TRACING WATER SOURCES ALONG THE BRAZOS RIVER ALLUVIAL AQUIFER WITH $^{234}U/^{238}U$ ACTIVITY RATIOS AND URANIUM CONCENTRATIONS

A Thesis

by

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ABSTRACT

The combined use of $^{234}U/^{238}U$ activity ratios and uranium concentrations can be used to trace water sources within a hydrological system. Additionally, the specific uranium concentration and isotopic signature of each source can be applied to mixing calculations to estimate the relative contribution of each source in a river. $^{234}U/^{238}U$ activity ratios and uranium concentrations were measured over a 6-month period in the Brazos River watershed along the Brazos River Alluvial Aquifer to determine where water in the Brazos River is sourced from and to estimate groundwater discharge to the Brazos River.

Results from this study indicate that lithology within the Brazos River watershed affects $^{234}U/^{238}U$ activity ratios and uranium concentrations along the studied stretch of river as there is a change from carbonate rocks to siliciclastic rocks downstream and an associated change in $^{234}U/^{238}U$ activity ratios. Rain was found to have a negligible effect on $^{234}U/^{238}U$ activity ratios of sources within the area, and only dilutes the concentration of uranium in these sources. $^{234}U/^{238}U$ activity ratios and uranium concentrations suggest water in the Brazos River near Bryan/College Station, Texas is sourced from Lake Whitney, groundwater, and tributaries. Groundwater appears to discharge from the alluvial aquifer to the river at a steady rate with slight increases in groundwater contributions as discharge increases in the Brazos River. This study demonstrates the utility of uranium as a natural tracer of water sources.

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Professor Franco Marcantonio [advisor] and Peter Knappett of the Department of Geology and Professor Brendan Roark of the Department of Geography.

All work for the thesis was completed by the student, under the advisement of Franco Marcantonio of the Department of Geology.

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1. INTRODUCTION

Protecting water as a natural resource is becoming increasingly important as the human population continues to grow. So, many studies of hydrological systems seek to answer questions such as how much water can be sustainably extracted from an aquifer, where are recharge waters sourced from, what is the potential for contamination, and what is the best remediation method to apply to a contaminated hydrologic system. Results from these types of studies are used by water managers and planners to make informative decisions regarding long term sustainability of water resources. Traditionally, flow in hydrological systems has been quantified based solely on hydraulic data such as hydraulic conductivities and hydraulic heads to produce a flow model following the principles of Darcy's Law. However, recent developments and improvements of many environmental tracer methods have proved their ability to address questions regarding water conservation measures. One such tracer that can be used to increase understanding of specific hydrological systems is uranium. Specifically, the combined use of the $^{234}U/^{238}U$ activity ratio and uranium concentration measured from the dissolved load of natural freshwaters has been used to identify source waters contributing to the flow of river water, estimate the relative contribution of each source water, establish weathering mass balances, trace hydrological processes that occur in rivers and monitor any changes of those processes through time (Chabaux et al., 2001; Grzymko et al., 2007; Kaufman et al., 1969; Kraemer and Brabets, 2012; Kronfeld and Adams, 1974; Osmond et al., 1974; Riotte and Chabaux, 1999; Ryu et al., 2009).

Numerous published studies have reported that $^{234}U/^{238}U$ activity ratios of natural waters located around the world are in secular disequilibrium due to radiation damage in rocks by the emission of α-particles as ^{238}U decays, facilitating leaching of ^{234}U (Camacho et al., 2010; Chabaux et al., 2001; Chabaux et al., 2003; Durand et al., 2005; Grzymko et al., 2007; Kaufman et al., 1969; Kraemer and Brabets, 2012; Kronfeld and Adams, 1974; Kronfeld and Vogel, 1991; Osmond et al., 1974; Riotte and Chabaux, 1999; Ryu et al., 2009). In these studies, spatial and temporal variations of $^{234}U/^{238}U$ activity ratios and uranium concentrations were analyzed to determine the parameters that control the origin and magnitude of the dissolved uranium flux carried by these waters. Results from these prior studies suggest that the climate and lithology of a river's drainage basin are the parameters that primarily influence the river's $^{234}U/^{238}U$ activity ratio and uranium concentration. As these parameters change over a river's drainage basin, so does the $^{234}U/^{238}U$ activity ratio and uranium concentration in the river's water. Consequently, waters derived from a similar environment within a hydrological system will have a distinct uranium signature apart from waters derived from a different environment. Since uranium behaves conservatively under oxic conditions, these separate water sources defined by its uranium signature can be used in mixing calculations to determine the relative contribution of each source within river water.

In Texas, the Brazos River Alluvial Aquifer (BRAA) is an invaluable resource that provides water for irrigation, domestic, stock, and commercial use (Shah et al., 2007). As water demands are expected to increase in the future, it is vital that the hydrogeological characteristics and processes that occur in this aquifer are thoroughly understood. Here, we utilize $^{234}U/^{238}U$ activity ratios and uranium concentrations measured within the Brazos River's Watershed to expand on the previous work completed on the interactions between the Brazos River and its alluvial aquifer. From September 2016 to March 2017, the Brazos River was sampled biweekly at its intersection with Hwy 21, Hwy 60, and Hwy 105. Yegua Creek was sampled concurrently with the Brazos River to analyze its contribution of uranium in the Brazos River. Additionally, water samples were obtained from Lake Whitney and the BRAA as they may represent major water sources to the Brazos River within the area of this study. The measured uranium concentrations and $^{234}U/^{238}U$ activity ratios at the sampling sites will be used along with USGS discharge data to estimate relative proportions of each source in the Brazos River at Hwy 21.

1.1 Previous work on the Brazos River and its alluvial aquifer

Previous studies of the Brazos River and its alluvial aquifer were performed to determine the groundwater to surface water interactions. Cronin and Wilson (1967) completed one of the first detailed studies of the Brazos River and its alluvial aquifer from Lake Whitney Dam to Richmond, TX. Their study documented the regional geology, hydrologic properties of the alluvial aquifer, groundwater movement, groundwater and surface water quality, and availability of groundwater in the alluvial aquifer. Subsequent studies have expanded on this original work utilizing a variety of hydrological methods. Most of these studies agree that the Brazos River is a gaining stream near College Station, Texas (Alden and Munster, 1997; Turco et al., 2007; Wrobleski, 1996).

The Texas A&M University Brazos River Hydrogeologic Field Site was constructed to determine the transport of non-point source agricultural chemicals applied at the surface into alluvial aquifers. So, the objective of many studies following the construction of this site was to quantify groundwater movement in the alluvial aquifer. Wrobleski (1996) provides an aquifer characterization at the Texas A&M field site using daily water level measurements and pump-test data. Results from this study gives estimates of transmissivity, hydraulic conductivity, specific yield, and storativity values within the aquifer. These values suggest that the alluvial aquifer acts as a semi-confined aquifer due to less permeable material in the upper parts of the aquifer. Additionally, it was concluded that during normal flow conditions groundwater moves toward the river but as river stage increases the flow of groundwater shifts in a more downstream direction. These findings agree with a study where two in-situ permeable flow sensors were used to assess the river-floodplain aquifer interactions at the Texas A&M University Hydrogeologic Field Site (Alden and Munster, 1997). Data from these two flow sensors provided continuous measurements of the magnitude and direction of the groundwater velocity in the BRAA. Again, results from this study indicates that the groundwater velocity shifts towards a downstream direction with increasing river stage.

