PEDERNALES RIVER 2017 STORM WATER SAMPLING

The Meadows Center for Water and the Environment
January 2018

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The Meadows Center for Water and the Environment
Texas State University

MEMBER THE TEXAS STATE UNIVERSITY SYSTEM

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Performing Agency:

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LIST OF ACRONYMS

BC: Barons Creek Sampling Site at Old San Antonio Road

BMP: Best Management Practices

BSEAGCD: Barton Springs Edwards Aquifer Conservation District

DOC: Dissolved Organic Carbon

FB: Fredericksburg Sampling Site at HWY 87

GMWL: Global Meteoric Water Line

JC: Johnson City Sampling Site at HWY 281

LBJ: LBJ Sampling Site at Klein Road

LCRA: Lower Colorado River Authority

NLCD: National Land Cover Database

NVSS: Non-Volatile Suspended Solids

PC: Particulate Carbon

PP: Particulate Phosphorous

SRP: Soluble Reactive Phosphorous

TDS: Total Dissolved Solids

Total N: Total Nitrogen

Total P: Total Phosphorous

TSS: Total Suspended Solids

USGS: United States Geological Survey

EXECUTIVE SUMMARY

In conjunction with the project "How Much Water is in the Hill Country", a preliminary sampling program was conducted during a major storm event on August 7th, 2017. Storm water samples were collected at three locations in the main channel of the Pedernales River and one location on Barons Creek to determine if excessive amounts of nutrients and solids were entering the river system. Storm water samples were compared to water quality during base flow conditions.

Major findings indicate there were large increases in nutrient and sediment loading in the river during the storm event. The areas in and upstream of the City of Fredericksburg appeared to contribute the highest concentrations of nutrients and suspended solids during the early parts of the event. Elevated concentrations were measured downstream as the storm surge proceeded towards Johnson City.

A more robust sampling program is needed to further delineate storm water runoff quality and identify specific areas where best management practices (BMPs) could be implemented to minimize nutrient and solids loading to the river and ultimately Lake Travis. Potential BMPs identified in the report "How Much Water is in the Pedernales, Conservation Strategies, Management Approaches and Action Plan" (Wierman, et al, 2015) should be considered.

INTRODUCTION AND PURPOSE

Nutrient and sediment loading from storm water runoff events into Hill Country streams can lead to degradation of the water ways. Nutrient loading from nitrogen and phosphorous compounds can cause algae and aquatic plants to grow wildly, choke up the waterway and use up large amounts of oxygen required to support other aquatic species. Sediment loading can reduce sunlight penetrating the water. Sediment loading can also result in the deposition of sediment in the stream bed and, in the case of the Pedernales River, increased sedimentation in Lake Travis.

In conjunction with the project "How Much Water is in the Hill Country?", base flow water quality samples have been collected and analyzed for inorganic parameters to aid in understanding groundwater/surface water interactions. By definition, base flow in streams is totally supported from groundwater discharge and water quality reflects groundwater quality. Results of previous base flow sampling events in the Pedernales River Basin can be found in Zappitello (2016).

Storm water sampling during a precipitation event provides an opportunity to characterize the quality of runoff from the land surface. Previous sampling events, such as in Onion Creek (Smith, et al, 2011), indicate an increase in phosphorous, nitrogen and total suspended solids (TSS) during storm events. These increases are primarily attributable to human land use activities such as agriculture, wastewater treatment and runoff from impervious cover, but some increases may be natural.

The purpose of this study is to perform an initial, screening level storm water sampling program to determine if there are water impacts to the river from rain events and secondly, to develop recommendations for future investigations, if warranted.

It is recognized that every storm water runoff event is somewhat unique. Rainfall distribution and intensity vary from storm to storm. Antecedent soil moisture conditions are a significant factor in the volume and quality of runoff. Seasonality can be a factor. For example, spring/early summer runoff is likely higher in nutrients from urban and agricultural fertilizer application as compared to late summer or fall. Given these variables, this study and its conclusions are general in nature and may not be representative of other storm events but are useful on a screening level.

SAMPLING PROGRAM

Samples were collected during two storm events in 2017: May 19-20 and August 7-8. Surface water grab samples were collected at four locations during each event. Three of the locations are at or near fixed, continuous measurement gauging stations on the Pedernales River: two maintained by the United States Geological Survey (USGS) and one by the Lower Colorado River Authority (LCRA). The fourth location is on Barron's Creek, downstream of the city of Fredericksburg on Old San Antonio Road. Samples were also collected at Hammett's Crossing during the May event but not during the August event due to access issues with high water. Sampling locations are included in Figure 1 and shown in Table 1.

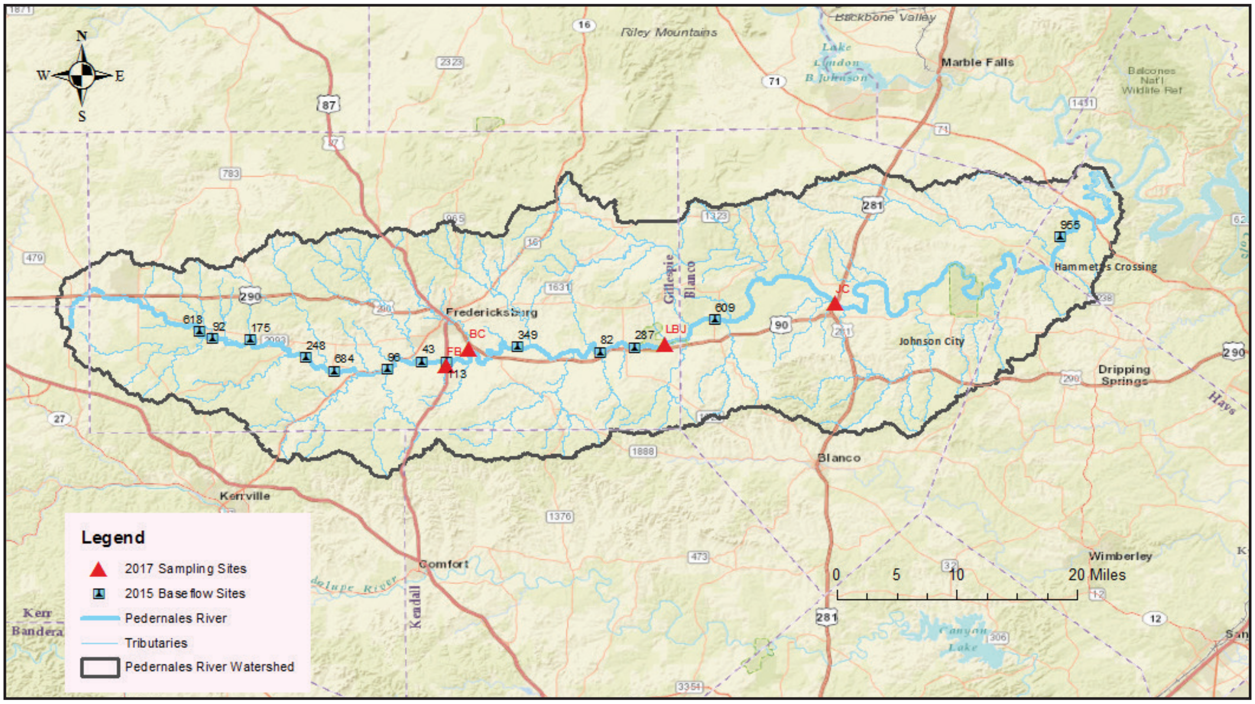


Figure 1. Sampling locations.

Sampling Site Designation	Station Designation	Location (listed upstream to downstream)
FB	USGS 08152900	Highway 87 near Fredericksburg, TX https://waterdata.usgs.gov/nwis/uv?site_no=08152900
BC	n/a	Old San Antonio Road south of Highway 290
LBJ	LCRA 3343	LBJ Ranch near Stonewall (Klein Road) http://hydromet.lcra.org/full.aspx
JC	USGS 08153500	Highway 281 near Johnson City, TX https://waterdata.usgs.gov/nwis/uv?site_no=08153500

Table 1. Sampling Locations

During sample collection, river discharge was noted from the sites respective webpage, except Barons Creek as there is not a station at that location. Immediately upon grab sample collection, field parameters of pH and specific conductivity were measured using hand held field meters. Meters were calibrated each morning. Two one-half gallon containers were collected for each sample and kept on ice until delivered to Dr. Benjamin Schwartz's laboratory at Texas State University in San Marcos, TX. Field measurements are included in Appendix A.

Samples were analyzed for the parameters included in Appendix A. These parameters were selected to compare with base flow sampling by Zappitello (2016). The parameters are also representative of naturally occurring parameters and various nitrogen and phosphorous compounds that may be either natural or the results of human activities. A summary of the parameters is included in Table 2. Laboratory quality control information is included in Appendix B.

Parameter	Parameter Description
Sodium, Potassium, Magnesium, Calcium	Naturally occurring cations used in general water classification. Abnormally large concentrations may indicate natural brines, industrial brines, or sewage.
Chloride, Sulfate	Naturally occurring cations used in general water classification. Point source pollution includes wastewater treatment plants and industrial discharges. Runoff from fertilized agricultural lands also contributes sulfates to water bodies. Discharge from water softeners can be a significant source of chloride.
Fluoride	Natural fluorides occur in rocks in some areas. Another source of fluorides in streams and reservoirs is releases from wastewater treatment plants, since most public water supplies add fluoride to drinking water to reduce dental decay.
Total Dissolved Solids	Primarily from dissolution processs in carbonate rock units. Agriculture and urban runoff are also sources.
Total Suspended Solids	Suspended solids consist of an inorganic fraction (silts, clays, etc.) and an organic fraction (algae, zooplankton, bacteria, and detritus) that are carried along by water as it runs off the land. Both contribute to turbidity, or cloudiness of the water. The geology and vegetation of a watershed affect the amount of suspended solids
Non-volatile Suspended Solids	Non-volatile Suspended Solids is a measurement of the total solids, including both the suspended solids and the dissolved solids which are obtained by separating the solid and liquid phase by evaporation.
Total Nitrogen (N), Ammonia (NH3), Nitrate (NO3), Nitrite (NO2), Ammonium (NH4)	Various forms of dissolved nitrogen compounds. Primarily from agriculture and urban runoff but may be naturally occurring. Ammonium ions are a waste product of the metabolism of animals. Aquatic life and fish also contribute to ammonia levels in a stream. NH3 is the principal form of toxic ammonia.

