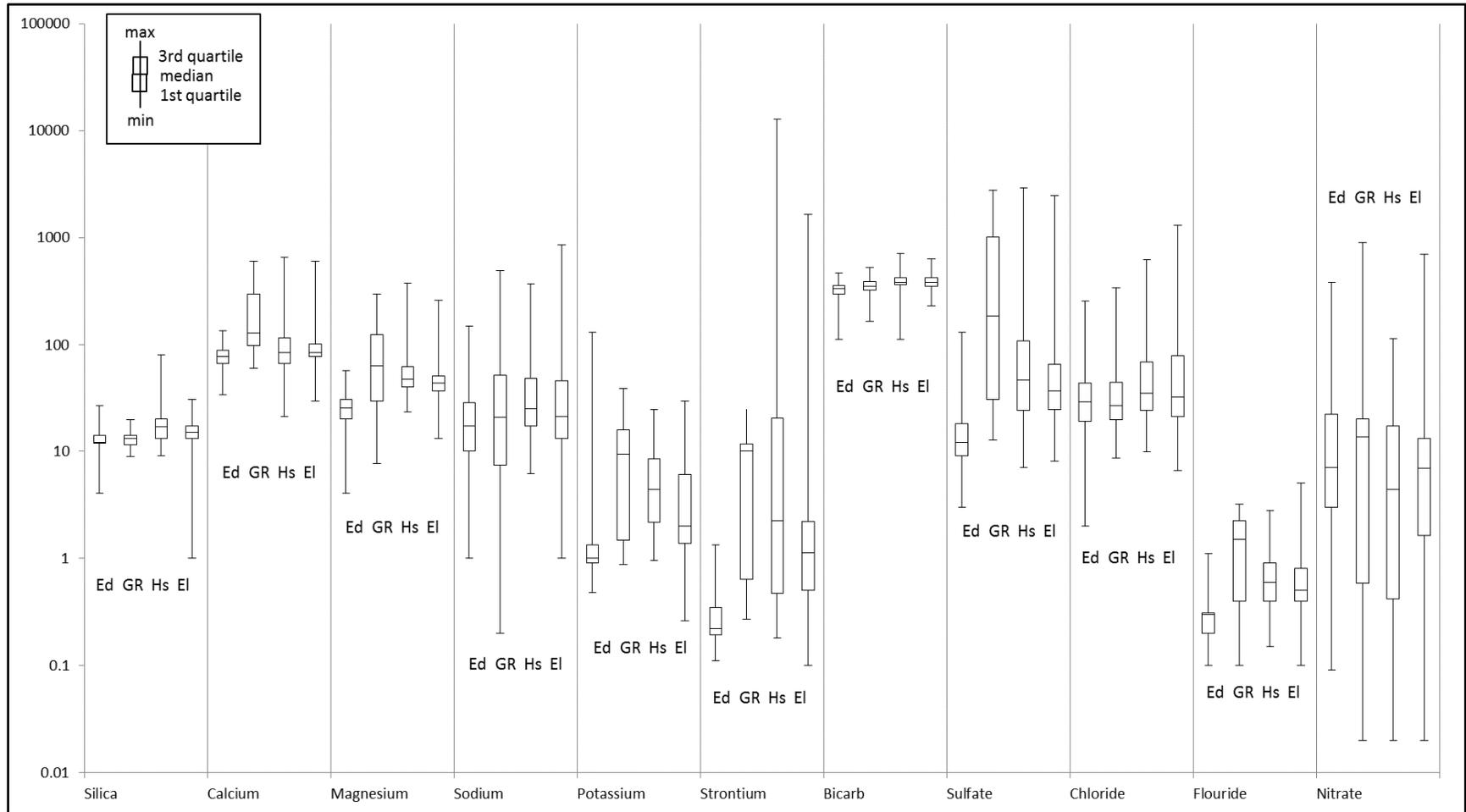


Figure 49. Box and whisker plot of well chemistry from TWDB database. Hydrogeologic units are listed as Edwards (Ed), Glen Rose (GR), Hensell (Hs), and Ellenburger (EI).

5. DISCUSSION

5.1. Hydrogen & Oxygen Stable Isotopes

While the spring and well samples plot on the GMWL, the tributary and main river samples plot along an evaporitic trend. The linear trend suggests that the tributary and river waters are supplied by groundwater from headwater springs away from the main river channel, and the most significant natural impact on the isotopic ratios was evaporation. The fact that all samples lie on an evaporitic line with a source signature of homogenized groundwater supports the idea that the samples were collected during groundwater-sourced baseflow conditions, and that none of the samples represent contribution from recent runoff or an isotopically different body of water. The gradient between groundwater values and evaporitically enriched samples was useful to identify near-spring samples. Samples collected from known springs are all located in the southeast quadrant of the watershed, and the tributary samples with minimally enriched isotope values indicate that a wider geographic extent of near-spring samples was collected. Near-spring samples were likely collected very close to spring-fed headwaters, even though access restrictions prohibited direct observation and sampling of many springs. Spatial analysis of sample enrichment allows linkage of spring and near-spring samples (low $\delta^{18}\text{O}$, shown in blue on Figure 7) with surface geology. Springs locations relative to geologic units are summarized on the stratigraphic column in Figure 50. Springs in the western portion of the watershed are located near the contact between the Segovia and Fort Terrett members of the Edwards limestone. These are probably the result of gravity fed springs emerging along the geologic contact. Two near-spring samples collected in the south-central portion of the watershed appear to originate from

the contact between the Edwards Fort Terrett and the Upper Glen Rose. Several intermediate-enriched samples in the north-central portion of the watershed are located downstream of more enriched samples and appear to indicate groundwater contributions from the Hensell. The known springs in the southeast portion of the watershed originate from the Edwards Fort Terrett, the contact between the Edwards Fort Terrett and the Upper Glen Rose, the Hensell, and the Sycamore. Near-spring samples in the southeast come from the Upper Glen Rose, the Lower Glen Rose, the Cow Creek, the Hensell, the Cow Creek and Hensell undivided, and the Sycamore. Near-spring samples in the northeast come from the Hensell, the Honeycut (Ordovician, Ellenburger), and the San Saba (Cambrian). The geologic locations of springs indicate groundwater contributions from the Edwards-Trinity Plateau Aquifer, the Trinity Aquifer, and the Ellenburger-San Saba Aquifer.

Period	Group	Formation	Member	Aquifer	Springs
Cretaceous	Fredericksburg	Edwards	Segovia	Edwards-Trinity Plateau	~
			Fort Terrett		~
	Trinity	Glen Rose	Upper Glen Rose	Upper Trinity	~
			Lower Glen Rose	Middle Trinity	~
		Hensell			~
		Cow Creek			~
		Hammett			
		Sligo		Lower Trinity	~
		Sycamore			
		Pennsylvanian	Canyon	Undivided rocks	
Smithwick					
Bend	Marble Falls		Marble Falls	~	
Ordovician	Ellenburger	Honeycut		Ellenburger - San Saba	~
		Gorman			
		Tanyard			
Cambrian	Moore Hollow	Wilberns	San Saba		~
			Point Peak		
			Morgan Creek		
		Welge		Welge-Lion Mountain	
		Riley	Lion Mountain		
			Cap Mountain		
Hickory	Hickory				
Precambrian	Undivided rocks				

Figure 50. Stratigraphic column adapted from Wierman et al. 2010 and Standen and Ruggiero (2007) with locations of springs indicated by ~.