A more extensive study by Turco et al. (2007) employed the methods of hydrograph separation and differential gaging along a stretch of the Brazos River from McLennan County to Fort Bend County, Texas. Historical discharge data encompassing the years 1966-2005 was used in their hydrograph separation technique to estimate the percentage of baseflow within the total stream flow. Their results indicate that baseflow increases as the Brazos River crosses the aquifer outcrops of Carrizo-Wilcox, Queen City, Sparta, and Yegua-Jackson while no appreciable increase in baseflow occurs as the Brazos River crosses the Gulf Coast aquifer. Additionally, synoptic discharge measurements were used to identify where the Brazos River was gaining and losing water to its alluvial aquifer at 35 different stretches along the Brazos River. Similar to their other results, the strongest gaining stretches occurred where the Brazos River crossed the outcrops of the Carrizo-Wilcox, Queen City, Sparta, and Yegua-Jackson aquifers.

A recent study completed on the Brazos River from Bryan to Navasota used multiple methods to compare water exchange between the Brazos River and its alluvial aquifer (Rhodes, 2016). This study provided estimates of groundwater discharge to the Brazos River on two stretches of the Brazos River between Hwy 21 to Hwy 60 and Hwy 60 to Hwy 105, using complementary methods including continuous differential gaging with fixed gaging stations and mass flux estimates based on measurements of Total Dissolved Solids (TDS) and major ions in the BRAA and river over time. These methods agreed that groundwater discharge to the river increases with increasing river discharge along the stretch between Hwy 21 and Hwy 60. Conversely, most methods suggest that groundwater discharge to the river decreases with increasing river discharge at the stretch between Hwy 60 and Hwy 105.

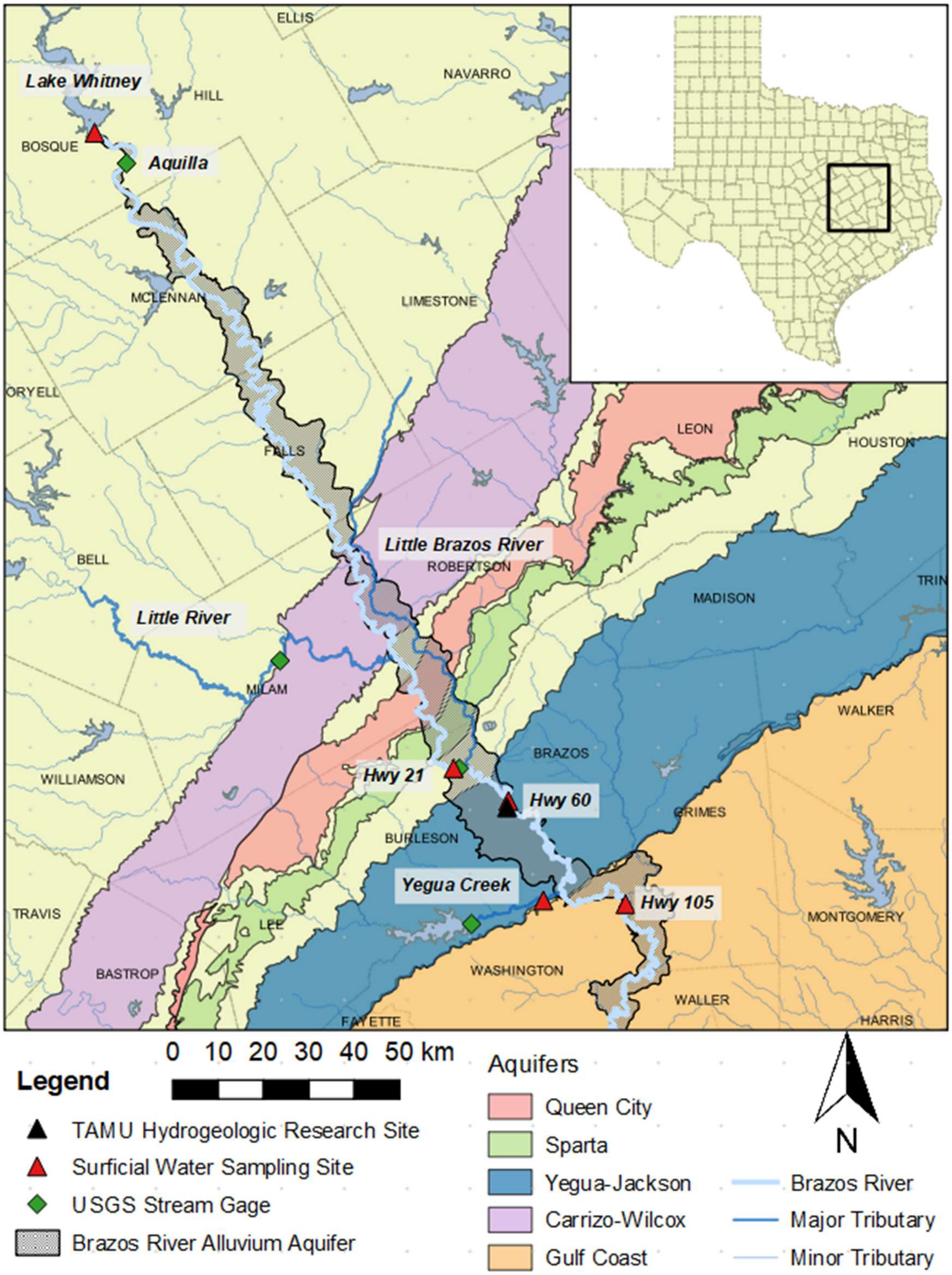

Figure 1. *Map of the study area showing aquifers and the confluence of major tributaries with the Brazos River. Additionally, the locations of sampling sites and USGS stream gages are shown.*

2. DESCRIPTION OF STUDY AREA

The area of this study is located along a stretch of the Brazos River, extending from Lake Whitney Dam in Bosque County to southern Brazos County where the Brazos River intersects Hwy 105 (figure 1). The climate is subtropical, humid over the entirety of this study area which is characteristic of hot, humid summers and mild winters (TWDB, 2012). On average, January experienced the coldest monthly lows of 41.2 ºF and August experienced the hottest monthly highs of 96.2 ºF over the 30-year period from 1981-2010. Historical monthly climate data shows that precipitation falls regularly throughout the year. In general, average monthly precipitation is low during the summer and there are gradual increases in precipitation during spring and autumn (NOAA, 2017). Water samples were obtained from various locations within the Brazos River's watershed over the duration of six months, from September 2016 to March 2017, to assess the significance of the spatial and temporal variability of uranium concentrations and $^{234}U/^{238}U$ activity ratios measured along this stretch of the Brazos River. Daily discharge data reported by the United States Geological Survey (USGS) was utilized to perform source mixing calculations. Locations of the field sampling sites and USGS stream gages are shown in Figure 1.