Parameter	Parameter Description
Phosphorus	Rainfall can cause varying amounts of phosphates to wash from agricultural soils into nearby waterways. Phosphate will stimulate the growth of plankton and aquatic plants which provide food for fish. This may cause an increase in the fish population and improve the overall water quality. However, if an excess of phosphate enters the waterway, algae and aquatic plants will grow wildly, choke up the waterway and use up large amounts of oxygen.
Total Reactive Soluble Phosphorus	Ortho-phosphate (soluble reactive phosphorus) and total phosphorus. Ortho-phosphate is the chemically active dissolved form of phosphorus that is taken up directly by plants. Ortho-phosphate levels fluctuate daily. Orthophosphate is a readily available to the biological community and typically found in very low concentrations in unpolluted waters.
Particulate Phosphorous (PP)	A portion of particulate phosphorus is contained in organic matter such as algae, plant and animal tissue, waste solids, or other organic matter. Microbial decomposition of organic compounds can convert organic particulate P to dissolved P. Some of the P in soil mineral particles can also be converted to dissolved P both in the water column and during chemical and physical changes in bottom sediment. Only the most tightly bound forms of particulate phosphorus such as aluminum-bound phosphorus are not generally available for algal growth. Because phosphorus changes form, most scientists measure total phosphorus rather than any single form to determine the amount of nutrient that can feed the growth of aquatic plants such as algae.
Stable Water Isotopes	N, O and B isotopes to evaluate nitrate pollution in water. Tracers in watershed hydrology. Interpret spatial patterns and temporal changes in pollution sources.
Soluble Reactive Phosphorus (SRP)	Soluble Reactive Phosphorus is a measure of orthophosphate, the filterable (soluble, inorganic) fraction of phosphorus, the form directly taken up by plant cells. Orthophosphate is produced by natural processes and is found in sewage.
Particulate and Dissolved Organic Carbon	Derived from decaying organic matter and living organisms. Can provide a food source for some aquatic organisms. Particulate organic carbon (POC) is generally the form of carbon that most readily undergoes sedimentation and in-ecosystem loss.
Common manmade sources include: • Cropland • Forestry harvest • Grazing land • Industrial discharge • Mining • Septic systems • Wastewater treatment plants • Construction • Urban runoff	

Table 2. Summary of Analytical Parameters

AUGUST 7-8, 2017 STORM EVENT

The target precipitation event is a fast-moving, heavy precipitation event that encompasses the entire watershed and the river is at or near base flow conditions prior to the storm. The May event started as a basin wide rainfall event, but quickly lost momentum. The August event was basin wide and generated considerable runoff. Figure 2 is a snap shot of Doppler radar showing storm intensity as the August storm moved from north to south. See Figure 3 for the distribution of rainfall during the August event.

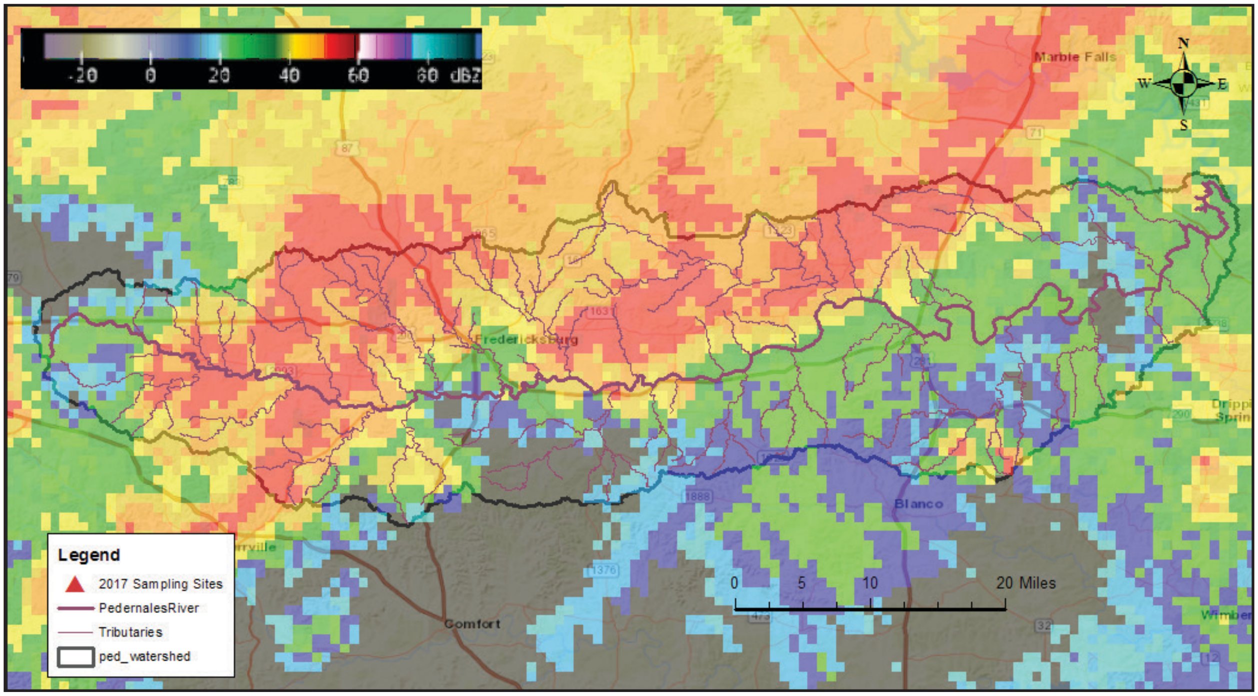


Figure 2. Doppler radar from August 7, 2017.

The August 7 event was of short duration, but very intense. The majority of the precipitation fell between 04:00 and 06:30. Total precipitation ranged from a trace to over 5 inches across the watershed. The highest rainfall totals were north of Hwy 290 in the Fredericksburg area (Figure 3). Figure 4 shows the precipitation hydrograph as well as the surface water discharge at the three gauging/sampling locations.

The initial water samples (-3 suffix) were collected shortly after the rainfall ceased, but several hours after the intense rainfall that occurred around 06:00. The -3 samples were obtained at the initial rise of the discharge hydrograph. The water quality from these samples is likely representative of water from the subwatersheds immediately upstream of the sampling location, prior to mixing in the river channel. Water quality may be representative of land use/land cover near the sampling locations. Samples obtained later in the event should exhibit some degree of mixing in the main channel as the storm surge moved downstream.

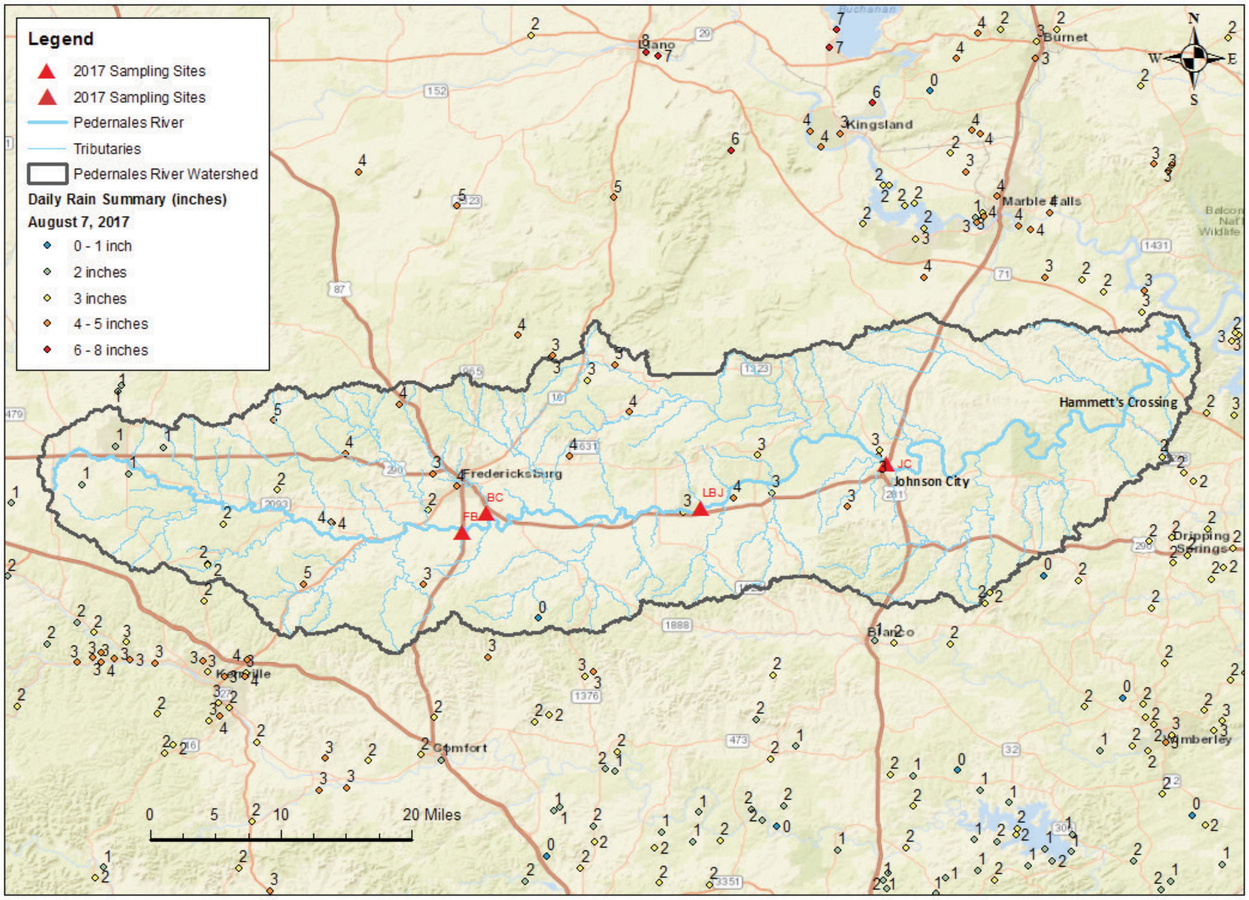


Figure 3. Precipitation totals for August 7, 2017.

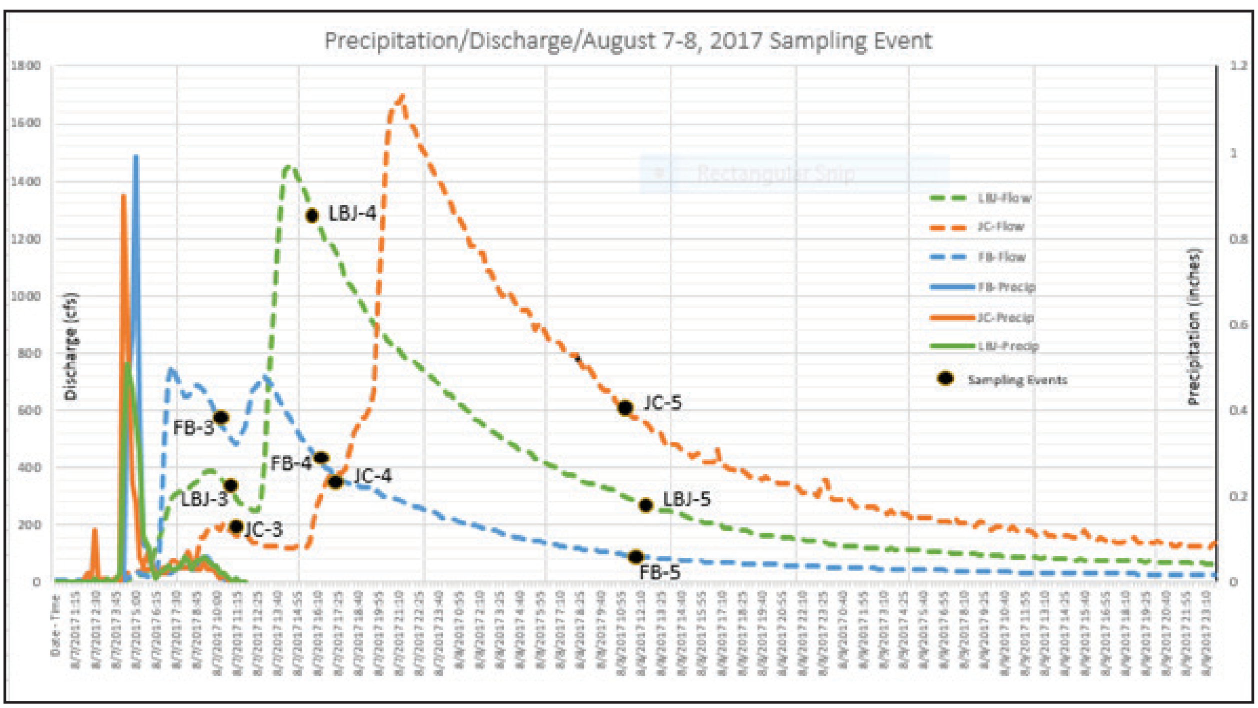


Figure 4 Precipitation and River Discharge Hydrographs, August 7 -9, 2017.