Isotopic ratios are generally more enriched in the western portion of the watershed. This could be, in part, due to variation in climate across the river basin, or an artifact of where access allowed samples to be collected. The precipitation gradient in Texas extends from humid in the east to arid in the west, and the geographic extent of this

watershed is large enough to encompass a subtle change in climate. The mean annual precipitation ranges from 34 inches in the east to 26 inches in the west (PRISM 2014). This variation in climate could also affect vegetation dynamics and the level of transpiration. The channel morphology could also contribute, because wide and shallow bedrock streams tend to enhance evaporation compared with narrower and more-shaded streams; however, a morphological analysis was beyond the scope of the observations collected during this study.

5.2. Principal Component Analysis and Geochemistry

When the stable isotope results are combined with the PCA, a regional groundwater signature emerges and evaporation appears to be the dominant driver of chemistry once the water is flowing above ground. Some variation is present in the groundwater chemistry, but the variation does not appear linked to any specific geologic unit. Two samples, a spring and a near-spring tributary, are located on the Hensell Sand and have higher sulfate concentrations, likely due to contributions from the Lower Glen Rose. Other chemistry variations are not consistent among samples from the same geologic unit.

One of the goals of the PCA was variable reduction, so this discussion will focus on the water chemistry variables that most strongly influenced the PCA. For PC1 those analytes were Cl^- , Na^+ , K^+ , and PP. PC2 included $\delta^{18}\text{O}$, $\delta^2\text{H}$, SC, Ca^{2+} , and T.

Chloride, sodium, and potassium all have very similar spatial patterns in concentration across the river basin in the subwatersheds and in the river (Figure 8 through Figure 13). There is a strong linear relationship between Cl^- and Na^+ of $\text{Cl}^- = 1.3475(\text{Na}^+) + 5.603$ with an R^2 of 0.9246 (Figure 51), and a strong linear relationship

between Cl^- and Na^+ plus K^+ of $\text{Cl}^- = 1.22(\text{Na}^+ + \text{K}^+) + 4.8512$ with an R^2 of 0.9159 (Figure 52). This indicates that these ions come from the same source: salts. The most evident pattern in the concentrations of these ions is that they are elevated in subwatersheds which contain cities. Assuming that these ions came from the same source, only chloride is discussed in more detail because of its utility in hydrologic studies. Cl^- is a conservative ion and does not react with the natural system. For this reason, it is sometimes used as a tracer in water flow studies. Cl^- can originate in natural or manmade sources. Cl^- is added to drinking water in water softeners and then ends up in human wastewater. It is also found in fertilizer and livestock feed and supplements. Cl^- accumulates by evapotranspiration in groundwater irrigated fields, even if the groundwater is not particularly high in chloride. This is an active agricultural area and fields in the region are irrigated from groundwater. The 1962 study linked high Cl^- concentrations with locations overlying the Hensell Formation (Holland and Hughes 1964), but the current results do not show a consistent relationship between Hensell samples and elevated chloride. In addition, the reduced levels of Cl^- in the river in 2015 versus 1962 seem to reflect a difference in human activity rather than changes in geologic setting, and may be due to advances in wastewater treatment practices. The EPA secondary maximum contaminant level for Cl^- is 250 mg/L due to salty taste (EPA 2015), and all samples were below this limit.

Particulate phosphorus was also elevated near cities (Figure 28 - Figure 29), although some samples were elevated in particulate matter due to localized human impact such as an impoundment and sediment retention near a spring orifice. Nutrients (compounds containing nitrogen or phosphorus) are important components of the

biological aquatic system, but are often associated with human impact due to elevated levels found in treated wastewater effluent. The common theme among the variables strongly linked to PC1 seems to be human impact.

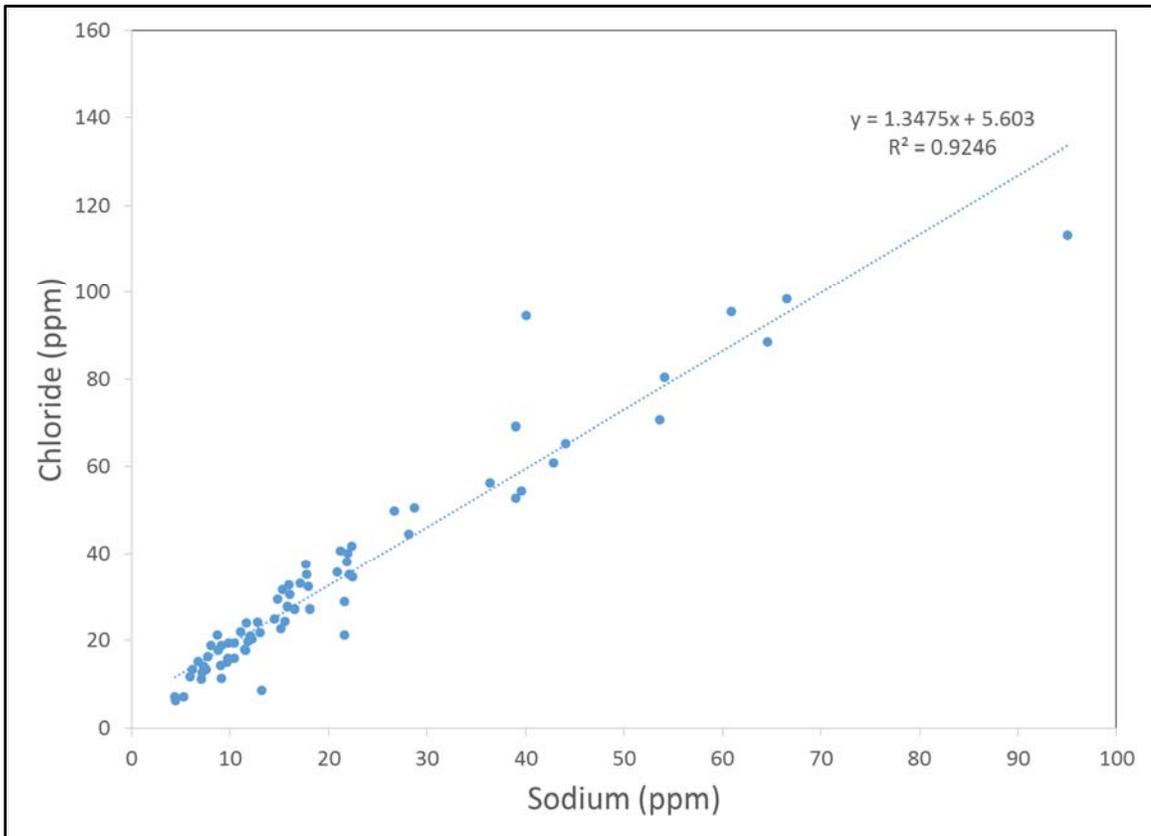


Figure 51. Linear trend between chloride and sodium.