The BRAA bounds both sides of the Brazos River along this stretch and is categorized as a heterogeneous, unconfined to semi-confined aquifer (Wrobleski, 1996). The thickness of the aquifer ranges from negligible to 168 feet and has a maximum width of 7 miles (Shah et al., 2007). It is composed of alluvial gravel, sand, silt, and clay from channel and flood plain deposits. In general, coarser sediment is located at the bottom of the aquifer while finer sediment is located at the upper portion of the aquifer. However, many isolated beds of sand deposited in stream channels pinch out and grade laterally and vertically into finer flood plain deposits (Cronin and Wilson, 1967). The BRAA is recharged primarily by infiltration of rainwater that falls onto the surface of the floodplain. Other sources of recharge include infiltration of stream water, irrigation water, and groundwater from the underlying abutting aquifers (Cronin and Wilson, 1967). On the other hand, groundwater in the BRAA is lost through discharge to the Brazos River, evapotranspiration, and pumping wells.

Bedrock underlying the BRAA consists of late cretaceous to quaternary sedimentary rock (Cronin and Wilson, 1967). From Lake Whitney Dam, the Brazos River flows over limestone or chalk until it reaches the southern city limits of Waco, where the Brazos River flows over siliceous rock until it reaches its mouth in the Gulf of Mexico. Several major and minor aquifers underlie the BRAA and are hydraulically connected to it (Turco et al., 2007). These include the Carrizo-Wilcox, Queen City, Sparta, Yegua-Jackson, and Gulf Coast aquifer. Generally, the geologic formations that comprise these aquifers strike approximately perpendicular to the BRAA and dip slightly towards the Gulf Coast. Comparable to the BRAA, these aquifers are composed of interbedded clays, silts, sands, and gravels (George et al., 2011).

The furthest upstream source of water to the Brazos River that was sampled for this study was Lake Whitney. Water samples were obtained from Lake Whitney during three sampling campaigns, approximately two months apart. Two samples were collected on each campaign at two separate locations near Lake Whitney Dam to determine whether the reservoir is well-mixed with respect to uranium. Flow to the Brazos River below Lake Whitney is regulated by releases from Lake Whitney Dam. USGS stream gage 08093100 is located on the Brazos River near Aquilla, Texas directly downstream from Lake Whitney approximately 10 km away. This gage primarily records the discharges from Lake Whitney Dam as there is not a major tributary between the dam and the gage.

Downstream from Lake Whitney, the Brazos River was sampled at its intersection with Hwy 21, Hwy 60, and Hwy 105 (Figure 2). Water samples were collected at each of these field sites biweekly over the duration of this study, for a total of 14 samples at each site (28 weeks), to measure variations in uranium concentration and $^{234}U/^{238}U$ activity ratio of water in the Brazos River as it moves downstream. USGS stream gage 08108700 is located on the Brazos River at State Hwy 21 and was used to track daily discharge for the field sampling site at Hwy 21. No discharge data was available for the sites at Hwy 60 and Hwy 105.

Two major tributaries that flow into the Brazos River between the most upstream river sampling site (Hwy 21) and the most downstream (Hwy 105) are the Little Brazos River and Yegua Creek. The confluence of the Little Brazos River with the Brazos River is located between the sampling sites at Hwy 21 and Hwy 60 (Figure 2). Since the results from a study conducted by Turco et. al. (2007) showed that the Little Brazos River did not have a substantial contribution to the overall stream flow to the Brazos River between Hwy 21 and College Station, the Little Brazos River was not sampled regularly. Nonetheless, three water samples were collected from the Little Brazos River at its intersection with Hwy 21 near the end of the regular sampling period in late January, early February, and early March. The confluence of Yegua Creek with the Brazos River is located between the sampling sites at Hwy 60 and Hwy 105 (Figure 2). Water samples were obtained at Yegua Creek biweekly on the same day samples were taken from the Brazos River to explain the impact Yegua Creek has on the uranium concentration and $^{234}U/^{238}U$ activity ratio in the Brazos River. Flow in Yegua Creek is largely controlled by reservoir releases from Lake Somerville where USGS stream gage 08110000 located on Yegua Creek near Somerville, Texas records the discharge of these releases.

Additionally, to evaluate the flow contribution from the BRAA to the Brazos River, groundwater samples were acquired at the Texas A&M Hydrogeologic Research Site, located along the Brazos River near Hwy 60. At this site, there are 36 monitoring wells divided in 9 separate well nests that are oriented parallel and perpendicular to the river (Figure 2). In each well nest, there are 4 monitoring wells labeled 1, 2, 3, and 4 that are located at approximate depths of 7.2 m, 11.0 m, 14.8 m, and 18.3 m, respectively (Munster et al., 1996). Each monitoring well has a screen 6 inches in length that ensures the water sampled in that well is representative of the groundwater located at that depth in the alluvial aquifer. The shallowest well in each nest does not penetrate below the water table on a typical year, so only the three deepest wells were sampled to determine the spatial variability in uranium signatures. Additionally, monitoring wells A3-4, B3-4, C2-4, C3-4, and C3-3 could not be sampled because these wells had transducer instruments recording data in them. Groundwater samples were collected at this site during three sampling campaigns, approximately two months apart, to monitor temporal variability in the uranium signature of each well sampled.