Figure 5. Barons Creek sampling location at Old San Antonio Road, Fredericksburg (August 7, 2017).

Figure 6. August 7, 2017 flood damage to Old San Antonio Road Bridge at Barons Creek.

Figure 7. Fredericksburg sampling location at Hwy 87 (August 8, 2017).

Figure 8. LBJ sampling location at Klein Road (August 7, 2017).

Figure 9. JC sampling location at Hwy 281 in Johnson City.

LAND COVER

Storm water quality is often related to land cover/use. Figure 10 illustrates the National Land Cover Data for the Pedernales River watershed. Data from FB likely reflects runoff quality from cultivated crop land and developed cover in the City of Fredericksburg. Site BC represents primarily urban runoff from the City of Fredericksburg. Also, the City of Fredericksburg municipal wastewater treatment plant also discharges into Barons Creek approximately one mile upstream of Site BC. The area upstream of the LBJ site has a significant amount of crop land and pasture land. The area immediately upstream of the JC site is mostly contained within the Towhead subwatershed. The land cover of the subwatershed is primarily shrub/scrub and evergreen forest. The majority of urban runoff from Johnson City enters the Pedernales River just downstream of the JC sampling point (Wierman, et al, 2017).

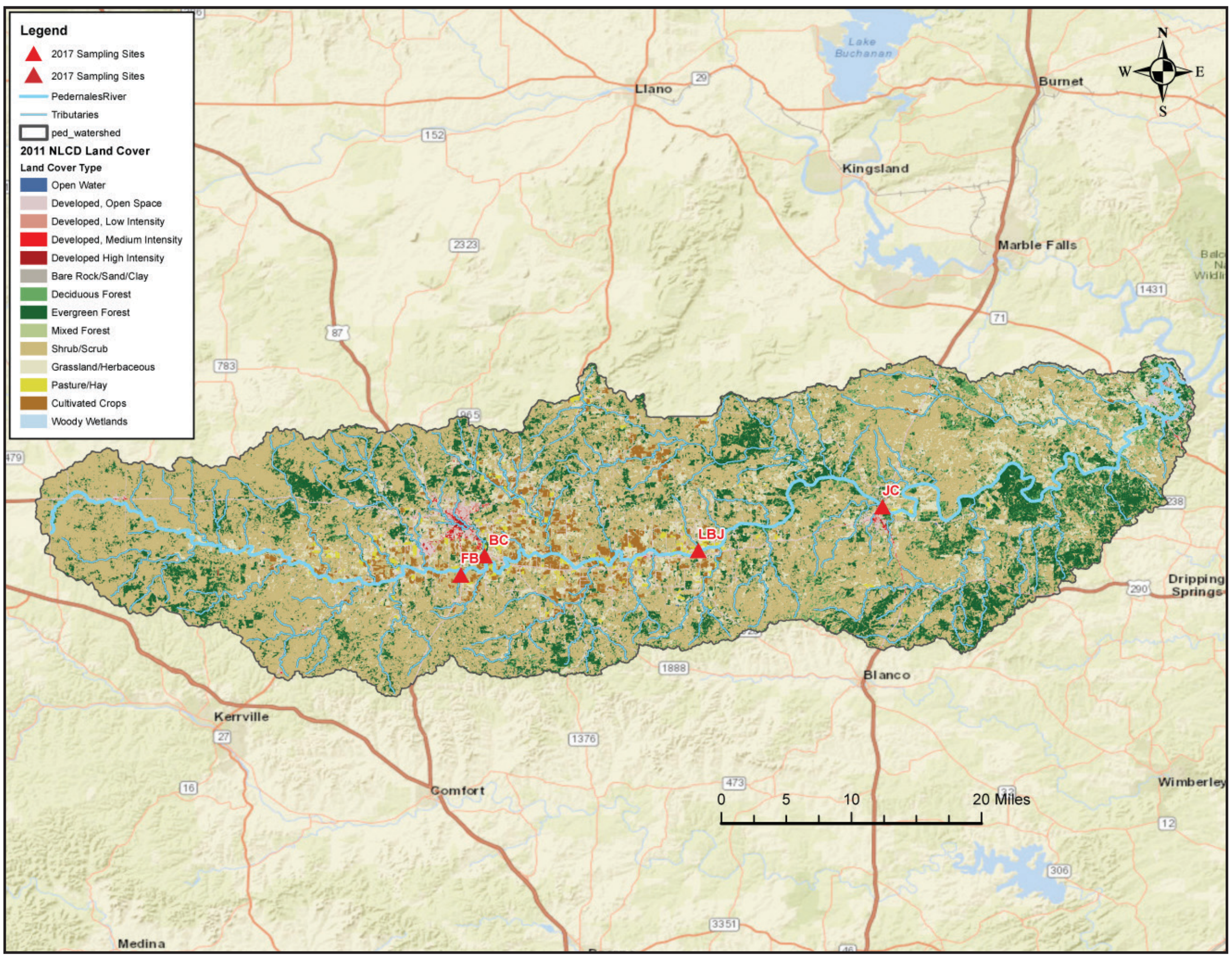


Figure 10. Pedernales Watershed NLCD Land Cover, 2011 (Wierman, et al, 2017).

Runoff water quality can also be influenced by the surficial geology. The central area of the watershed is underlain by the Hensel Sand (Wierman, 2017). Area underlain by the Hensel Sand is the only area in the watershed suitable for cultivated crops. Fertilizers rich in nitrogen and phosphorous are usually applied to the crop lands which increases the likelihood of nutrient enriched runoff. Increased sediment loads are common from cultivated lands.

SAMPLING RESULTS

Analytical results from the current storm water sampling events were compared to samples collected during base flow conditions. Base flow occurs when all surface water in the river is being contributed by groundwater. Base flow samples collected in August 2015 by Zappitello (2016) were collected from the main channel. Discharge rates during the 2015 sampling at FB and JC were 2 cfs and 18 cfs respectively (Zappitello, 2016). The results from thirteen samples were used to represent base flow water quality conditions for parameters analyzed in 2015 to compare to 2017 storm water samples. Base flow results from 2015 are included in Appendix C.

Average base flow concentrations of main channel samples are compared to US EPA (US EPA, 2001) recommended boundaries for trophic classification of streams for total phosphorus and total nitrogen Table 3.

Variable	Oligotrophic-mesotrophic boundary	Mesotrophic-eutrophic boundary	Pedernales River base flow
Total Phosphorus	0.025	0.075	0.024
Total Nitrogen	0.70	1.50	0.048

Table 3. Boundaries for Trophic Classification (all values expressed in milligrams per liter)

Based on the 2015 base flow sampling, the river would be classified as oligotrophic with regards to total nitrogen and borderline oligotrophic-mesotrophic when compared to total phosphorus. Oligotrophic water bodies have low nutrient concentrations usually resulting in very low algae content and clear water.

Representative parameters from each group are described in the following discussion. The representative parameters are calcium (major cations), chloride (major anions), total nitrogen (total N-nitrogen compounds), total phosphorous (total P-phosphorous compounds), total dissolved solids (TDS), total suspended solids (TSS) and carbon (particulate and dissolved organic carbon). Mean base flow concentrations are also shown on the parameter concentration graphs.

Calcium

Calcium concentrations were generally within the range of base flow concentrations for all samples. Sodium, potassium and manganese displayed similar trends. These cations are naturally occurring in the carbonate geology of the basin.

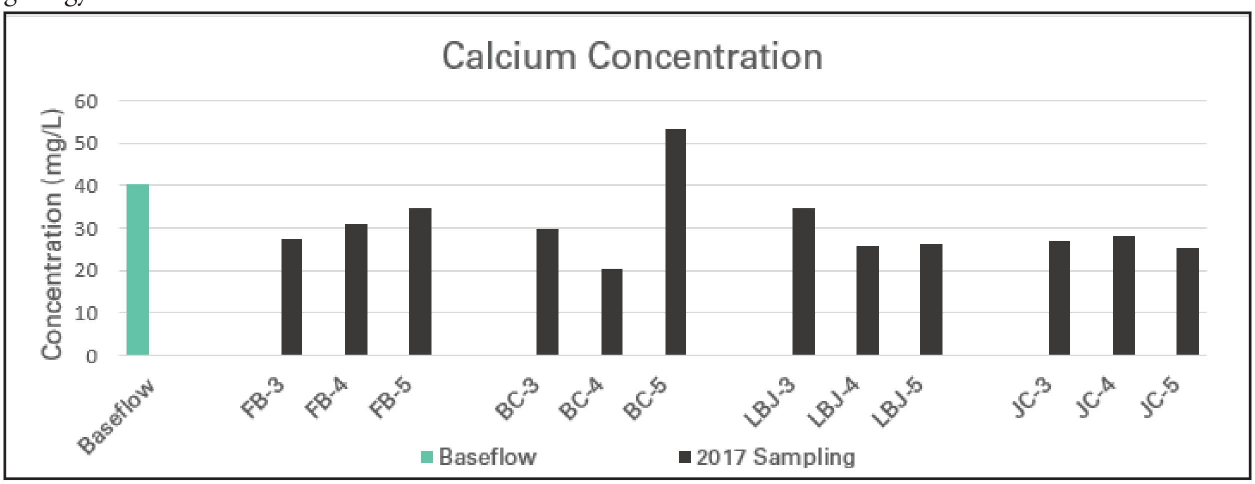


Figure 11. Calcium Concentrations - Base flow and August 7-8, 2017 Storm Water

Chloride

Chloride concentrations were at or below base flow concentrations throughout the event. Decreasing concentrations were observed at FB, LBJ and JC, probably the result of dilution from rainfall. Concentrations increased significantly at BC during the event, even as discharge was decreasing. The same trend was observed in sulfate concentrations. Runoff from the developed areas in the City of Fredericksburg as well as effluent discharge from the Fredericksburg wastewater treatment plant may have caused the increases observed.