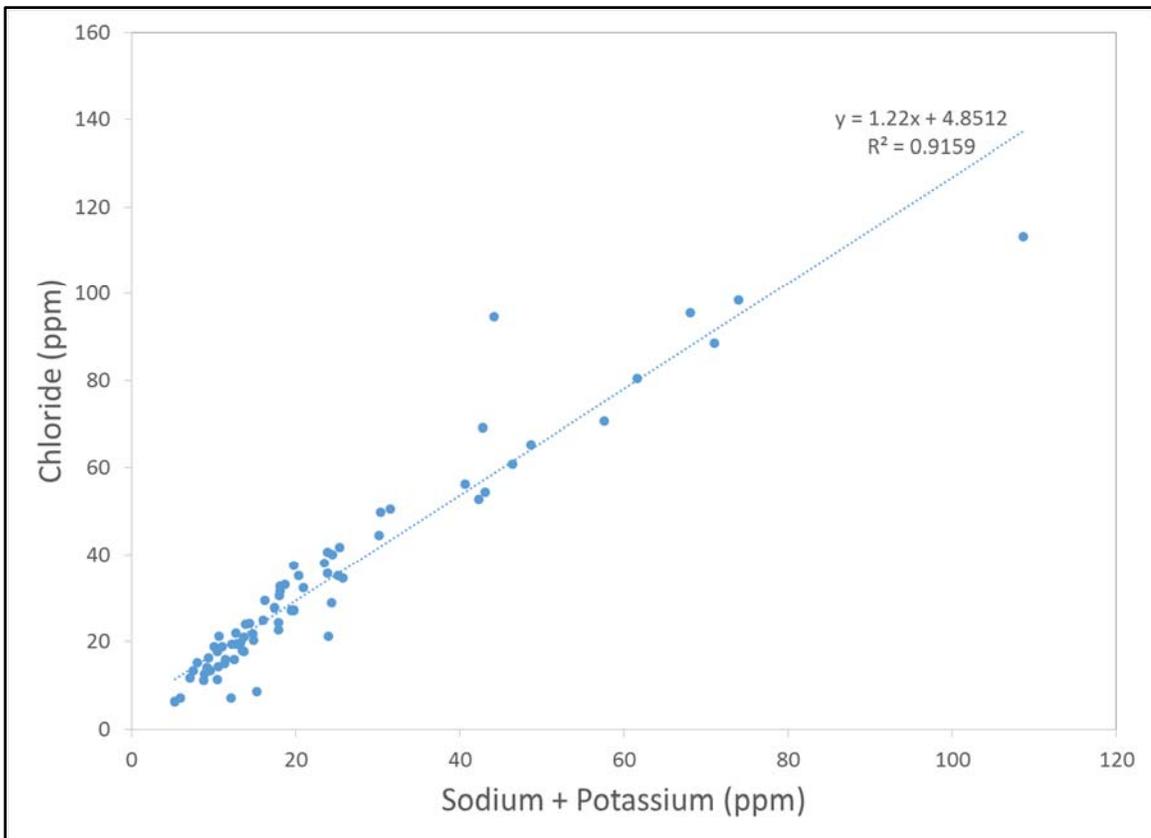


Figure 52. Linear trend between chloride and sodium plus potassium.

Increased conductivity is often linked to groundwater and mineral dissolution. High levels of calcium are typical in carbonate groundwater, also due to dissolution of bedrock. Temperature is another indicator of groundwater, since the sun tends to warm cool spring water quickly during low-flow conditions such as the time period when this study was conducted. All of these PC2 variables can also have human influenced sources, but they seem to follow natural patterns within the Pedernales River watershed. They are also grouped with stable isotopes in the PCA. Since stable isotopes appear strongly linked to amount of groundwater influence, it seems reasonable that these analytes are indicative of groundwater contributions in this watershed.

Of potential interest for water quality considerations is the source of nitrate in the river. NO_3^- concentrations in the river were higher in the west (Figure 24 - Figure 25),

near the headwaters of the Pedernales River, which concurs with findings from Strickland (2009). Strickland (2009) proposed that groundwater was a significant source of NO_3^- -N in the river, and this may be supported by the 2015 results including the PCA. NO_3^- loads along PC2 (Figure 32) which seems to group the dominant influence of groundwater on the water samples. NO_3^- was also present in elevated concentrations downstream of the Johnson City wastewater treatment plant, though the levels were below the EPA primary maximum contaminant level limits. The concentration of NO_3^- in Barons Creek downstream of the Fredericksburg wastewater treatment plant was greatly reduced from the concentration measured there during the 1962 study, possibly indicating improved treatment processes and the success of watering golf courses on improving the water quality of the direct effluent discharge to the creek. The statistical grouping along with elevated concentrations near the headwaters supports the suggestion that a main source of NO_3^- in the river is groundwater during baseflow conditions, though the inputs from wastewater treatment plants are likely also important.

5.3. Regional Aquifer Geochemistry

In both the piper diagram (Figure 48) and the box and whisker plot (Figure 49), the well chemistry among the various aquifers overlaps in chemical composition. Some moderate variation occurs within wells from the same aquifer, for example Glen Rose, Hensell, and Ellenburger wells have a larger range of sulfate. However, the amount of overlap of the geochemistry makes aquifer identification based on geochemical signature difficult. The well data should be interpreted with caution since screened intervals may cross vertical aquifer boundaries. The overlap in aquifer chemistry supports the regional groundwater signature indicated by the hydrogen and oxygen stable isotopes and the

PCA. The location of springs relative to the surface geology is very important for identifying source aquifers when the geochemistry is similar.

5.4. Historic Flows

Decreasing flow trends in the Pedernales River at Fredericksburg, Live Oak Creek, and Barons Creek (Figure 44 - Figure 46) could be a result of changing climate conditions or of human impact from the city of Fredericksburg. Human impacts on creek flows could result from diversions, wastewater discharge, and groundwater pumping from wells which can impact spring discharge volumes (Hunt et al. 2012). The wastewater discharge practices have changed in Fredericksburg since 1995 (personal communication with J. Horry, City of Fredericksburg Water/Wastewater Superintendent, 24 Nov 2015). The city wastewater treatment plant is located adjacent to Barons Creek, and all treated effluent was previously discharged into the creek. In 1995, some reclaimed effluent began to be used to water a golf course in the Live Oak Creek subwatershed and since 2009 an additional golf course in the Palo Alto subwatershed. Some treated wastewater continues to be discharged into Barons Creek, and volumes vary depending on time of year and weather. The increasing mean annual discharge trend in the Pedernales River at Johnson City (Figure 47) could be hypothesized to be due to increased city well usage and a consequential increase in treated wastewater discharge; however, the USGS gage is upstream of the confluence with the creek where Johnson City treated effluent is discharged. Increased flows may be due to several years with high levels of precipitation between 1986 and 2008 in contrast with 1940 through 1986. The contrast between the increasing trend at Johnson City and the decreasing trend at Fredericksburg is due to the difference in time periods represented because when the

USGS gage data at Johnson City is evaluated from 1980 to 2014, the resulting mean annual discharge trend is decreasing. The decreasing trend in flows since 1980 may be influenced by several recent dry years in a row, including the most severe one-year drought on record in 2011 (Nielsen-Gammon 2011).

5.5. Implications and Future Work

Identifying the sources of water to the Pedernales River is important for managing water quantity and quality within the river, and will be used to provide direction and delineate priority areas for long-term conservation efforts by organizations such as The Mitchell Foundation.

Gain/loss stream discharge volume studies can identify subtle interactions between the surface and the subsurface, for example Pleasant Valley Spring in the Blanco River immediately to the south of the Pedernales River; this type of study would contribute greatly to this geochemical analysis. A comparison of creek flow volumes with the 1962 flows, combined with this water chemistry study, will allow for a more thorough comparison of temporal changes in the river basin. Information about the relative amounts of contributions where the water chemistry varies will also support an evaluation of dilution in the river and contribute to knowledge about the volumes of water coming from the various geologic sources.

While the baseflow volumes are important for consistent use of the river water, large influxes of water occur during precipitation events within the river basin. The Pedernales River is a flashy system, and floods often result from rain storms in the area. Surface run-off during precipitation events often carries a higher load of contaminants and suspended sediment. Understanding the dynamics of the system during precipitation

and flooding events will contribute to planning for the changes in water quality that inevitably follow floods and inputs of surface run-off. Precipitation could also impact the amount of groundwater in the system and the volume and chemical characteristics of groundwater inputs.