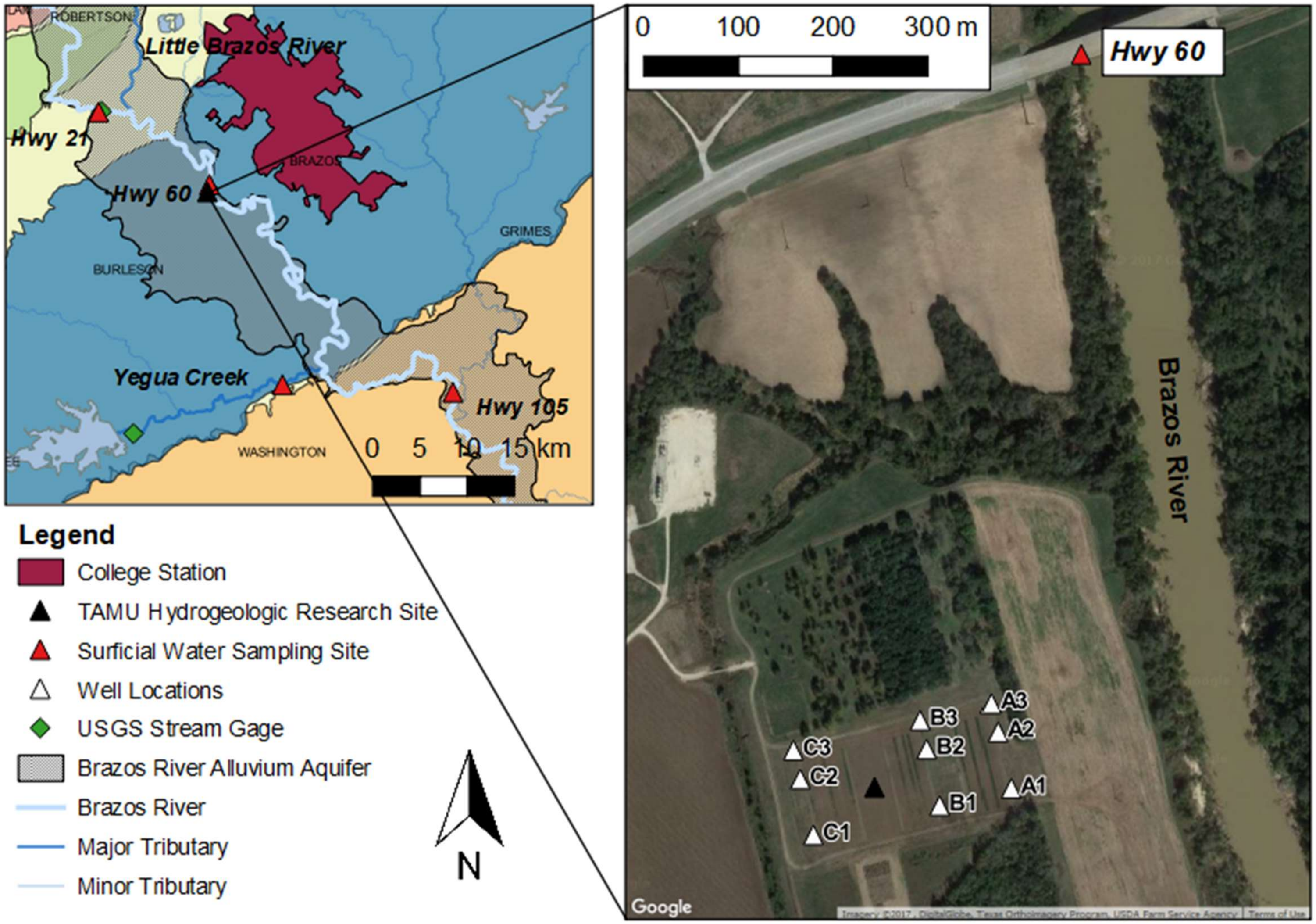

Figure 2. *Map of the Texas A&M Hydrogeologic Research Site showing locations of the nine well nests.*

3. METHODOLOGY

3.1 Field sampling methods

Surficial water samples were collected at field sampling sites Hwy 21, Hwy 60, Hwy 105, Yegua Creek, Little Brazos River, and Lake Whitney. Each sample was obtained near the river bank or lake shore by wading into the water as was safely to do so. Approximately 20 mL of water was collected with a syringe, passed through a 0.2 μm nylon filter, and stored in 20 mL HDPE scintillation vials. Prior to filtration, water was flushed through the syringe three times before collection. Each sample was acidified in the field at the time of collection with 20 μL of ultra-pure nitric acid.

All groundwater samples were collected at the Texas A&M Hydrogeologic Research Site with a Masterflex E/S Portable Sampler. Teflon tubing attached to the sampler was lowered to the bottom of each monitoring well with a weight fastened on the end of the tubing. The Teflon tubing was flushed with groundwater for at least 5 minutes before a sample was collected. Approximately 20 mL of water was collected for each groundwater sample and was filtered and acidified following the methods of the surficial water samples.

3.2 Analytical procedure

Each water sample was analyzed for its $^{234}U/^{238}U$ activity ratio and uranium concentration using the Element XR Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Texas A&M University. Prior to analyzing, each 20-mL water sample was diluted to 2% HNO_3 by adding the appropriate amount of ultra-pure nitric acid. To determine the $^{234}U/^{238}U$ activity ratio, approximately 5 mL of a water sample was sub-sampled for analysis on the ICP-MS. Abundance sensitivity corrections were checked by measuring the half masses of $^{235.5}U$, $^{234.5}U$, and $^{233.5}U$, however the abundance sensitivity at mass ^{234}U was consistently lower than 1 ppm/amu for each sample analyzed. Instrumental mass fractionation corrections were applied to the results of each sample by correcting the measured $^{238}U/^{235}U$ ratio to its natural value ($^{238}U/^{235}U = 137.88$). Associated analytical uncertainties for the $^{234}U/^{238}U$ activity ratios were calculated and were generally around 1% on the 2σ level when the uranium concentration was about 1 ppb. Additionally, blanks were analyzed to correct for any uranium contamination from sampling methods which was found to be negligible. To validate the results, a CRM U500 standard ($^{238}U/^{235}U \approx 1$) was diluted to about 1-2 ppb and analyzed between every 7 samples. Over the course of this study, this standard was analyzed 26 times yielding a mean $^{238}U/^{235}U$ ratio of 1.003 (0.3% difference from the theoretical value of 1, i.e., a 0.1%/amu fractionation correction) and an external reproducibility of 0.8% which confirms the accuracy of the results for this study.

Determination of the uranium concentration in each sample was obtained by an isotope dilution analysis where 1 mL aliquot of a sample was spiked with 35 µL of ^{236}U spike with known concentration and isotopic composition. The weight of the sample and spike was recorded and the $^{236}U/^{238}U$ ratio was measured on the ICP-MS. The uranium concentration was calculated using the equation (Faure and Mensing, 2005):

$$U_N = \frac{AW_N}{AW_S} * \frac{Ab_S^{236} - R_m Ab_S^{238}}{R_m Ab_N^{238} - Ab_N^{236}} \frac{U_S * Wt_S}{Wt_N}$$

where U_N is the uranium concentration of the sample in ppb, AW_N and AW_S are the atomic weights of uranium in the sample (238.0508) and the spike (236.0000), Ab_S^{236} and Ab_S^{238} are the relative abundances of ^{236}U (0.9993) and ^{238}U (0.0002) in the spike, Ab_N^{238} and Ab_N^{236} are the relative abundances of ^{238}U (0.9927) and ^{236}U (0.0000) in the sample, R_m is the measured $^{236}U/^{238}U$ ratio of the sample and spike mixture, Wt_S and Wt_N are the weights in grams of the spike and sample, and U_S is the uranium concentration of the spike in ppb (15.63 ppb).

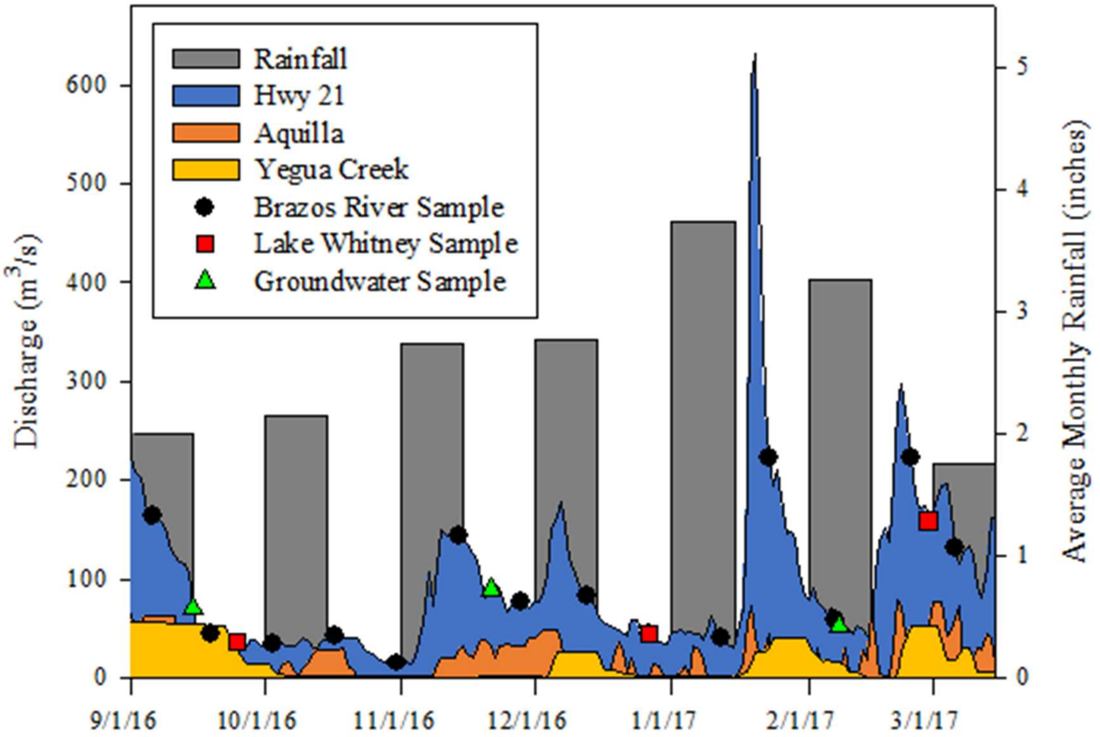

Figure 3. *Daily mean discharge from USGS stream gages at Hwy 21, Aquilla, and Yegua Creek. Dates samples were obtained are also shown along with the average monthly rainfall near College Station, TX.*