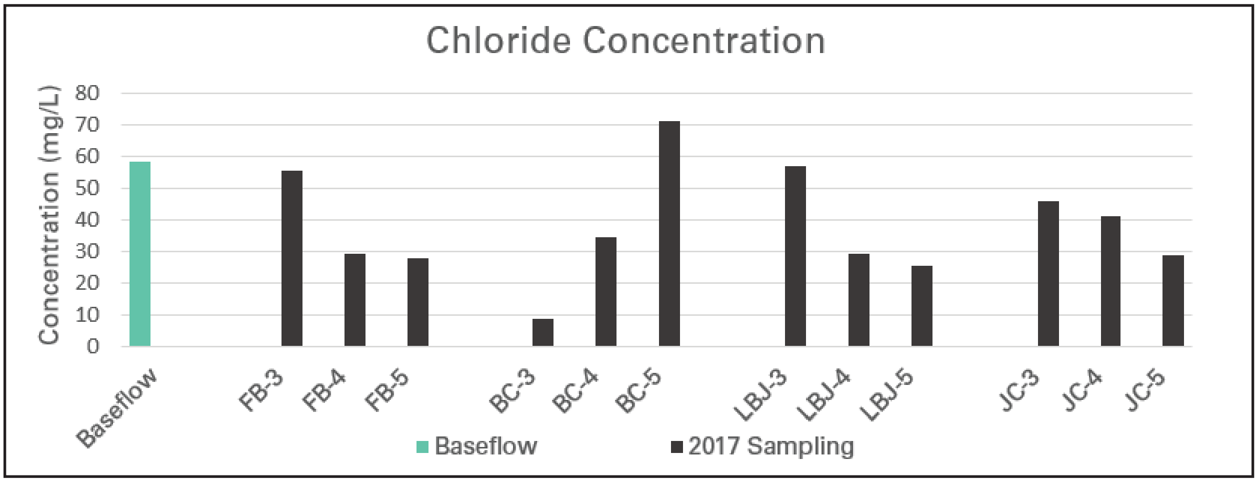


Figure 12. Chloride Concentrations - Base flow and August 7-8, 2017 Storm Water

Total P

Initial Total P concentrations were significantly above background levels at FB, BC and LBJ. Concentrations increased at JC towards the end of the storm surge. The increases at JC are likely the result of the storm surge moving downstream carrying phosphorous from upstream. SRP and particulate phosphorous showed similar trends. The sources of phosphorous at FB, BC and LBJ are likely urban runoff, effluent discharge from the Fredericksburg wastewater treatment plant and upstream agricultural runoff.

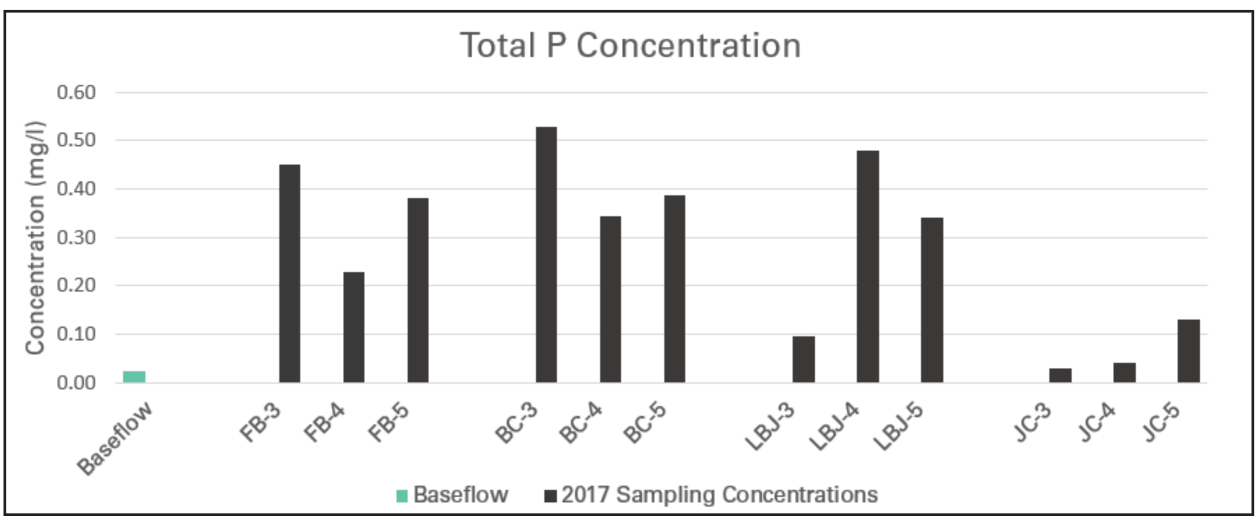


Figure 13. Total P Concentrations - Base flow and August 7-8, 2017 Storm Water

Total N

Concentrations of total N were significantly above base flow levels at FB and BC, with lower levels measured at LBJ and JC. Similar to total P concentrations, the sources of nitrogen at FB, BC and LBJ are likely urban runoff, effluent discharge from the Fredericksburg wastewater treatment plant and upstream agricultural runoff.

Initial total P concentrations were significantly above background levels at FB and BC. Concentrations increased at LBJ and to a lesser degree at JC. The increases at LBJ and JC are likely the result of the storm surge moving downstream. SRP and particulate phosphorous showed similar trends. The sources of phosphorous at FB and BC are likely urban runoff, effluent discharge from the Fredericksburg wastewater treatment plant and upstream agricultural runoff.

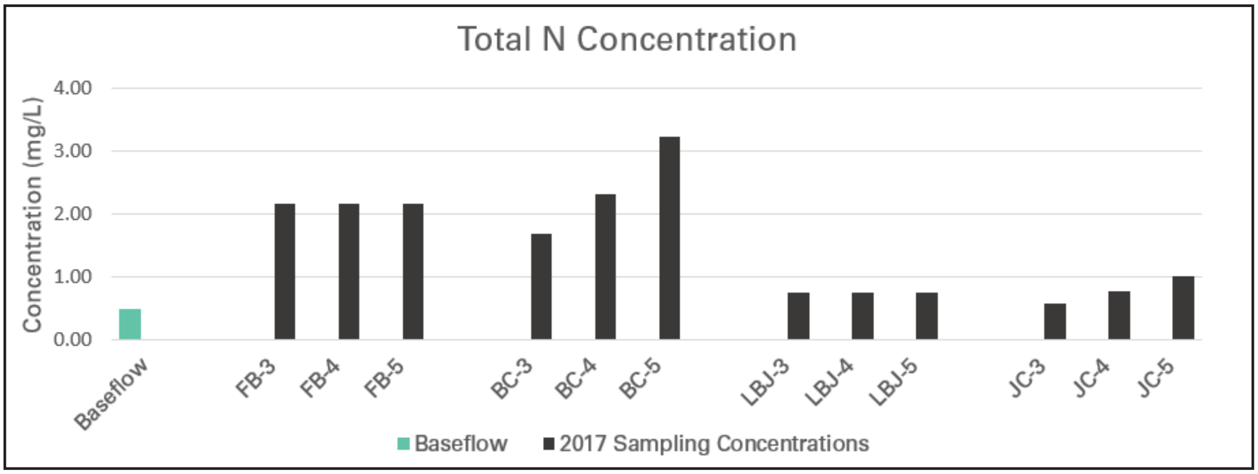


Figure 14. Total N Concentrations - Base flow and August 7-8, 2017 Storm Water

Solids

TDS concentrations (Figure 15) declined in all of the main channel sites throughout the storm event. Concentrations were generally in the 200-300 mg/l range. The decline in concentrations is likely due to dilution by precipitation. Concentrations at BC more than doubled during the storm event, from 169 mg/l to 371 mg/l as the runoff event subsided.

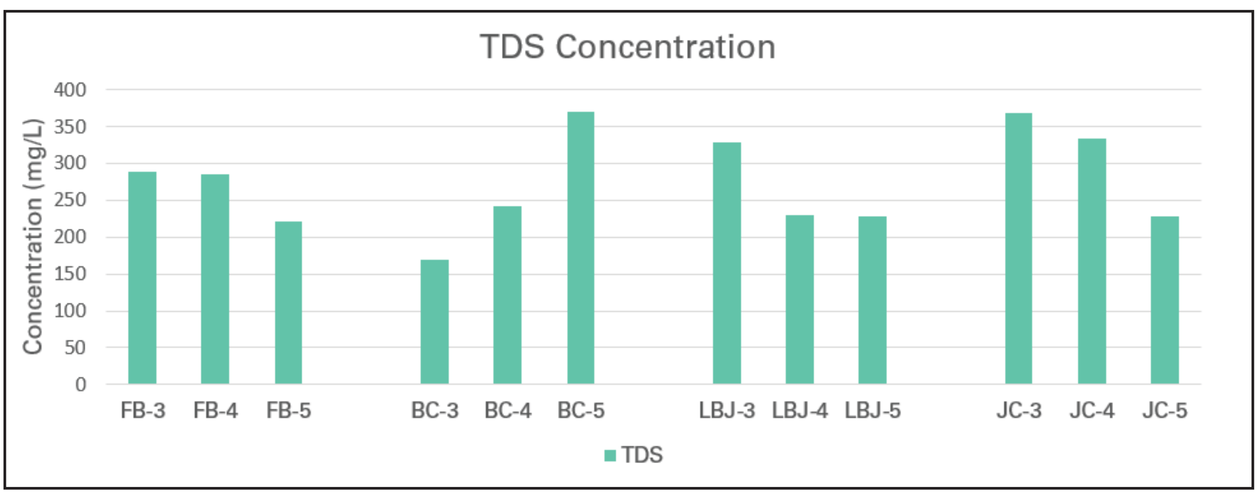


Figure 15. Total Dissolved Solids Concentrations - Base flow and August 7-8, 2017 Storm Water

It appears the majority of TSS originated in the Fredericksburg area, then proceeded downstream towards LBJ and JC. The highest TSS concentrations were measured in the first samples collected at FB and BC, then quickly decreased at those sites. As the storm surge moved downstream, TSS concentrations became elevated at LBJ, followed by JC. Figure 16 illustrates the progression of TSS downstream. Rainfall totals were highest north and west of the City of Fredericksburg which may have produced additional sediment load.

The elevated TSS concentrations measured in the Fredericksburg area at FB and BC may have several natural and manmade origins. Urban runoff from impervious areas and construction sites in the city can contribute to TSS. Runoff from cultivated agricultural lands is also a source.

The area around and upstream of Fredericksburg is underlain by the Hensel Sand. The Hensel Sand is more easily eroded than the carbonate rocks underlying the rest of the watershed. Erosion of tributary and main river channels in areas of surficial Hensel Sand also contribute to TSS.