6. CONCLUSIONS

The water quality in the Pedernales River is generally good. Although total dissolved solids at a few sites are above EPA drinking water limits of 500 mg/L (approximately 781 $\mu\text{S SC}$), all other ion and nutrient concentrations meet drinking water limits. Headwater springs are the source of the Pedernales River during baseflow conditions and are very important to the health of the river. Water in the springs originates from several geologic units with similar carbonate geochemistry. Due to somewhat homogeneous aquifer chemistry, interpreting the groundwater source is dependent on the geologic location of springs. The geochemical groundwater signature indicates surface locations that are near springs and allows enhanced spatial analysis of spring locations when exact spring access is limited due to restricted private property. By overlaying the spring locations with surface geology, and therefore identifying host geologic unit and source aquifer, groundwater in the Pedernales River was determined to originate from the Edwards-Trinity Plateau Aquifer, the Trinity Aquifer, the Marble Falls Aquifer, and the Ellenburger-San Saba Aquifer.

Combining naturally occurring geochemical tracers like major ions and stable isotopes with principal component analysis is a powerful tool for evaluating geochemical trends. Groundwater has a distinct regional signature with respect to stable hydrogen and oxygen ratios. The isotopic gradient from groundwater to river water follows an evaporitic trend and indicates a strong evaporation control on water chemistry within the watershed. Some of the major ion concentrations are elevated near cities and may reflect human impacts from treated wastewater discharge. When the overall geochemical dataset for the 2015 synoptic watershed sampling is analyzed for statistically relevant patterns

using PCA, human impact and proximity to springs seem to be the dominant factors controlling water chemistry. This information will be useful for water conservation and planning because Pedernales River and tributary flows have been decreasing since the 1980's, severe drought has affected the region, and population in central Texas is increasing.

APPENDIX SECTION

Table 4. Field data collected during water sampling.

Site	Date	Time	Type	SC	T (from SC)	pH	T (from pH)	DO (mg/L)	Total Depth (m)	Flow	Clarity	Algae	Color	Surface	Odor
20	8/27/2015	11:16	tributary	655	27.6	7.8		5.37	0.5	med	clear	0	clear	clear	none
43	8/28/2015	14:45	main	755	31.2	8.28			1	med	cloudy	0	clear	clear	none
73	8/28/2015	15:06	tributary	537	30.8	8.8			0.1	very low	clear	15	clear	clear	none
75	8/28/2015	15:25	tributary	643	29.1	7.57			0.2	low	clear	10	clear	clear	none
82	8/29/2015	14:39	main	664	33	8.98			0.3	med	cloudy	10	green	scum	none
92	8/27/2015	15:30	main	530	35.8			5.8		very low	cloudy	0	grey	debris	none
96	8/28/2015	11:55	main	660	26.8	8.12			0.2	med	slightly cloudy	0	clear	clear	none
113	8/28/2015	14:33	main	758	29.8	8.15			>1	med	cloudy	0	clear	clear	none
129	8/29/2015	12:42	tributary	549	30	8.08			0.2	low	clear	60	green	scum	none
135	8/28/2015	11:46	tributary	589	28.1	7.87		6.75	0.6	low	clear	0	clear	clear	none
175	9/10/2015	9:56	main	758	24.1	7.13	24.1		0.3	low	clear	10	clear	clear/ scum/ algae	none
195	8/29/2015	12:18	tributary	540	25	7.75		5.3	0.3	low	clear	0	green	clear	none
248	9/10/2015	10:45	main	595	28.1	8.74	27.4		0.2	med	clear	5	tan	clear/ scum/ algae	none
285	8/28/2015	17:10	tributary	937	22.6	7.18		3.2	0.02	low	clear	30	clear	algae	none
287	8/28/2015	16:56	main	736	33.5	8.31		6.2	>1	high	cloudy	0	green	debris & scum	fishy
349	8/29/2015	13:56	main	664	30.5	8.75			1	low	muddy	0	brown	clear	none
393	8/27/2015	12:55	tributary	640	29.3	7.73		7.32	1	low	clear	2	clear	clear	none
403	9/10/2015	14:32	tributary	669	28.7	7.47	28.1		0.2	low	cloudy	0	tan	clear/ foam/ sheen	none
457	8/28/2015	17:40	tributary	1201	25.3	7.98			0.2	very low	clear	30	clear	clear	none
521	9/10/2015	10:23	tributary	604	23.3	8.17	23.2		0.02	low	clear	0	clear	clear	none
524	8/28/2015	13:13	tributary	680	28	7.35			0.05	low	clear	10	clear	clear	none
609	8/28/2015	13:57	main	649	31	8.46		7.75	0.3	med-high	cloudy	0	brown	foam	musky
618	8/27/2015	14:50	main	390	36.8	8.96		6.3	0.05	med	clear	0	clear	clear	none
683	9/10/2015	11:40	tributary	412	31	7.89	29		0.1	none	clear	0	clear	vegetation	none
684	8/28/2015	10:33	main	644	28	8.19			0.1	low	clear	0	clear	clear	none
710	8/28/2015	17:20	tributary	850	28.5	7.38				none/low	clear	10	clear	scum, sheen	none
713	9/10/2015	13:31	tributary	972	27.8	7.62	27.1		0.3	none	clear	2	clear	clear/ debris	none
718	8/29/2015	9:10	tributary	970	24	7.91		5.5	0.1	very low	cloudy	0	brown	some scum	none
728	8/29/2015	11:56	tributary	648	26.8	8.03		5.5		med	clear	5	brown/clear	clear	none
731	8/28/2015	8:22	tributary	671	22.7	7.45		3.69	0.03	low	clear	0	clear	clear	none
732	8/27/2015	15:50	tributary	518	32.4	7.83		6.34	0.5	med	clear	0	clear	clear	none
733	8/28/2015	9:41	tributary	632	25.7	7.74		4.2	0.25	low	clear	0	clear	clear	none
744	8/28/2015	14:00	tributary	545	33.7	8.74			0.2	none/low	clear	50	clear	clear	none
754	8/28/2015	13:45	tributary	648	27.3	7.53			0.05	low	clear	35	clear	clear	none
762	8/28/2015	17:29	tributary	751	24.4	7.14		4.43	0.3	low	clear	5	clear	clear	fishy/acrid
766	8/29/2015	14:21	tributary	757	28.3				0.3	low	clear	0	clear	clear	none
767	8/29/2015	9:59	tributary	773	23.1	8.15			0.2	med	clear	0	clear	clear	none
772	8/28/2015	11:03	tributary	502	27.6	7.92		5.56	0.4	low	clear	0	clear	clear	none
779	8/27/2015	12:25	tributary	674	29.1	7.03		5.81	0.3	none	clear	90	clear	algae	none
788	8/28/2015	17:05	tributary	913	29.6	8.14			0.25	low	clear	10	clear	clear	none
789	8/28/2015	14:18	tributary	912	27.8	7.26			0.5	none/low	clear	5	clear	slight pollen	none
793	8/28/2015	11:40	tributary	631	25.7	7.68			0.5	med	cloudy		clear	scum	none
794	8/28/2015	10:15	tributary	646	28.3	7.8		4.8	1	none	slightly cloudy	0	green	scum	none
796	8/28/2015	16:20	tributary	638	31.1	8.18		8.13	0.2	low	cloudy	25	brown	debris, scum, foam	cow poop
808	8/28/2015	12:08	tributary	530	29.3	8.22			0.25	low	clear	0	clear	clear	none
810	8/28/2015	15:45	tributary	595	26.7	8.12				med	clear	10	clear	clear	none
812	8/28/2015	11:12	tributary	620	24.6	7.99			0.2	low/med	clear	0	clear	clear	none
815	8/28/2015	14:44	tributary	531	28.9	7.29		3.53	0.1	low	clear	0	clear	small amount foam	rotten egg
816	8/28/2015	14:17	tributary	450	33	8.18		7.92	0.2	low	clear	4	clear	scum	none
818	8/27/2015	17:02	tributary	519	29.3	7.63		5.31	0.02	low	clear	0	clear	clear	rotten egg
832	8/29/2015	10:24	tributary	800	23.7	8.26		7.9	0.3	med	clear	10	clear	clear	none
835	8/29/2015	11:30	tributary	588	25.6	7.4		4.27	0.3	low	clear	50	clear	some scum	none
836	8/28/2015	11:25	tributary	574	29.7	8.52			0.05	low	clear	5	clear	clear	none
840	8/27/2015	11:40	tributary	527	29.2	7.95		7.45	0.9	med	clear	0	clear	clear	musky
841	9/10/2015	12:16	tributary	614	32.2	7.85	29.4		0.1	none	cloudy	0	green/tan	clear/ scum	none
851	8/27/2015	16:10	tributary	450	33.2	8.09		8.78	0.02	med	clear	0	clear	clear	none
852	9/10/2015	16:39	tributary	431	30.9	8.26	30.4		0.1	med	clear	0	clear	clear	none
863	8/27/2015	13:20	tributary	670	26.3	7.48		4.34	0.1	med	clear	0	clear	some scum	none
868	8/27/2015	12:45	tributary	455	34.3	8.75		5.23	0.1	low	clear	25	clear	clear	none
878	8/28/2015	12:31	tributary	505	30.1	8.4			0.05	low	clear	10	clear	clear	none
879	8/28/2015	16:47	tributary	633	31.4	8.4			0.5	low	clear	15	clear	clear	none
880	8/28/2015	16:17	tributary	1137	27.8	8.47			0.35	very low	muddy	0	brown	clear	none
881	8/28/2015	16:33	tributary	896	30.1	8.44			0.3	low	clear	10	clear	clear	none
883	8/28/2015	12:54	tributary	625	28.8	7.7		5.64	0.4	low	clear	0	clear	scum	none
884	8/28/2015	13:31	tributary	538	29.9	7.8			0.2	low	clear	40	clear	clear	none
887	8/27/2015	16:30	tributary	580	29.9	7.35		4.01	0.1	low	clear	0	clear	clear	none
888	9/10/2015	8:59	tributary	682	24.8	7.21	24.3		0.3	low	clear	2	clear	clear/ scum/ foam/ sheen	none
889	8/29/2015	10:48	tributary	900	25.6	8.3		7.55	0.3	med	clear	30	clear	clear	none
898	8/28/2015	13:34	tributary	508	31.6	7.98		5.58	0.4	low	clear	5	clear	small amount foam/ debris	fishy
900	8/28/2015	9:27	tributary	610	24.3	8.2		5.3	0.1	low	clear	0	clear	clear	none