4. RESULTS

4.1 Discharge

Daily mean discharge measurements were obtained from USGS stream gages at various locations within the Brazos River watershed (Figure 3). During the sampling period from September 2016 to March 2017, daily discharge at Hwy 21 ranged from a low of 14 m^3/s on 11/3/16 to a high of 685 m^3/s on 1/19/17. Beginning in September, discharge fell to its lowest point during early November in the Brazos River. Two small peaks in discharge followed in early November and early December due to precipitation that fell at those times. After the spike in December, discharge continued to fall until mid-January when discharge reached its highest peak after heavy rainfall. Subsequently, discharge fell rapidly before its final spike in mid-February, at which point there was a general decrease in discharge until the final sampling period on 3/6/17. Overall, small variations were observed with discharge from September to mid-January compared to the large variations in mid-January to March which correlates to a steady base flow component contributing to overall discharge at the beginning of the sampling period followed by an increasing runoff component late in the sampling period.

Daily discharge for the Brazos River near Aquilla, Texas and for Yegua Creek roughly follow a similar pattern of highs and lows observed in the discharge at Hwy 21, but in contrast, the deviations are the result of controlled releases from their reservoirs. Generally, after a storm event water is released into Yegua Creek at a steady rate whereas water is released from Lake Whitney at an unsteady rate as shown by the smooth decline in discharge for Yegua Creek and the spiked nature in discharge at Aquilla (Figure 3).

4.2 Brazos River $^{234}U/^{238}U$ activity ratios and uranium concentrations

Water samples were obtained from the Brazos River where it intersects with Hwy 21, Hwy 60, and Hwy 105 to determine what hydrological processes affected uranium concentrations and $^{234}U/^{238}U$ activity ratios as the water moves downstream (Table 1). Over the course of this study, uranium concentrations varied temporally by approximately 70% while $^{234}U/^{238}U$ activity ratios varied by 9%. The lowest and highest uranium concentrations were measured at Hwy 105, from 0.77 ppb when discharge was high to 1.60 ppb when discharge was low. Similarly, uranium concentrations were high at low discharge and were low at high discharge at sampling locations Hwy 21 and Hwy 60. The lowest $^{234}U/^{238}U$ activity ratio was observed at Hwy 105 with a value of 1.21 whereas the highest activity ratio was observed at each of the Brazos River sampling sites with a value of 1.32. Overall, there was a good correlation (r^2=0.60) between uranium concentrations and discharge and a weak correlation (r^2=0.27) between $^{234}U/^{238}U$ activity ratios and discharge at Hwy 21 (Figure 4).

Additionally, uranium concentrations exhibited a wide range of spatial variability along this stretch of the Brazos River. For instance, each sampling period showed little variability at the stretch between Hwy 21 and Hwy 60 within measured uranium concentrations but the stretch between Hwy 60 and Hwy 105 showed significantly more

Table 1. *$^{234}U/^{238}U$ activity ratios and uranium concentrations measured in the Brazos River at Hwy 21, Hwy 60, and Hwy 105 along with discharge measured at Hwy 21.*

Brazos River

Date	**Discharge Hwy 21** Bryan, TX (m^3/s)	**Hwy 21** $^{234}U/^{238}U$ activity ratios	U concentration (ppb)	**Hwy 60** $^{234}U/^{238}U$ activity ratios	U concentration (ppb)	**Hwy 105** $^{234}U/^{238}U$ activity ratios	U concentration (ppb)
9/6/2016	163	1.28 ± 0.02	0.86	1.30 ± 0.02	0.97	1.29 ± 0.01	0.84
9/19/2016	44	1.32 ± 0.01	1.33	1.32 ± 0.01	1.35	1.25 ± 0.02	0.82
10/3/2016	34	1.29 ± 0.01	1.30	1.30 ± 0.01	1.37	1.23 ± 0.01	1.33
10/17/2016	43	1.31 ± 0.01	1.57	1.29 ± 0.02	1.52	1.28 ± 0.01	1.37
10/31/2016	15	1.28 ± 0.01	1.57	1.31 ± 0.01	1.52	1.32 ± 0.01	1.60
11/14/2016	144	1.27 ± 0.01	1.03	1.28 ± 0.01	0.97	1.26 ± 0.01	1.01
11/28/2016	77	1.31 ± 0.02	1.34	1.29 ± 0.02	1.22	1.29 ± 0.02	1.23
12/13/2016	84	1.29 ± 0.01	1.22	1.27 ± 0.02	1.20	1.27 ± 0.01	1.04
12/27/2016	45	1.26 ± 0.01	1.20	1.27 ± 0.01	1.21	1.29 ± 0.01	1.27
1/12/2017	40	1.27 ± 0.02	1.08	1.27 ± 0.02	1.07	1.29 ± 0.02	1.33
1/23/2017	222	1.25 ± 0.02	1.09	1.28 ± 0.01	1.08	1.25 ± 0.01	0.93
2/7/2017	59	1.29 ± 0.02	1.34	1.29 ± 0.02	1.32	1.26 ± 0.02	1.13
2/24/2017	222	1.25 ± 0.02	0.93	1.29 ± 0.01	0.91	1.21 ± 0.01	0.77
3/6/2017	131	1.30 ± 0.01	1.18	1.27 ± 0.01	1.13	1.27 ± 0.01	1.10

variability. Uranium concentrations varied spatially from 0.5% to 11% between Hwy 21 and Hwy 60 and from 0.5% to 49% between Hwy 60 and Hwy 105.