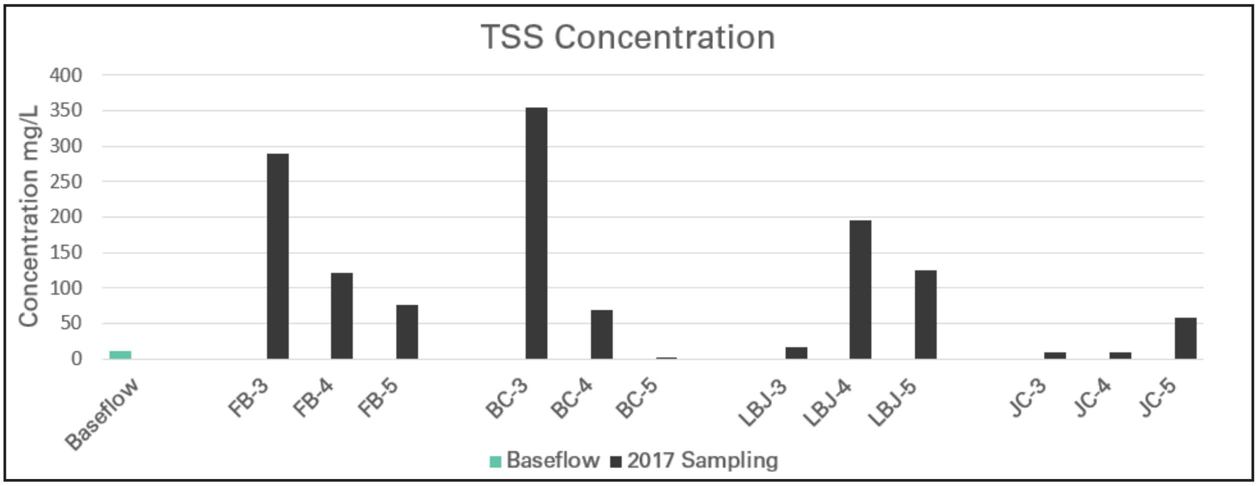
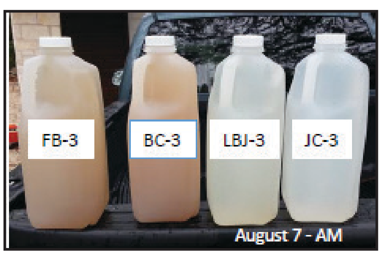


Figure 16. Total Suspended Solids Concentrations - Base flow and August 7-8, 2017 Storm Water



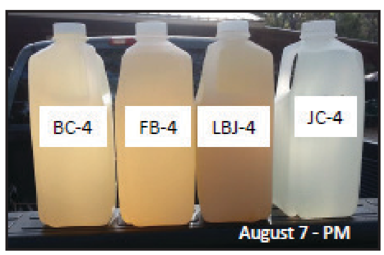


Figure 17. Sample bottles – August 7-8, 2017. Note progression of TSS downstream. BC and LBJ becoming less turbid. JC shows increasing turbidity.

Carbon

Total particulate carbon was highest at FB, likely reflecting the high rainfall totals upstream of this sampling point. Initial levels at BC were elevated with respect to base flow levels, but decreased to below background. The initial high levels were likely be the result of a "first flush" of the impervious cover areas in the subwatershed.

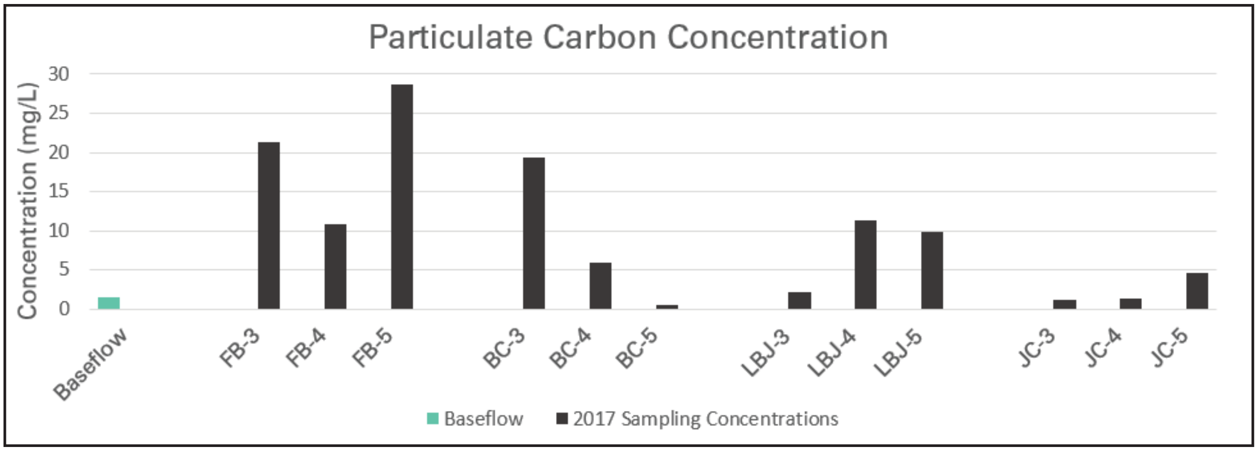


Figure 18. Particulate Carbon Concentrations - Base flow and August 7-8, 2017 Storm Water

Dissolved organic carbon concentrations were slightly above background levels. Concentrations were fairly consistent throughout the storm.

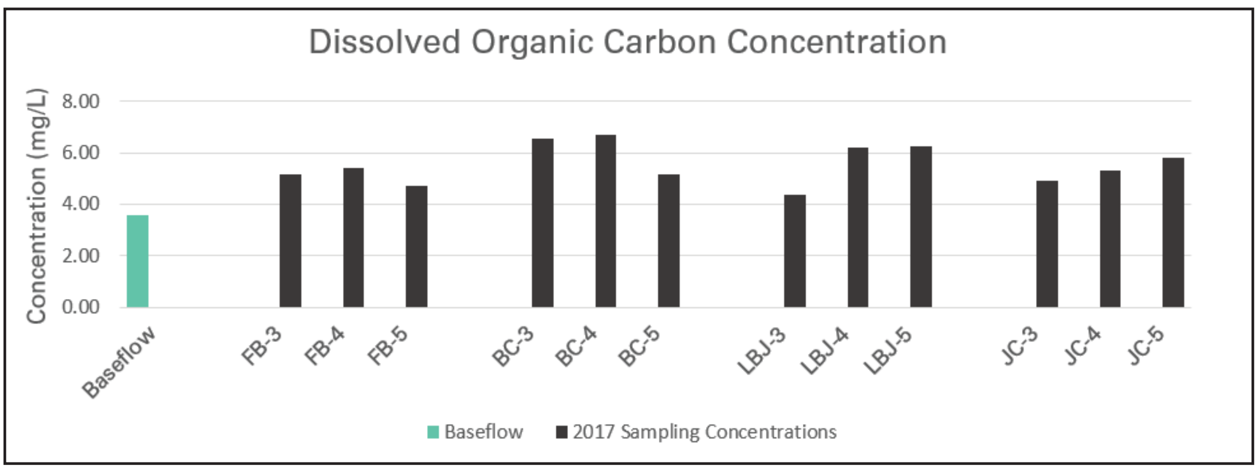


Figure 19. Dissolved Organic Carbon Concentrations - Base flow and August 7-8, 2017 Storm Water

Constituent Loading Rates

Loading rate is defined as concentration multiplied by discharge. In the case of this study, loading rates are driven by discharge and sample timing, not concentration. Loading rates decreased throughout the storm at FB due to declining discharge. Loading rates increased during the middle of the runoff event at LBJ as the surge from upstream Fredericksburg. Samples at JC were obtained at increasing discharge rates, therefore the loading rates continued to rise. Samples were collected near the peak discharge (therefore at peak loading rates) at FB and LBJ. Samples were not obtained at peak discharge at JC, therefore peak loading rates on the accompanying figures understate the peak loading rate at JC. There is not a discharge measuring station at Barons Creek and site conditions were not safe for manually measuring discharge , therefore loading rates are not available.

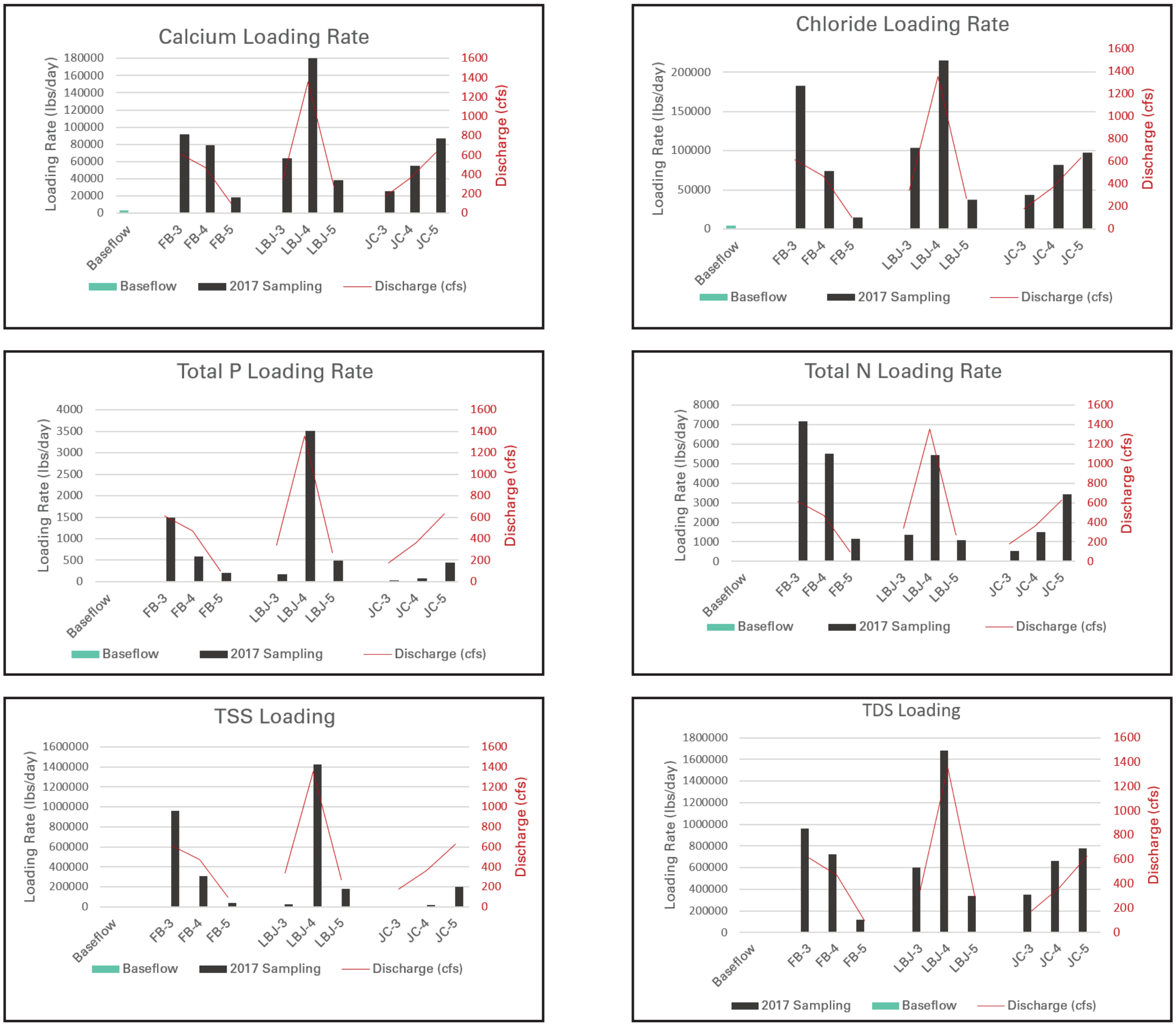


Figure 20. Constituent Loading Rates for Calcium, Chloride, Total P, Total N, TDS and TSS – August 7-8, 2017

COMPARISON TO ONION CREEK STORM WATER SAMPLING

Storm water sampling was conducted by the Barton Springs Edwards Aquifer Conservation District (BSEACD) in 2011 as part of the Onion Creek Recharge Project in Northern Hays County. Five storm events were sampled (Smith, B. A. 2011). There were four parameters common to the BSEACD and 2017 Pedernales sampling events. To compare the data, whisker plots of the data from each study are shown on Figures 21 -24. Whisker plots display mean, minimum, maximum, and quartile ranges. All of the Onion Creek data from five storm events were used to create the figures. Base flow from 2015 is also shown where available.