Site	Date	Time	Type	SC	T (from SC)	pH	T (from pH)	DO (mg/L)	Total Depth (m)	Flow	Clarity	Algae	Color	Surface	Odor
901	8/27/2015	15:10	tributary	373	33.5	8.1		5.64	0.01	very low	clear	0	clear	some scum	none
906	9/10/2015	13:05	tributary	535	27	7.71	26.6		0.1	med	clear	0	clear	clear	none
913	8/28/2015	10:54	tributary	370	27	8.18			0.1	med	clear	0	clear	clear	none
918	9/10/2015	11:02	tributary	484	27.6	8.53	25.4		0.3	very low	clear	0	clear	clear/ debris	none
920	8/28/2015	9:00	tributary	785	24.9	7.72		3.8	0.1	med	clear	0	clear	clear	none
940	8/29/2015	20:02	spring	608	22.6	7.3	23.4		0.5	med-low	clear	0	clear	clear	none
941	8/28/2015	9:40	well	1242	28.6	7.93		5.1							
943	8/29/2015	16:30	spring	631	21.7	7.14	21.3		0.01	low	clear	0	clear	clear	none
951	8/28/2015	12:06	tributary	1223	27.2	7.95		5.83	0.08	med	clear	0	light green brown	some foam	effluent
952	8/28/2015	12:17	main	648	29.7	8.58		9.65	>1	med-high	cloudy	0	green	small amount debris	
953	8/27/2015	14:15	spring	590	25.9	7.11		4.2	0.1	med	clear	25	clear	10% scum	none
954	8/27/2015	10:00	spring	644	25.1	7.01		5.76	0.03	low	clear	0	clear	clear	none
955	8/27/2015	10:25	main	516	30.6	8.31		7.29	2	high	clear	0	clear	clear	none
956	8/27/2015	15:02	spring	557	27.4	7.65		2.05	0.4	high	clear	0	clear	clear	none
957	8/28/2015	9:34	tributary	673	22.2	7.55		5.21	0.4	low-med	clear	2	clear	clear	none
958	8/27/2015	9:30	spring	442	24.2	7.27		5.52		low	clear	0	tan	clear	none
959	8/27/2015	10:05	spring	492	23.5	7.78		3.32		low	clear	0	clear	clear	none
960	8/27/2015	10:35	spring	615	23.4	7.06			0.15	low	cloudy	0	brown	clear	none
961	8/27/2015	11:05	well	1709	25.7	6.97		1.68			clear	0	clear	clear	rotten egg, gym
962	9/10/2015	16:04	well	579	29.1	7.48	28								
971	9/10/2015	15:50	spring	807	22.8	7.16	22.2		0.2	low	clear	0	clear	clear	none
684D	8/28/2015	10:33	duplicate	644	28	8.19			0.1	low	clear	0	clear	clear	none
898D	8/28/2015	13:35	duplicate	508	29.8	8.02		5.73	0.4	low	clear	5	clear	light debris foam	fishy
940D	8/29/2015	20:04	duplicate	608	22.6	7.3	23.4		0.5	med-low	clear	0	clear	clear	none
953D	8/27/2015	14:20	duplicate	595	26	7.04		4.4	0.1	med	clear	25	clear	10% scum	none
957D	8/28/2015	9:35	duplicate	674	21.9	7.52		5.27	0.4	low-med	clear	2	clear	clear	none
971D	9/10/2015	15:52	duplicate	807	22.8	7.16	22.2		0.2	low	clear	0	clear	clear	none

Table 5. Chemistry data for all water samples. *Second row indicates detection limits.