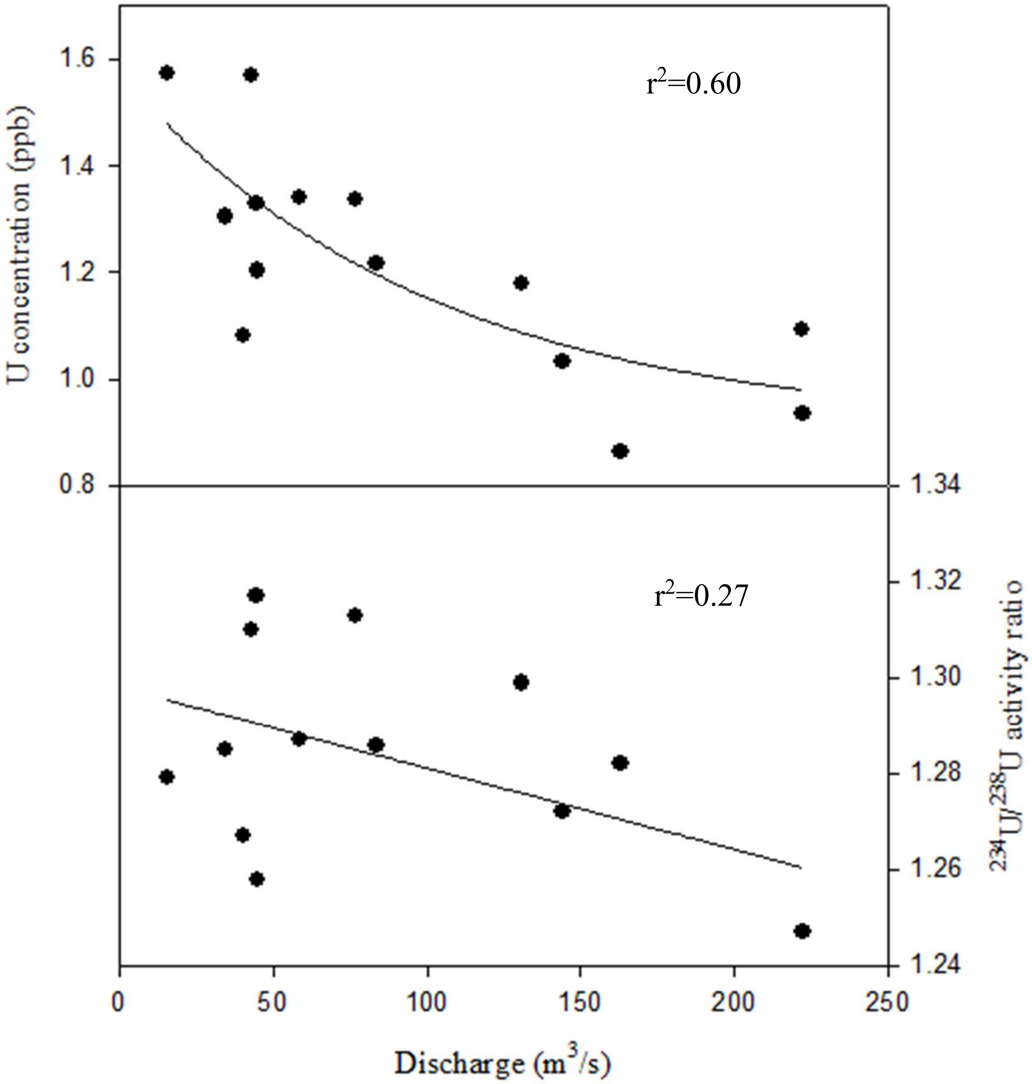

Figure 4. *Discharge at Hwy 21 plotted against U concentrations (above) and* $^{234}U/^{238}U$ *activity ratios (below) measured at sampling site Hwy 21. Line shown in plots is a regression line with best fit.*

4.3 Lake Whitney, tributary, rainwater, and groundwater $^{234}U/^{238}U$ activity ratios and uranium concentrations

Tables 2 and 3 show all measured $^{234}U/^{238}U$ activity ratios and uranium concentrations in Lake Whitney, Yegua Creek, Little Brazos River, rainwater, and groundwater. Water samples were obtained from Lake Whitney on three separate occasions, approximately two months apart, and at two locations near Lake Whitney Dam to analyze the spatial and temporal variability in uranium concentrations and $^{234}U/^{238}U$ activity ratios at this source. Over the course of this study, uranium concentrations varied by approximately 28%, from a low of 1.13 ppb to a high of 1.50 ppb, while the $^{234}U/^{238}U$ activity ratio varied by 4%, from a low of 1.32 to a high of 1.37. Generally, there was good spatial agreement among uranium concentrations and activity ratios during each sampling period. The lowest uranium concentrations were observed during late September whereas the highest were observed during late February. The lowest $^{234}U/^{238}U$ activity ratios were observed during late February whereas the highest were observed during late December.

Tributary water samples were collected from Yegua Creek and the Little Brazos River. Yegua Creek was sampled on the same day as the Brazos River to analyze a major tributary's contribution of uranium to the Brazos River. Yegua Creek showed the largest variations within uranium concentrations and $^{234}U/^{238}U$ activity ratios compared to the other surficial water sampling sites. Uranium concentrations varied temporally by 185%, from a low of 0.07 ppb to a high of 1.71 ppb and exhibited a good correlation with discharge (r^2=0.86; Figure 5). $^{234}U/^{238}U$ activity ratios varied temporally by 13%,

Table 2. *$^{234}U/^{238}U$ activity ratios and uranium concentrations in Yegua Creek, Little Brazos River, Lake Whitney, and rainwater.*

Tributaries

Date	Discharge Yegua Creek Somerville, TX (m^3/s)	$^{234}U/^{238}U$ activity ratios	U concentration (ppb)	$^{234}U/^{238}U$ activity ratios	U concentration (ppb)
		Yegua Creek		Little Brazos River	
9/6/2016	57	1.09 ± 0.04	0.07		
9/19/2016	54	1.13 ± 0.05	0.08		
10/3/2016	8	1.20 ± 0.04	0.13		
10/17/2016	2	1.12 ± 0.03	0.31		
10/31/2016	0.02	1.09 ± 0.01	1.71		
11/14/2016	0.1	1.11 ± 0.01	1.27		
11/28/2016	2	1.10 ± 0.02	0.26		
12/13/2016	26	1.14 ± 0.02	0.18		
12/27/2016	3	1.06 ± 0.02	0.42		
1/12/2017	2	1.05 ± 0.02	0.45		
1/23/2017	31	1.15 ± 0.03	0.22	1.12 ± 0.03	0.30
2/7/2017	17	1.08 ± 0.04	0.22	1.14 ± 0.02	0.71
2/24/2017	52	1.10 ± 0.04	0.17		
3/6/2017	17	1.09 ± 0.03	0.24	1.17 ± 0.02	0.79

Lake Whitney

		Lake Whitney 1		Lake Whitney 2	
9/25/2016		1.35 ± 0.01	1.13	1.35 ± 0.01	1.16
12/27/2016		1.37 ± 0.01	1.50	1.37 ± 0.01	1.30
2/28/2017		1.32 ± 0.02	1.46	1.33 ± 0.02	1.43

Rain

		Rain 1		Rain 2	
2/20/2017		1.13 ± 0.10	0.05	1.00 ± 0.10	0.06

Table 3. *^{234}U/^{238}U activity ratios and uranium concentrations in groundwater at the Texas A&M Hydrogeologic Research Site.*