The results indicate that all storm water samples were significantly elevated above background levels. The results indicate a similar mean value for TDS. The mean TSS value for the Pedernales River samples was greater than Onion Creek and the Pedernales River displayed a significantly greater range. Total P and Total N concentrations were generally higher in the Pedernales samples than the Onion Creek..

In general, the rainfall totals were much lower during the Onion Creek sampling events than the August 2017

Pedernales River sampling event. Levels of Total P, Total N and TSS were comparable between the two water bodies for storms of similar rainfall.

Onion Creek watershed is underlain by carbonate geologic units of the Glen Rose and Edwards Formations. Other than scattered low density grazing, there is little agriculture in the Onion Creek watershed. In contrast, there is much more land under cultivation, grazing and fruit production in the Pedernales River Watershed.

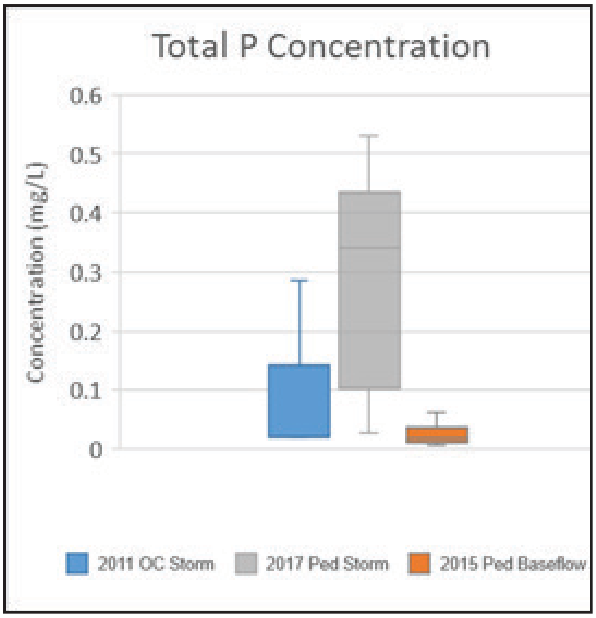


Figure 21. Total P results from 2011 Onion Creek storm samples, 2017 Pedernales River Storm Samples and 2015 Pedernales River Base Flow Samples.

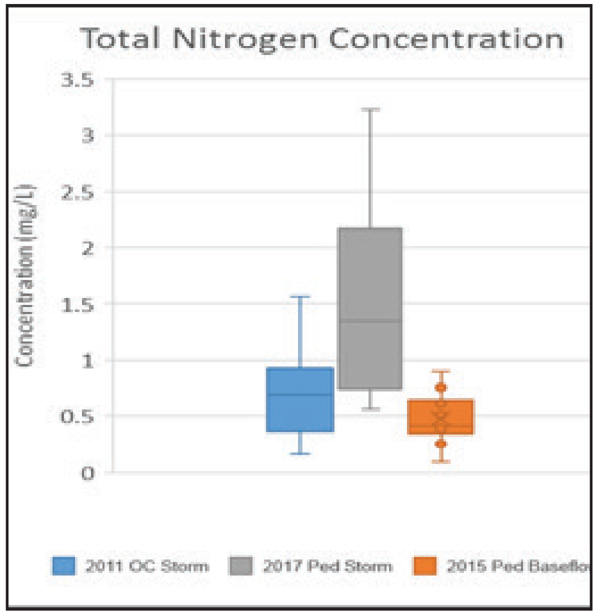


Figure 22. Total Nitrogen results from 2011 Onion Creek storm samples, 2017 Pedernales River Storm Samples and 2015 Pedernales River Base Flow Samples.

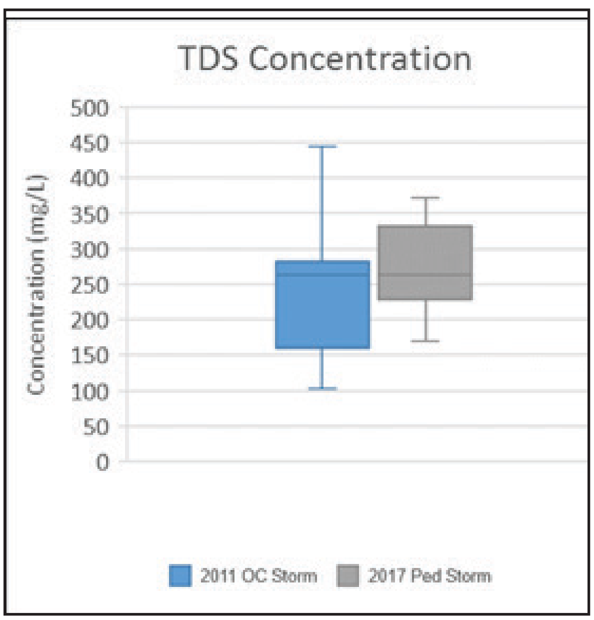


Figure 23. Total Dissolved Solids results from 2011 Onion Creek storm samples, 2017 Pedernales River Storm Samples and 2015 Pedernales River Base Flow Samples.

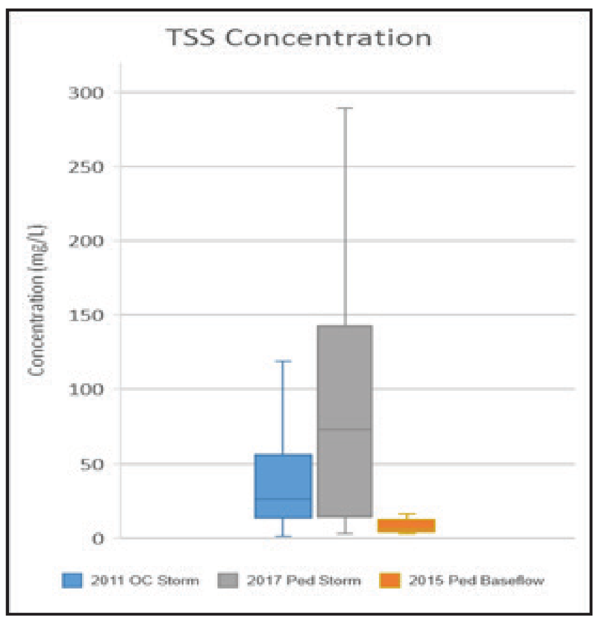


Figure 24. Total Suspended Solids results from 2011 Onion Creek storm samples, 2017 Pedernales River Storm Samples and 2015 Pedernales River Base Flow Samples.

Increased agricultural activity may result in higher TDS, Total P and Total N in the Pedernales samples. There may also be a bias in the Pedernales samples as the FB and BC sites are located near the City of Fredericksburg, a large source of nutrients. While there is significant residential development in the Onion Creek watershed, there are no large urban areas directly upstream of the Onion Creek sampling site.

STABLE WATER ISOTOPES

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. Evaporation and precipitation affect whether the hydrogen and oxygen isotopes are heavier or lighter. 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 (GMWL) is an equation that describes the relationship between hydrogen and oxygen isotopes. A straight line trending away from the GMWL toward more enriched isotopic values, but with a lower slope than the GMWL, indicates evaporative loss (Zapitello, 2016). The general equation for the GMWL is d2H = 8(d18O) + 10.

Figure 25 represents the 2015 base flow data (Zapitello, 2016) and the 2017 August storm water data. Both sets of data indicate more enriched isotopic values, likely from evaporative loss. The difference in the absolute values between the data sets may be indicative of warmer base flow temperatures than the storm flow data.