Site	F ⁻ (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ -NO ₃ (ppm)	NO ₃ ⁻ -N (mg/L)	SO ₄ ²⁻ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	Mg ²⁺ (ppm)	Ca ²⁺ (ppm)	δ ¹⁸ O VSMOW	δ ² H VSMOW	TSS (mg/L)	NVSS (mg/L)	TN (ug/L)	TP (ug/L)	PN (mg/L)	PC (mg/L)	DOC (mg/L)	NH ₄ (ug/L)	PP (ug/L)	SRP (ug/L)
*	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	+/- 0.05	+/- 0.2	2.5	10	100	5	9 ug/ total N	50 ug/ total C	5	2	25	5
20	1.7	17.7	0.2	0.3	0.1	16.8	11.5	2.1	37.4	66.3	-3.53	-23.0	1.4	1.0	273.9	4.2	0.0	0.4	1.7	66.0	2.6	0.0
43	2.1	80.0	0.4	0.0	0.0	27.5	52.2	4.2	42.0	38.2	0.03	-6.6	6.5	4.3	411.4	17.0	0.1	1.0	3.9	47.3	8.8	0.7
73	2.3	35.6	0.2	0.0	0.0	15.5	20.8	3.0	44.5	27.7	2.63	4.1	4.7	2.4	568.8	16.6	0.1	1.1	5.5	26.2	7.3	3.0
75	1.5	27.7	0.2	0.8	0.2	11.6	15.8	1.6	35.4	57.2	-2.71	-20.3	2.1	1.1	512.8	0.8	0.0	0.9	2.7	80.3	3.5	0.5
82	1.9	63.3	0.4	0.0	0.0	30.0	43.1	4.9	38.1	38.5	-0.78	-10.9	5.5	3.7	510.9	34.8	0.1	1.1	3.5	31.3	14.7	0.1
92	1.7	42.8	0.4	0.0	0.0	14.7	27.5	3.0	24.5	37.3	3.25	6.6	56.3	41.7	896.2	62.6	0.2	2.3	4.5	108.2	30.3	13.4
96	1.9	52.5	0.4	0.3	0.1	13.8	28.7	3.5	36.2	48.4	-0.73	-10.6	6.2	4.4	388.2	21.1	0.1	1.1	2.6	88.3	11.6	1.8
113	2.0	75.2	0.5	0.4	0.1	29.2	47.0	4.3	38.9	43.6	-0.34	-9.1	5.9	4.0	388.1	6.1	0.1	0.8	2.6	60.2	9.9	4.3
129	2.2	21.8	0.4	0.0	0.0	16.8	13.0	1.8	27.4	62.8	-1.96	-14.3	4.0	2.9	303.8	14.1	0.0	0.9	5.6	72.5	4.9	1.6
135	1.6	13.8	0.0	0.8	0.2	25.8	7.3	2.0	27.3	41.1	-3.40	-19.8	2.5	1.1	275.1	2.7	0.0	0.9	1.6	60.1	1.0	0.0
175	1.7	47.4	0.4	0.0	0.0	25.2	29.3	2.7	33.2	72.1	-0.93	-11.3	4.0	2.7	95.7	19.5	0.0	0.6	1.6	66.2	19.8	2.0
195	1.7	14.1	0.3	0.0	0.0	9.3	7.3	1.8	26.0	66.2	-1.68	-12.7	4.8	3.3	178.4	3.7	0.0	0.7	3.4	52.9	4.2	0.0
248	1.8	69.0	0.4	0.0	0.0	16.0	40.6	3.5	37.5	26.9	2.11	2.3	3.1	1.5	674.7	14.5	0.0	1.0	6.2	20.5	4.8	0.0
285	3.5	70.6	0.4	4.0	0.9	50.8	53.6	4.0	37.0	89.1	-2.80	-17.9	1.2	0.5	1026.1	4.1	0.2	1.6	1.0	120.0	5.6	5.9
287	2.0	77.1	1.3	0.0	0.0	31.2	51.0	4.8	43.2	39.3	-0.02	-6.8	12.5	8.5	613.9	40.9	0.0	2.3	3.5	62.2	25.2	3.1
349	2.1	68.9	0.4	0.0	0.0	28.6	45.5	5.3	35.1	37.7	-0.59	-9.9	16.0	10.7	392.3	38.3	0.4	3.3	3.5	16.4	45.8	3.6
393	1.8	15.9	0.0	0.4	0.1	14.8	10.4	2.1	42.4	58.0	-3.58	-23.4	3.5	1.9	338.0	15.4	0.0	0.7	2.4	43.4	0.9	2.1
403	2.0	21.3	0.3	0.0	0.0	2.1	8.7	2.0	33.2	77.3	-2.73	-17.1	10.6	3.9	126.6	24.2	0.0	1.2	5.3	91.4	15.9	2.1
457	3.3	98.5	0.5	1.1	0.2	78.9	66.5	7.4	73.2	42.1	-3.36	-19.8	3.8	1.1	722.9	27.3	0.3	2.0	2.8	71.6	18.8	2.5
521	1.3	27.2	0.2	4.0	0.9	14.5	18.1	1.6	25.8	64.6	-4.56	-26.9	8.8	6.1	1262.5	22.3	0.0	1.3	1.7	67.2	6.8	0.0
524	1.8	29.4	0.3	0.0	0.0	11.8	14.8	1.4	31.0	38.7	-3.45	-21.8	2.3	1.1	139.5	9.5	0.0	0.4	1.8	106.4	1.0	1.0
609	2.3	58.9	0.5	0.0	0.0	40.3	42.4	4.5	41.8	35.1	0.28	-6.2	10.7	6.9	549.5	34.0	0.2	2.1	3.8	48.8	16.7	1.8
618	1.5	47.3	0.3	0.0	0.0	13.9	31.7	2.8	16.2	20.9	3.33	9.1	12.8	9.1	756.5	13.5	0.2	1.8	6.2	32.1	3.5	2.6
683	1.3	7.0	0.0	0.0	0.0	3.1	4.4	7.7	15.9	51.8	0.29	-11.0	2.9	0.9	747.0	24.5	0.3	1.2	6.9	72.7	15.1	5.7
684	1.7	47.8	0.4	0.0	0.0	19.7	29.9	3.0	36.6	46.2	-0.26	-9.0	4.1	2.5	258.2	6.9	0.0	0.9	2.5	61.9	8.3	2.1
710	2.7	28.7	0.3	0.0	0.0	15.7	21.6	2.7	64.1	57.0	-3.36	-23.4	4.3	2.1	292.8	13.7	0.2	1.2	2.7	119.9	10.3	0.0
713	3.0	20.4	0.2	0.2	0.1	268.7	12.2	2.6	38.4	129.1	-2.86	-17.9	2.6	1.7	181.5	1.4	0.0	0.7	1.8	143.4	4.8	0.0
718	3.0	95.6	0.5	0.0	0.0	57.7	60.9	7.2	73.7	39.9	2.60	4.7	30.4	21.3	1111.7	64.9	0.4	2.8	6.3	214.9	78.0	0.0
728	2.1	32.2	0.3	0.0	0.0	21.3	17.9	3.0	34.1	70.2	-2.15	-15.5	1.6	1.0	281.2	10.0	0.1	0.8	2.1	61.5	6.2	0.0
731	1.5	18.8	0.3	0.0	0.0	11.5	8.1	2.0	27.8	81.3	-2.00	-16.7	97.4	62.9	193.8	82.4	0.9	12.0	4.7	110.0	97.9	2.1
732	1.5	24.0	0.2	0.2	0.0	43.1	11.7	2.2	17.4	59.1	-2.20	-15.6	1.1	0.8	100.7	9.9	0.0	0.3	1.5	41.6	0.3	0.0
733	1.4	40.1	0.4	0.0	0.0	20.6	21.9	2.6	39.4	45.4	-1.53	-13.8	1.4	0.6	347.1	7.0	0.0	0.5	3.5	58.4	5.5	0.0
744	2.5	31.6	0.5	0.0	0.0	13.9	15.3	2.8	43.0	42.1	0.13	-6.0	6.1	3.5	1037.1	31.8	0.7	4.5	9.3	104.9	21.7	16.2
754	1.4	14.9	0.0	2.1	0.5	11.0	9.7	1.7	29.3	75.0	-4.54	-26.8	1.4	0.6	674.7	12.3	0.0	0.8	1.7	79.1	3.3	1.6
762	2.8	21.2	0.2	13.0	2.9	61.6	21.6	2.4	33.4	88.4	-3.85	-23.1	1.2	0.6	3105.1	8.6	0.0	0.4	9.3	147.3	0.9	3.6
766	2.3	54.5	0.5	1.1	0.2	43.5	39.6	3.5	40.3	58.1	-2.14	-16.0	3.1	1.9	449.9	11.3	0.0	1.0	2.6	50.2	6.7	0.0
767	2.4	56.2	0.4	2.1	0.5	33.7	36.4	4.3	43.8	58.4	-2.70	-18.6	1.8	0.9	773.3	11.7	0.0	0.3	2.2	66.1	2.7	4.4
772	1.5	21.9	0.1	0.4	0.1	50.2	11.0	1.6	16.9	62.1	-1.77	-12.6	0.9	0.5	177.5	0.1	0.0	0.3	1.6	36.5	0.0	1.5
779	1.8	14.2	0.0	0.9	0.2	14.8	9.0	1.5	15.4	96.3	-4.28	-24.7	3.4	1.9	209.4	2.7	0.2	1.6	1.5	94.9	3.2	0.0
788	2.9	69.1	0.4	12.3	2.8	38.4	39.0	3.7	63.7	51.8	-2.35	-17.0	1.9	1.1	3082.8	8.4	0.1	0.9	2.0	72.1	3.0	2.0
789	3.2	60.9	0.7	0.0	0.0	81.4	42.9	3.5	46.5	80.3	-1.98	-15.0	5.4	3.4	219.9	26.6	0.2	1.1	3.2	165.1	25.7	6.1
793	2.0	30.5	0.2	0.0	0.0	16.5	16.0	2.0	38.7	51.7	-1.52	-13.1	4.7	2.9	190.7	8.4	0.0	1.0	2.4	70.2	7.9	3.4
794	1.5	41.7	0.3	0.0	0.0	12.4	22.4	3.0	36.8	53.0	-2.09	-17.9	4.9	2.9	190.4	10.4	0.1	1.4	2.1	53.3	11.9	0.0
796	1.1	8.5	0.0	0.2	0.0	3.1	13.2	2.0	35.7	64.5	-0.41	-5.0	28.2	19.1	779.5	29.1	0.3	3.9	3.9	115.8	30.4	2.1
808	1.9	35.0	0.4	0.2	0.0	25.0	17.7	2.6	33.0	40.3	-0.26	-8.5	5.0	3.2	381.9	12.5	0.1	1.2	3.2	75.3	11.7	0.0