Texas A&M Hydrogeologic Research Site								
Relative Depth	**Sample**	**Depth** (m)	**9/15/2016**		**11/21/2016**		**2/8/2017**	
			^{234}U/^{238}U activity ratios	U concentration (ppb)	^{234}U/^{238}U activity ratios	U concentration (ppb)	^{234}U/^{238}U activity ratios	U concentration (ppb)
Shallow	A1-2	11.1	1.25 ± 0.01	2.01	1.25 ± 0.01	1.58	1.24 ± 0.01	1.75
	A2-2	12.3	1.31 ± 0.01	2.36	1.26 ± 0.00	2.32	1.26 ± 0.01	2.13
	A3-2	13.0	1.30 ± 0.02	2.20	1.31 ± 0.01	2.82	1.29 ± 0.02	2.51
	B1-2	10.9	1.26 ± 0.01	1.98	1.22 ± 0.01	1.90	1.23 ± 0.01	1.60
	B2-2	11.5	1.30 ± 0.01	3.08	1.25 ± 0.01	3.15	1.24 ± 0.01	2.40
	B3-2	12.5	1.36 ± 0.01	3.22	1.46 ± 0.01	2.24	1.36 ± 0.01	2.03
	C1-2	10.9	1.33 ± 0.01	0.68	1.29 ± 0.01	0.84	1.28 ± 0.02	0.98
	C2-2	10.9	1.32 ± 0.01	3.04	1.28 ± 0.01	3.09	1.28 ± 0.01	3.14
	C3-2	10.9	1.31 ± 0.01	2.90	1.30 ± 0.02	2.96	1.30 ± 0.01	3.40
Intermediate	A1-3	14.6	1.28 ± 0.01	1.33	1.25 ± 0.02	1.20	1.24 ± 0.02	1.25
	A2-3	15.7	1.79 ± 0.01	2.11	1.56 ± 0.01	0.92	1.28 ± 0.01	0.78
	A3-3	17.0	1.26 ± 0.01	0.96	1.25 ± 0.01	0.56	1.26 ± 0.01	0.80
	B1-3	15.0	1.24 ± 0.01	0.06	1.56 ± 0.01	0.07	1.19 ± 0.01	0.25
	B2-3	15.8	1.26 ± 0.02	0.82	1.29 ± 0.01	0.93	1.25 ± 0.01	1.18
	B3-3	14.8	1.31 ± 0.04	2.37	1.32 ± 0.06	2.41	1.32 ± 0.03	2.49
	C1-3	16.6	1.25 ± 0.02	1.29	1.26 ± 0.02	1.36	1.27 ± 0.02	1.34
	C2-3A	12.4	1.29 ± 0.02	1.19	1.26 ± 0.02	1.16	1.25 ± 0.01	1.11
	C2-3B	16.4	1.28 ± 0.02	1.40	1.28 ± 0.01	1.47	1.25 ± 0.01	1.43
Deep	A1-4	17.8	1.35 ± 0.02	0.07	1.36 ± 0.02	0.12	1.30 ± 0.02	0.40
	A2-4	18.8	1.54 ± 0.07	0.49	1.41 ± 0.08	0.29	1.34 ± 0.04	0.35
	B1-4	18.7	1.35 ± 0.02	0.19	1.51 ± 0.05	0.16	1.35 ± 0.04	0.18
	B2-4	18.7	1.41 ± 0.02	0.03	1.45 ± 0.02	0.03	1.27 ± 0.03	0.17
	C1-4	20.3	1.98 ± 0.06	1.66	1.96 ± 0.04	1.40	1.88 ± 0.02	1.48

from a low of 1.05 to a high of 1.20 and showed no correlation with discharge (r^2=0.03; Figure 5). The Little Brazos River was not sampled regularly because it was shown previously to contribute a negligible amount of water to the Brazos River (Turco et al., 2007). However, three samples were collected to compare to the results from Yegua Creek. In the Little Brazos River, uranium concentrations varied from 0.30 ppb to 0.79 ppb while $^{234}U/^{238}U$ activity ratios varied from 1.12 to 1.17. These values are within the range of values obtained from Yegua Creek.

Two rainwater samples were collected during late February to determine the atmospheric contribution of uranium to surface water. The concentration of uranium in rain was low with measurements of 0.05 and 0.06 ppb for each of the two samples obtained. $^{234}U/^{238}U$ activity ratios for both samples were also low at 1.00 and 1.13 with large associated errors due to its low concentration.

All groundwater samples were collected at the Texas A&M University Hydrogeological Research Site on three separate sampling campaigns. There was significant spatial variability among uranium concentrations and $^{234}U/^{238}U$ activity ratios of groundwater in the Brazos River Alluvial Aquifer. Groundwater uranium concentrations varied by 197%, from 0.03 ppb to 3.40 ppb, while $^{234}U/^{238}U$ activity ratios varied by 50%, from 1.19 to 1.98. Moreover, significant spatial variability was seen in shallow, intermediate, and deep groundwater which correlate with wells labeled "-2," "-3," and "-4," respectively.

Additionally, there was significant temporal variability of uranium concentrations in groundwater, most notably in well rows A and B which are closer to the Brazos River. However, less temporal variability was observed in the $^{234}U/^{238}U$ activity ratio of each individual monitoring well with the exceptions of wells A2-3, A2-4, B1-3, B1-4, and B2-4. In these wells, the $^{234}U/^{238}U$ activity ratio started out relatively high in September and fell throughout this study.