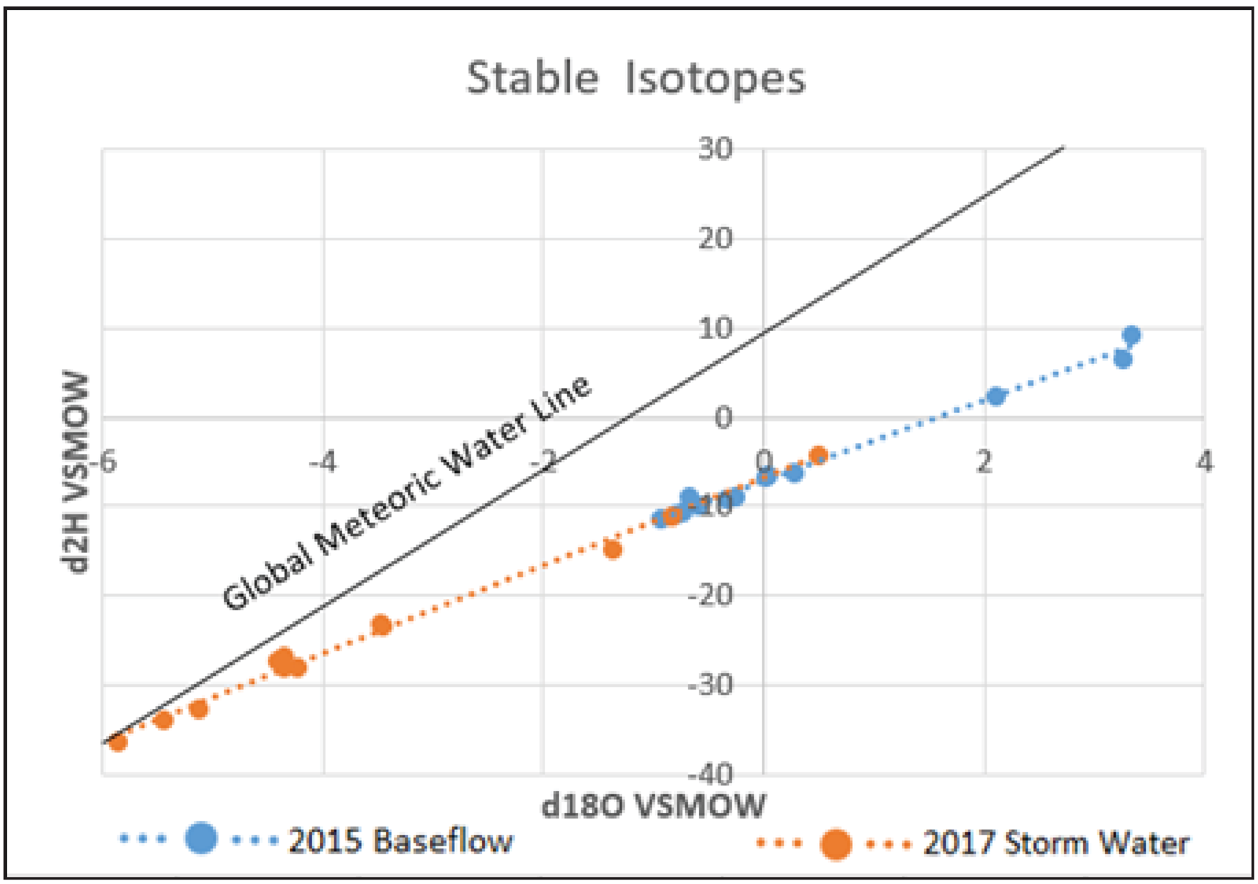


Figure 25. 2015 Base Flow and 2017 Storm Water Stable Isotopes

DISCUSSION AND PATH FORWARD

The goal of this study was to perform an initial, screening level storm water sampling program to determine if there are impacts to the river from rain events and secondly, to develop recommendations for future investigations, if warranted. The study accomplished this goal.

The results of this study are believed to be generally representative of runoff water quality trends. Major findings are that there are large increases in nutrient and sediment loading in the river during storm events. The areas in and upstream of the City of Fredericksburg appeared to contribute the highest concentrations of nutrients and suspended solids during the early parts of the event. High concentrations were measured downstream as the storm surge proceeded towards Johnson City. It should be noted that every storm event will have a slightly different runoff signature due to seasonality, rainfall distribution and intensity. Antecedent soil moisture conditions are a significant factor in the volume and quality of runoff.

A more robust sampling program is needed to further delineate storm water runoff quality and identify specific area where BMPs could be implemented to minimize nutrient and solids loading to the river and ultimately Lake Travis. Potential BMPs were identified in the report How Much Water is in the Pedernales, Conservation Stratagies, Management Approaches and Action Plan (Wierman, et al, 2015). Multiple subwatersheds upstream and immediately downstream of the City of Fredericksburg should be sampled. The constituents analyzed should be expanded to include several additional heavy metals and organic indicators of urban runoff. Additional parameters could include arsenic, lead, total petroleum hydrocarbons and poly nuclear aromatic compounds. A permanent discharge gauging station should be installed on Barons Creek near the confluence with the Pedernales River to facilitate loading measurements. Sampling frequency should be increased through an automated sampler or additional field staff.

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APPENDIX A

Analytical Results

See attached.

Appendice A. Analytical Results

Sample ID	Sample Date	Spec CondC µs/cm	Total N µg/L	Total P µg/L	NH4-N µg/L	SRP µg/L	PP ug/L	Particulate Nitrogen (mg/l)	Particulate Carbon mg/L	DOC mg/L	d2H VSMOW	d18O VSMOW	TDS mg/L	TSS mg/L	NVSS mg/L	Barium mg/L
Base Flow			410	19	44.7	1.9	14.2	0.1	1.5	3.3			n/a	7.6	5.1	n/a
BC-1	5/19/2017	694	324.02	254.13	132.40	248.41	14.27	0.00	0.53	2.18	-18.54	-2.95	435	<2.5	<2.5	0.00
BC-2	5/20/2017	227	1923.60	329.10	482.63	130.69	1025.89	0.00	8.25	6.45	-12.50	-2.75	168	110	19	0.67
BC-3	8/7/2017	180	1683.85	529.76	103.53	128.01	1802.99	0.22	19.39	6.55	-36.43	-5.86	169	355	36	0.00
BC-4	8/7/2017	327	2317.48	343.47	120.23	233.16	705.68	0.06	5.92	6.70	-33.90	-5.43	242	70	10	0.00
BC-5	8/8/2017	608	3228.81	386.02	193.43	370.62	97.40	0.00	0.46	5.15	-27.45	-4.41	371	3	<2.5	0.67
FB-1	5/19/2017	559	607.65	2.25	159.56	3.76	14.11	0.00	0.85	2.37	-14.28	-1.99	367	7	<2.5	0.00
FB-2	5/20/2017	571	631.79	9.24	158.16	6.18	15.27	0.00	0.81	2.36	-14.02	-1.99	360	6	<2.5	0.00
FB-3	8/7/2017	413	2164.65	450.80	322.03	84.46	2225.77	0.85	21.28	5.17	-26.92	-4.35	289	289	36	1.31
FB-4	8/7/2017	364	1268.53	228.48	265.22	29.51	1019.23	0.00	10.87	5.40	-23.39	-3.46	285	121	13	1.30
FB-5	8/8/2017	373	1885.19	380.27	129.28	13.20	1491.46	0.67	28.75	4.72	-23.13	-3.47	222	76	8	0.00
LBJ-1	5/19/2017	616	723.82	13.24	193.74	3.59	34.80	0.00	1.00	2.63	-14.87	-2.04	405	9	<2.5	0.00
LBJ-2	5/20/2017	600	774.69	25.43	302.68	8.77	104.85	0.07	2.08	2.63	-14.33	-2.00	387	22	4	0.00
LBJ-3	8/7/2017	542	745.32	94.33	154.25	10.03	379.88	0.13	2.18	4.37	-14.75	-1.38	329.2	16	4	0.00
LBJ-4	8/7/2017	348	1654.54	478.78	228.39	118.35	1842.25	0.22	11.27	6.23	-28.11	-4.24	230	195	28	0.00
LBJ-5	8/8/2017	295	1461.89	339.45	181.57	74.80	700.71	0.06	9.88	6.26	-32.65	-5.13	229	125	17	0.00
JC-1	5/19/2017	523	432.62	14.44	53.90	4.56	36.44	0.03	1.68	2.87	-10.92	-1.22	284	16	3	0.00
JC-2	5/20/2017	534	500.28	18.44	197.49	11.36	60.30	0.04	1.56	3.15	-9.99	-1.17	360	18	3	0.00
JC-3	8/7/2017	485	564.01	27.63	190.15	6.71	42.10	0.04	1.20	4.94	-4.19	0.49	368	10	<2.5	0.00
JC-4	8/7/2017	442	762.24	41.43	102.13	4.81	91.83	0.04	1.41	5.32	-11.09	-0.83	334	9	<2.5	0.00
JC-5	8/8/2017	332	1006.28	131.32	272.71	13.99	649.37	0.05	4.65	5.83	-28.05	-4.35	229	59	7	0.00

Sample ID	Sample Date	Flouride mg/L	Chloride mg/L	Nitrite-N (mg/l)	Bromide mg/L	Nitrate-N mg/L	Phosphate-P mg/L	Sulphate mg/L	Lithium mg/L	Sodium mg/L	Ammonium mg/L	Potassium mg/L	Magnesium mg/L	Manganese mg/L	Calcium mg/L	Strontium mg/L
Base Flow		1.8	54.8	n/a	0.5	0.02	n/a	23.4	n/a	34.6	0.047	3.6	33.2	n/a	40.5	n/a
BC-1	5/19/2017	2.12	67.10	0.00	0.42	0.43	0.64	34.86	0.00	44.26	0.00	4.49	41.71	0.00	61.83	0.00
BC-2	5/20/2017	0.90	12.16	0.00	0.00	2.26	0.47	9.45	0.00	9.65	0.00	3.70	9.71	0.00	20.12	0.00
BC-3	8/7/2017	1.20	8.93	0.00	0.00	2.16	0.58	8.71	0.00	20.44	0.00	5.38	13.28	0.00	29.98	0.00
BC-4	8/7/2017	1.41	34.46	0.00	0.00	7.05	0.74	16.30	0.00	7.43	0.00	4.52	6.14	0.00	20.55	0.00
BC-5	8/8/2017	2.22	71.25	0.33	0.42	12.74	0.99	31.33	0.00	42.92	0.00	6.45	28.71	0.00	53.30	0.00
FB-1	5/19/2017	1.80	45.17	0.00	0.38	1.41	0.00	27.31	0.00	28.32	0.13	2.51	40.69	0.00	47.39	0.00
FB-2	5/20/2017	1.80	44.72	0.00	0.38	1.44	0.00	26.85	0.00	28.06	0.00	2.54	40.11	0.00	46.28	0.00
FB-3	8/7/2017	2.02	55.21	0.00	0.00	2.01	0.00	22.15	0.00	34.29	0.00	5.29	19.34	0.00	27.56	0.00
FB-4	8/7/2017	2.09	29.12	0.00	0.00	1.48	0.00	16.00	0.00	18.48	0.00	3.94	22.11	0.00	31.17	0.00
FB-5	8/8/2017	2.16	28.04	0.00	0.00	1.40	0.00	15.71	0.00	17.92	0.00	3.58	22.32	0.00	34.50	0.00
LBJ-1	5/19/2017	2.01	56.90	0.00	0.41	1.07	0.00	31.96	0.00	38.05	0.16	3.65	42.15	0.00	42.32	6.68
LBJ-2	5/20/2017	2.01	55.98	0.00	0.42	1.05	0.00	31.71	0.00	37.41	0.43	3.29	41.19	0.00	42.28	5.37
LBJ-3	8/7/2017	2.30	56.69	0.00	0.49	0.41	0.00	25.99	0.00	39.79	0.00	4.54	36.46	0.00	34.74	0.00
LBJ-4	8/7/2017	1.92	29.39	0.00	0.00	1.78	0.00	17.35	0.00	21.88	0.00	5.82	18.99	0.00	25.88	0.00
LBJ-5	8/8/2017	1.48	25.72	0.00	0.00	1.92	0.00	14.68	0.00	17.63	0.00	5.02	13.12	0.00	26.26	0.00
JC-1	5/19/2017	2.00	48.45	0.00	0.39	0.00	0.00	32.35	0.00	32.98	0.00	2.96	40.54	0.00	32.87	5.95
JC-2	5/20/2017	1.96	47.88	0.00	0.37	0.00	0.00	31.40	0.00	32.05	0.00	3.07	39.70	0.00	32.57	5.83
JC-3	8/7/2017	2.39	45.92	0.00	0.44	0.00	0.00	27.44	0.00	31.04	0.00	3.64	36.57	0.00	27.09	4.46
JC-4	8/7/2017	2.41	41.26	0.00	0.43	1.02	0.00	25.43	0.00	27.60	0.00	3.66	30.65	0.00	27.99	0.00
JC-5	8/8/2017	2.08	28.78	0.00	0.00	1.74	0.00	19.08	0.00	18.86	0.00	4.96	18.94	0.00	25.52	0.00

APPENDIX B

Laboratory QA/QC Results

See attached.