Site	F ⁻ (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ -NO ₃ (ppm)	NO ₃ ⁻ -N (mg/L)	SO ₄ ²⁻ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	Mg ²⁺ (ppm)	Ca ²⁺ (ppm)	δ ¹⁸ O VSMOW	δ ² H VSMOW	TSS (mg/L)	NVSS (mg/L)	TN (ug/L)	TP (ug/L)	PN (mg/L)	PC (mg/L)	DOC (mg/L)	NH ₄ (ug/L)	PP (ug/L)	SRP (ug/L)
810	1.5	38.0	0.3	2.6	0.6	21.5	21.8	1.6	29.3	55.4	-3.94	-24.9	3.7	0.9	817.9	7.6	0.0	0.6	1.9	63.9	3.8	1.8
812	1.5	37.5	0.3	0.0	0.0	14.2	17.7	2.1	32.5	56.6	-1.53	-14.0	2.4	1.4	197.0	2.9	0.0	0.5	1.8	42.3	2.2	1.1
815	2.0	15.2	0.2	0.0	0.0	3.1	6.7	1.2	25.2	38.0	-1.91	-13.4	28.8	18.9	99.4	32.0	0.6	4.7	2.3	59.4	31.6	2.6
816	2.0	18.9	0.2	0.0	0.0	22.1	9.1	1.9	20.7	39.5	-0.49	-7.8	2.2	1.2	366.2	13.3	0.0	1.1	2.4	34.2	2.6	3.1
818	1.3	16.3	0.0	0.0	0.0	13.5	7.8	1.6	19.6	64.9	-3.14	-18.3	3.8	2.4	101.5	12.2	0.1	1.0	1.5	59.1	2.0	0.0
832	2.3	65.3	0.4	0.5	0.1	37.2	44.1	4.6	46.1	59.1	-2.67	-17.6	0.8	0.7	375.5	4.5	0.0	0.3	2.2	56.7	2.6	6.7
835	1.6	19.7	0.2	0.0	0.0	12.6	11.8	1.5	27.5	71.6	-3.30	-20.5	1.4	0.7	123.9	4.3	0.0	0.4	1.4	54.1	3.1	0.0
836	1.8	33.0	0.2	0.0	0.0	16.2	17.1	1.5	34.3	35.9	-1.98	-15.2	4.8	2.3	325.0	11.9	0.2	1.7	2.6	126.0	7.4	10.3
840	2.1	11.1	0.2	0.0	0.0	8.7	7.1	1.7	27.6	54.0	-3.56	-21.5	1.3	1.0	128.2	6.9	0.0	0.4	1.5	43.2	0.2	0.8
841	2.2	24.4	0.3	0.0	0.0	18.3	15.5	2.3	45.2	55.8	-1.55	-12.3	7.0	4.4	209.3	16.8	0.0	1.0	3.6	68.3	15.6	2.5
851	1.6	19.3	0.2	0.4	0.1	41.8	10.4	2.4	20.1	46.3	-0.36	-8.9	2.9	1.7	219.5	5.4	0.0	0.7	1.7	34.2	1.0	3.6
852	1.6	19.4	0.2	0.0	0.0	33.8	9.9	2.3	20.2	43.8	-0.70	-10.4	4.8	2.8	238.6	2.5	0.0	1.7	2.5	27.0	5.7	0.0
863	1.6	44.5	0.3	1.1	0.2	18.3	28.1	2.1	25.1	72.7	-4.11	-25.8	8.9	5.3	444.4	12.9	0.4	4.7	2.3	51.7	10.1	1.6
868	1.7	49.7	0.4	0.0	0.0	6.8	26.7	3.7	32.1	24.8	0.77	-4.6	8.6	4.2	1016.4	26.5	1.4	15.0	6.4	34.2	17.1	1.4
878	1.4	24.1	0.2	0.0	0.0	10.8	12.8	1.5	31.4	48.5	-1.49	-13.0	5.7	3.6	290.3	16.2	0.1	0.9	2.3	22.1	6.6	0.0
879	2.2	24.8	0.2	0.0	0.0	23.4	14.5	1.6	51.3	46.0	-2.42	-17.4	1.4	0.8	277.2	5.5	0.0	0.4	2.0	70.7	2.3	0.8
880	4.6	80.4	0.5	0.0	0.0	58.7	54.1	7.5	81.3	66.1	-0.41	-4.6	37.4	4.3	2621.7	71.1	0.9	7.8	12.0	175.3	159.2	76.5
881	2.2	94.6	0.3	0.6	0.1	26.4	40.1	4.1	71.0	39.5	-0.30	-7.1	3.3	2.0	588.9	8.6	0.3	2.7	4.3	114.0	10.0	4.6
883	1.6	18.0	0.0	0.2	0.0	14.3	11.5	2.0	41.7	32.6	-2.60	-16.8	3.6	2.1	298.7	8.2	0.2	2.2	2.0	57.7	9.2	0.0
884	1.6	32.7	0.4	0.0	0.0	18.7	15.9	2.1	28.1	45.9	-0.38	-8.4	2.0	1.0	260.5	17.8	0.0	0.4	2.9	27.0	5.0	0.5
887	1.3	17.7	0.2	0.0	0.0	22.6	8.8	1.7	14.1	73.8	-3.94	-23.0	1.7	1.1	75.4	6.7	0.0	0.6	1.2	94.8	0.9	0.0
888	2.9	22.7	0.3	0.0	0.0	49.7	15.1	2.7	23.8	81.5	-2.68	-18.2	4.4	2.4	0.0	15.8	0.0	0.7	1.9	150.0	17.6	0.0
889	2.2	88.6	0.5	0.0	0.0	45.8	64.5	6.5	39.0	57.6	-2.54	-17.8	1.0	0.8	287.2	442.5	0.0	0.3	2.2	46.6	4.0	365.9
898	1.7	35.0	0.2	0.2	0.0	16.6	22.1	3.0	27.6	39.8	-0.14	-6.8	1.2	0.6	270.8	4.5	0.0	0.6	1.4	21.9	2.9	1.9
900	1.9	40.5	0.3	0.0	0.0	12.4	21.2	2.7	41.8	41.8	-0.25	-8.5	2.4	1.3	325.8	14.1	0.0	0.6	3.6	36.7	4.9	0.0
901	1.6	27.2	0.3	0.0	0.0	6.2	16.5	2.9	17.5	27.9	2.20	1.8	4.7	3.0	532.1	10.7	0.1	0.9	4.0	24.7	6.2	0.0
906	3.0	34.4	0.3	0.0	0.0	13.5	22.4	3.3	21.5	51.2	-2.96	-17.5	0.9	0.5	117.6	12.3	0.0	0.0	1.4	32.0	0.5	8.5
913	1.4	16.0	0.0	0.0	0.0	5.5	9.8	1.6	22.9	32.1	-2.13	-16.7	1.7	0.9	172.6	6.1	0.0	0.6	2.0	29.2	3.8	0.3
918	1.5	50.6	0.3	0.3	0.1	10.7	28.7	2.8	35.9	22.8	2.30	3.7	1.7	1.0	594.8	14.3	0.0	0.6	6.9	31.3	7.9	0.0
920	2.6	52.8	0.4	1.9	0.4	28.7	39.0	3.3	43.1	57.5	-2.76	-20.5	1.6	0.9	631.2	10.6	0.0	0.5	1.6	80.3	1.5	5.6
940	1.5	13.3	0.0	0.0	0.0	14.1	6.2	1.3	26.7	35.9	-4.62	-25.3	0.7	0.2	91.7	2.0	0.0	0.3	1.3	93.6	0.0	0.9
941	5.2	113.9	0.9	2.9	0.6	76.2	212.3	11.0	15.1	35.6	-4.42	-25.8	1.1	0.7	699.4	2.3	0.0	0.2	0.4	4.1	0.0	0.0
943	1.5	11.7	0.0	2.1	0.5	13.7	5.9	1.2	23.7	90.4	-4.63	-25.5	7.2	3.4	542.7	2.9	0.0	1.4	0.9	67.2	3.7	0.9
951	2.6	113.2	0.2	40.6	9.2	64.1	95.0	13.6	45.1	85.4	-3.92	-22.3	4.4	2.5	12420.6	2007.8	0.0	1.6	4.3	1096.0	41.3	2341.5
952	2.1	54.4	0.3	0.9	0.2	35.9	37.2	4.4	39.3	39.6	1.15	-0.9	15.2	9.4	833.6	41.2	0.2	2.8	3.5	43.7	57.2	87.0
953	1.5	41.2	0.3	3.4	0.8	18.3	27.8	1.8	21.7	62.9	-2.90	-20.7	6.2	3.7	1052.5	7.0	0.0	1.3	1.9	47.8	4.1	0.0
954	1.4	12.6	0.0	1.5	0.3	20.4	7.2	1.7	22.6	82.9	-4.38	-24.9	0.8	0.6	460.8	2.3	0.2	3.0	0.9	73.5	3.2	1.1
955	1.7	29.2	0.3	0.0	0.0	26.1	17.4	2.9	29.8	39.8	-0.68	-9.0	4.7	3.0	305.0	8.4	0.0	0.9	2.2	18.7	7.0	0.0
956	1.4	32.4	0.3	0.8	0.2	29.3	19.5	3.1	30.7	47.9	-0.84	-9.3	7.9	5.9	393.1	15.2	0.0	0.9	1.5	34.1	4.8	13.4
957	1.9	21.1	0.1	2.5	0.6	16.1	12.0	1.6	35.1	37.0	-4.27	-23.8	1.2	0.7	690.7	2.5	0.0	0.6	1.3	61.9	2.9	0.0
958	1.2	7.1	0.0	8.0	1.8	11.3	5.2	0.7	18.8	56.1	-4.66	-26.3	0.9	0.6	2076.4	7.8	0.0	0.2	1.1	35.3	0.0	0.0
959	1.2	6.3	0.0	5.1	1.2	9.0	4.5	0.8	22.2	65.1	-4.74	-26.5	0.8	0.5	1375.7	2.0	0.1	0.4	1.2	43.7	0.2	1.6
960	1.3	11.3	0.0	3.7	0.8	9.8	9.1	1.3	30.8	77.4	-4.79	-26.7	2801.5	1289.9	65353257.6	54.9	7.5	105.5	1.6	260.1	1540.6	44.6
961	11.8	23.1	0.0	0.0	0.0	472.3	16.5	13.4	103.8	185.8	-4.58	-26.9	1.0	0.7	342.1	3.1	0.0	0.2	0.6	503.8	1.2	0.0
962	1.7	12.1	0.0	2.4	0.5	24.6	6.8	1.5	27.6	65.5	-4.34	-24.0	0.7	0.4	593.3	0.0	0.0	0.3	0.8	73.1	0.0	2.6
971	2.1	13.3	0.0	0.7	0.1	109.9	7.6	2.0	39.0	98.7	-4.47	-24.4	1.0	0.3	194.8	1.2	0.0	0.3	0.8	131.2	0.0	0.0
684D	1.7	47.6	0.4	0.0	0.0	19.5	29.3	3.3	35.9	43.5	-0.28	-9.1	2.7	1.7	224.9	21.9	0.1	0.8	2.9	57.7	10.8	2.8
898D	1.6	34.7	0.2	0.2	0.0	16.6	22.1	3.0	27.5	39.7	-0.15	-6.9	1.2	0.0	244.2	8.2	0.1	0.6	1.6	23.6	2.8	4.7