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Parameter	Results (mg/L)	MDL (mg/L)	Coefficient of Determination (r^2)	Date Analyzed	Analyst	Method
Anions						
Flouride	1.04	1	99.9583	10/1/2017	GT	EPA 300.1 A
Chloride	1.1087	1	99.9543	10/1/2017	GT	
Nitrite (NO_2-N)*	1.0622	1	99.9621	10/1/2017	GT	
Bromide	1.043	1	99.9671	10/1/2017	GT	
Nitrate (NO_3-N)**	1.0526	1	99.9665	10/1/2017	GT	
Phosphate (PO_4-P)***	1.2353	1	99.9573	10/1/2017	GT	
Sulfate	1.0842	1	99.9709	10/1/2017	GT	

	Results (mg/L)	Expected (mg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	5.3811	5		107.622	90-110%
Matrix Spike_1	0.9817	1		98.17	90-110%
Matrix Spike_2	49.1167	50		98.2334	90-110%
Sample Dup_1	49.9223		**Avg.**	49.92765	
Sample Dup_2	49.933		**%RPD=***	0.02143101	0-20%

*Relative percent difference

Parameter	Results	MDL	Coefficient of Determination (r^2)	Date Analyzed	Analyst	Method
Cations						
Lithium	0.0963	0.1	99.9795	10/1/2017	GT	Standard Methods 2320B
Sodium	0.1567	0.1	99.9764	10/1/2017	GT	
Ammonium [*b]	0.1003	0.1	100	10/1/2017	GT	
Potassium	0.1904	0.1	99.9908	10/1/2017	GT	
Magnesium	0.129	0.1	99.99	10/1/2017	GT	
Manganese	0.1089	0.1	100	10/1/2017	GT	
Calcium	0.1364	0.1	99.9888	10/1/2017	GT	
Strontium	0.0987	0.1	99.9626	10/1/2017	GT	
Barium	0.09961	0.1	99.9825	10/1/2017	GT	

[b]Quadratic fit

	Results (mg/L)	Expected (mg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	25.0173	25		100.0692	90-110%
Matrix Spike_1	1.1043	1		110.43	90-110%
Matrix Spike_2	79.7254	80		99.65675	90-110%
Sample Dup_1	18.86		**Avg.**	18.8253	
Sample Dup_2	18.786		**%RPD=***	0.41752323	0-20%

*Relative percent difference

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Parameter	Results (µg/L)	MDL (µg/L)	Date Analyzed	Analyst
Total Nitrogen	39.9785	40	9/4/2017	GT

Method

Crumpton et al. 1992

	Results (µg/L)	Expected (µg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	1087.805	1000		108.7805	90-110%
Matrix Spike_1	96.6154	100		96.6154	90-110%
Matrix Spike_2	15746.58	15000		104.9772	90-110%
Sample Dup_1	762.2374		**Avg.**	760.3377	
Sample Dup_2	758.438		**%RPD=***	0.499699	0-20%

*Relative percent difference

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Parameter	Results (µg/L)	MDL (µg/L)	Date Analyzed	Analyst
Total Phosphorus	4.9789	5	9/4/2017	GT

Method
Wetzel & Likens 3rd edition

	Results (µg/L)	Expected (µg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	98.674	100		98.674	90-110%
Matrix Spike_1	9.671	10		96.71	90-110%
Matrix Spike_2	501.457	500		100.2914	90-110%
Sample Dup_1	9.2419		**Avg.**	8.98815	
Sample Dup_2	8.7344		**%RPD=***	5.646323	0-20%

*Relative percent difference

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Parameter	Results (µg/L)	MDL (µg/L)	Date Analyzed	Analyst
Ammoniun-N (NH_4-N)	5.0134	5	9/25/2017	GT

Method
Wetzel & Likens 3rd edition

	Results (µg/L)	Expected (µg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	101.6421	100		101.6421	90-110%
Matrix Spike_1	10.9124	10		109.124	90-110%
Matrix Spike_2	500.7684	500		100.1537	90-110%
Sample Dup_1	292.38		**Avg.**	288.514	
Sample Dup_2	284.648		**%RPD=***	2.679939	0-20%

*Relative percent difference

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Parameter	Results (µg/L)	MDL (µg/L)	Date Analyzed	Analyst
Soluble Reactive Phosphate-Phosphorus (PO_4-P)	0.9879	1	9/27/2017	GT

Method

Standard Methods 4500-PE.

	Results (µg/L)	Expected (µg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	98.5113	100		98.5113	90-110%
Matrix Spike_1	9.468	10		94.68	90-110%
Matrix Spike_2	506.454	500		101.2908	90-110%
Sample Dup_1	74.8008		**Avg.**	72.75765	
Sample Dup_2	70.7145		**%RPD=***	5.616317	0-20%

*Relative percent difference

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Parameter	Results (µgP/L)	MDL (µgP/L)	Date Analyzed	Analyst
Particulate Phosphorus	9.134	10	9/27/2017	GT

Method
QuickChem 10-115-01-1-Q

	Results (µgP/L)	Expected (µgP/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	92.974	100		92.974	90-110%
Matrix Spike_1	45.674	50		91.348	90-110%
Matrix Spike_2	1456.617	1500		97.1078	90-110%
	PP/L				
Sample Dup_1	14.109		**Avg.**	15.2285	
Sample Dup_2	16.348		**%RPD=***	14.7027	0-20%

*Relative percent difference

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Parameter	Results N/C (µg/L)	MDL N/C (µg/L)	Date Analyzed	Analyst
Particulate Nitrogen/Particulate Carbon	9.689/61.134	10/62	10/1/2017	GT

Method

EPA Method 440.0, 1997

	Results (µg/L)	Expected (µg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
	Carbon				
LCS	2231.04	2200		101.41091	90-110%
	Nitrogen				
Matrix Spike_1	87.012	88		98.877273	90-110%
	Carbon				
Matrix Spike_2	100.013	100		100.013	90-110%
	Nitrogen mg/L	**Carbon mg/L**			
Sample Dup_1	0.0945	2.9206	**N Avg.**	0.0919265	
	Nitrogen mg/L	**Carbon mg/L**	**N %RPD=***	5.4967665	0-20%
Sample Dup_2	0.0894	2.995	**C Avg.**	2.9578	
			C %RPD=*	2.5166503	0-20%

*Relative percent difference

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Parameter	Results (mg/L)	MDL (mg/L)	Date Analyzed	Analyst
Dissolved Organic Carbon	4.894	5	9/29/2017	GT

Method
Shimadzu Co. TOC-NPOC

	Results (mg/L)	Expected (mg/L)		%Recovery	Acceptable Range
Lab Blank	0	0		0	<20
LCS	50.31	50		100.62	90-110%
Matrix Spike_1	5.064	5		101.28	90-110%
Matrix Spike_2	15.65	15		104.3333	90-110%
Sample Dup_1	6.55		**Avg.**	6.0105	
Sample Dup_2	5.471		**%RPD=***	17.95192	0-20%

*Relative percent difference

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Parameter	Results d2H VSMOW	Results d18O VSMOW	d2H MDL (mg/L)	d18OMDL (mg/L)	Date Analyzed	Analyst
d2H VSMOW/ d18O VSMOW	1.11	0.35	1.8	0.3	9/16/2017	GT

Method
Picarro ANO36

	d18O Results (mg/L)	d18O Expected (mg/L)	%Recovery	Acceptable Range
Lab Blank	0	0	0	<20
LCS	-158.89	-159	99.93081761	90-110%
Matrix Spike_1	-9.15	-9.2	99.45652174	90-110%
Matrix Spike_2	-235.11	-235	100.0468085	90-110%

	d2H VSMOW	d18O VSMOW			
Sample Dup_1	-26.92	-4.35	**d2H Avg.**	-26.53	
Sample Dup_2	-26.134	-4.21	**%RPD=***	2.963514029	0-20%
			d18O Avg.	-4.28	
			%RPD=*	3.160732237	0-20%

*Relative percent difference

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Parameter	Date Analyzed	Analyst	Method
Total Dissolved Solids	8/10/2017	MG	M2540C-2005

	Results (mg/L)	Expected (mg/L)		%Recovery	Acceptable Range
Blank	<10	<10			
QCS	982	751-1200			
Sample	329.2				
Sample Duplicate	333.6		**%RPD**	1.3	0-5%
			Dup Average	331.4	

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Parameter					Date Analyzed	Analyst	Method
Total Suspended Solids					8/10/2017	MG	M2540D-2005

	Results (mg/L)	Expected (mg/L)		%Recovery	Acceptable Range
Blank	<2.5	<2.5			
QCS	98.6	77.1-110			
Sample	45.7				
Sample Duplicate	47.9		%RPD	4.7	0-5%
			Dup Average	46.8	

APPENDIX C

2015 Baseflow Analytical Results

See attached.

Appendix C. Main Channel Base Flow Analytical Results*

Site	Fluoride mg/l	Chloride mg/l	Bromide mg/l	NO3-- NO3 mg/l	NO3--N mg/l	Sulfate mg/l	Sodium mg/l	Potassiu m mg/l	Magnesiu m mg/l	Calcium mg/l	δ18O VSMOW	δ2H VSMOW	TSS mg/l	NVSS (mg/L)	TN (ug/L)	TP ug/l	PN ug/l	PC ug/l	DOC mg/l	NH4 mg/l	PP ug/l	SRP ug/l
43	2.1	80.0	0.4	0	0.00	27.5	52.2	4.2	42	38.2	0.03	-6.6	6.5	4.3	411.4	17.0	0.1	1	3.9	47.3	8.8	0.7
82	1.9	63.3	0.4	0	0.00	30	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	0.00	14.7	27.5	3	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	0.10	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	0.10	29.2	47	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
175	1.7	47.4	0.4	0	0.00	25.2	29.3	2.7	33.2	72.1	-0.93	-11.3	4.0	2.7	95.7	19.5	0	0.6	1.6	66.2	19.8	2
248	1.8	69.0	0.4	0	0.00	16	40.6	3.5	37.5	26.9	2.11	2.3	3.1	1.5	674.7	14.5	0	1	6.2	20.5	4.8	0
287	2.0	77.1	1.3	0	0.00	31.2	51	4.8	43.2	39.3	-0.02	-6.8	12.5	8.5	613.9	40.9	0	2.3	3.5	62.2	25.2	3.1
349	2.1	68.9	0.4	0	0.00	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
609	2.3	58.9	0.5	0	0.00	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	0.00	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
684	1.7	47.8	0.4	0	0.00	19.7	29.9	3	36.6	46.2	-0.26	-9	4.1	2.5	258.2	6.9	0	0.9	2.5	61.9	8.3	2.1
955	1.7	29.2	0.3	0	0.00	26.1	17.4	2.9	29.8	39.8	-0.68	-9	4.7	3.0	305.0	8.4	0	0.9	2.2	18.7	7.0	0

* Data Source: Zapitello, 2016

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