Site	F ⁻ (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ -NO ₃ (ppm)	NO ₃ ⁻ -N (mg/L)	SO ₄ ²⁻ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	Mg ²⁺ (ppm)	Ca ²⁺ (ppm)	δ ¹⁸ O VSMOW	δ ² H VSMOW	TSS (mg/L)	NVSS (mg/L)	TN (ug/L)	TP (ug/L)	PN (mg/L)	PC (mg/L)	DOC (mg/L)	NH ₄ (ug/L)	PP (ug/L)	SRP (ug/L)
940D	1.6	13.1	0.0	0.2	0.0	13.8	6.2	1.7	27.2	79.4	-4.62	-25.7	1.0	0.8	81.7	2.9	0.0	0.2	1.2	191.8	0.0	3.1
953D	1.4	41.0	0.3	3.4	0.8	18.2	27.6	2.0	21.9	64.1	-2.97	-20.8	5.7	3.9	1071.7	4.4	0.2	2.4	1.9	44.2	2.6	0.0
957D	1.9	21.3	0.1	2.5	0.6	16.3	11.9	1.6	35.1	35.3	-4.24	-23.8	1.5	0.8	694.5	2.0	0.0	0.5	1.1	76.4	3.2	0.0
971D	2.1	13.3	0.0	0.7	0.2	109.4	7.5	2.0	39.1	99.1	-4.49	-24.6	0.4	0.3	147.6	7.2	0.0	0.0	0.9	97.2	0.0	0.0
BS1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	-4.10	-22.9	0.4	0.3	0.0	3.1	0.0	0.0	0.4	0.0	0.0	0.0
SB2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.1	-4.18	-23.4	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0

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