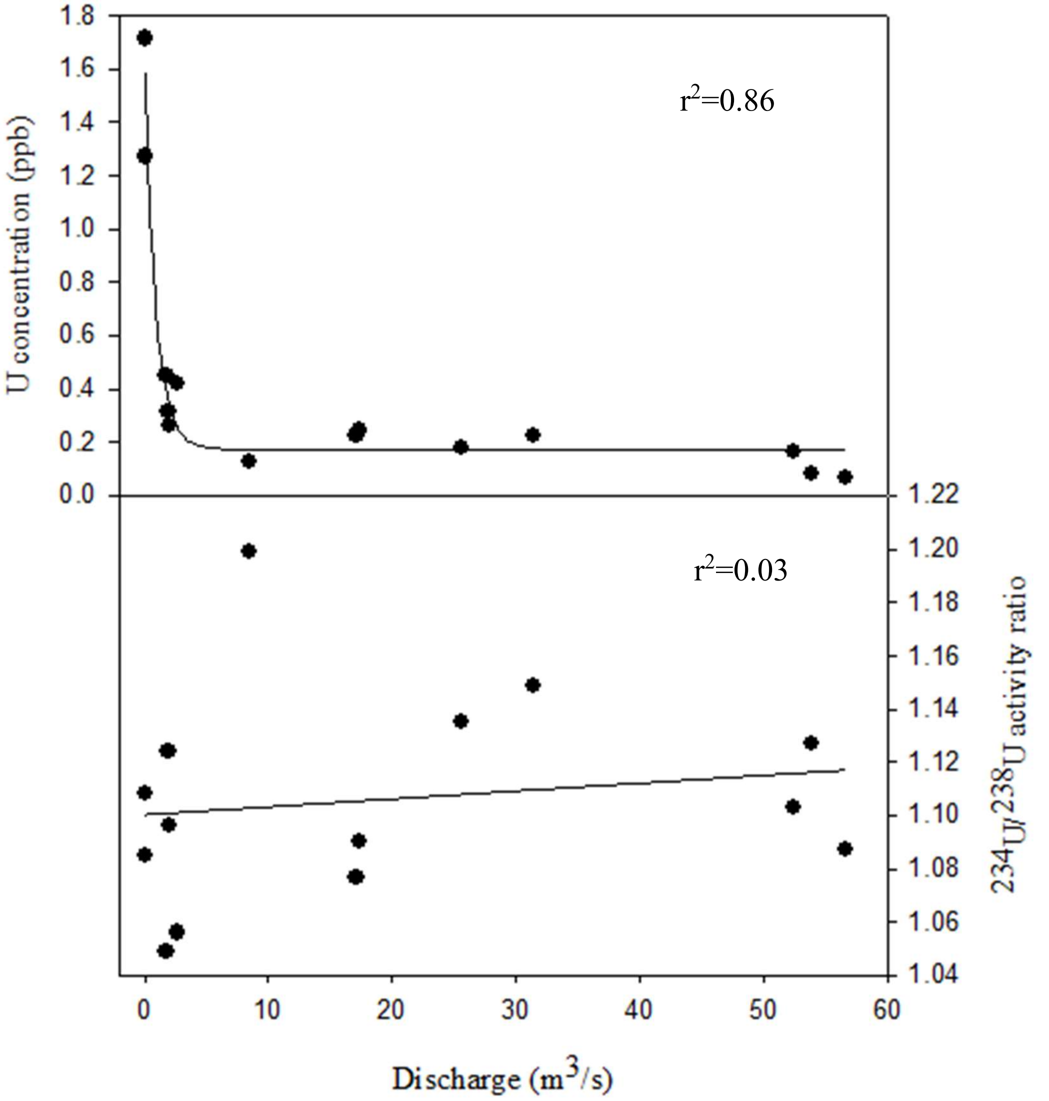

Figure 5. *Discharge at Yegua Creek plotted against U concentrations (above) and $^{234}U/^{238}U$ activity ratios (below) measured at sampling site Yegua Creek. Line shown in plots is a regression line with best fit.*

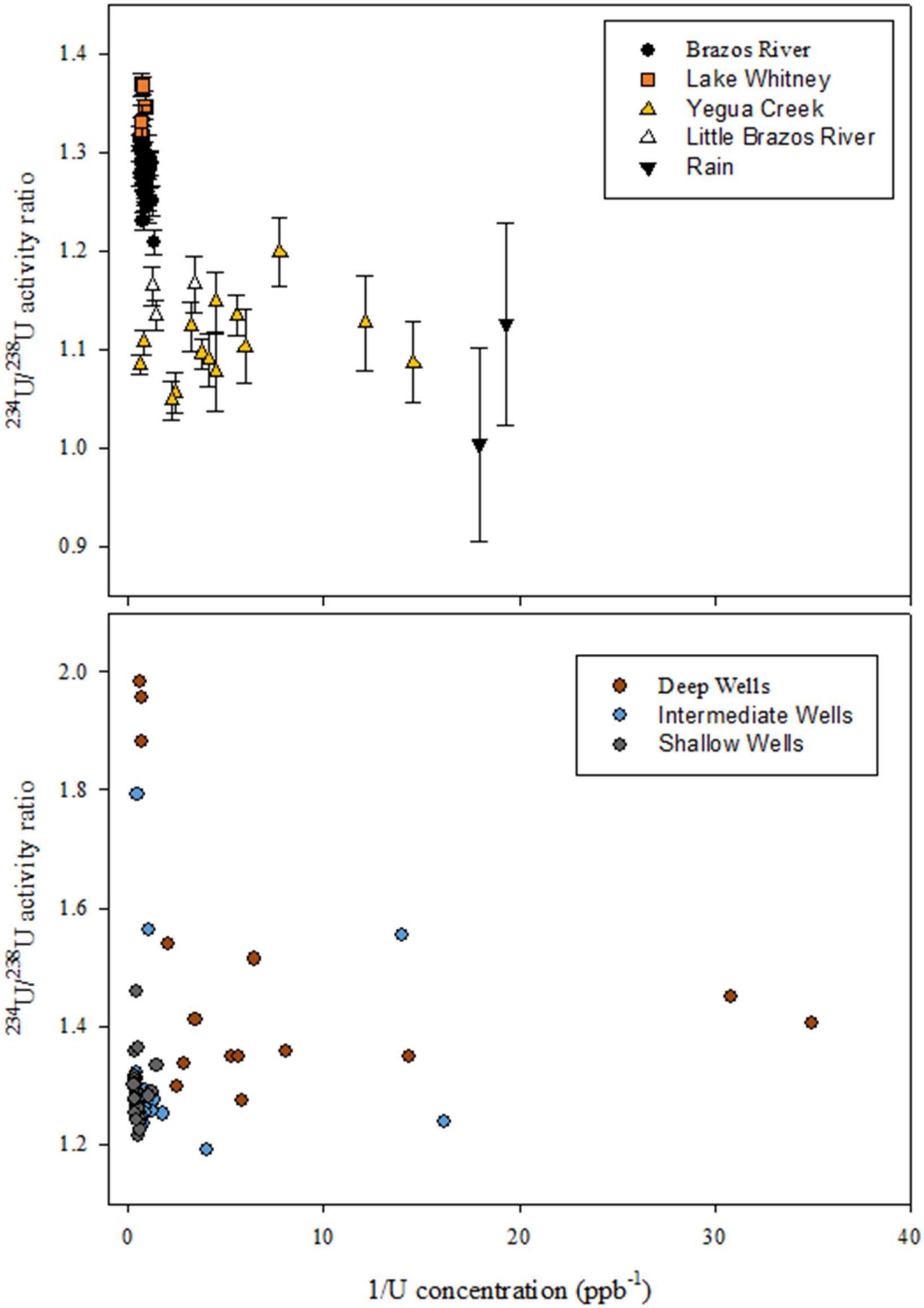

Figure 6. *$^{234}U/^{238}U$ activity ratios plotted against the reciprocal of the uranium concentration for surface waters (top) and groundwaters (bottom).*

5. DISCUSSION

5.1 ^{234}U/^{238}U activity ratios and uranium concentrations in the Brazos River

As stated earlier, ^{234}U/^{238}U disequilibria is observed in natural waters because radiation damage caused to rocks by the emission of α-particles as ^{238}U decays facilitates leaching of ^{234}U. Additionally, factors such as climate and lithology have been shown to influence the degree of ^{234}U/^{238}U disequilibria in river systems (Chabaux et al., 2001; Durand et al., 2005; Grzymko et al., 2007; Kraemer and Brabets, 2012; Pande et al., 1994; Plater et al., 1992; Riotte and Chabaux, 1999; Sarin et al., 1990). These factors may also exert control on the uranium isotopic signature and concentration in the Brazos River.

Figure 6 is a plot of the ^{234}U/^{238}U activity ratio against the reciprocal of the uranium concentration for all surficial water and groundwater samples analyzed in this study, respectively. Clearly there is significant spatial variability of uranium within the waters along this stretch of the Brazos River. Before a discussion on ^{234}U/^{238}U activity ratios and uranium concentrations in the Brazos River can take place, it is important to note the atmospheric contribution of uranium to river systems. The two rainwater samples collected had the lowest uranium concentrations and ^{234}U/^{238}U activity ratios compared to any of the other surficial water samples. Due to the extremely low uranium concentrations, rain will only dilute the uranium concentration of water sources in the Brazos River's watershed and will not affect the ^{234}U/^{238}U activity ratio of those sources. This implies that all the uranium carried by a river comes from the surrounding rocks and soils as has been previously noted (Chabaux et al., 2001; Chabaux et al., 2003; Chabaux et al., 2005; Riotte and Chabaux, 1999).

Further evidence of this is supported by the observation that there is a good negative correlation between discharge and uranium concentrations in the Brazos River as well as in Yegua Creek (Figures 4 and 5). Any significant increases of discharge in the Brazos River or Yegua Creek is due to increased rainfall in the Brazos River's watershed which then dilutes the concentration of uranium in these waters. Comparison between the temporal changes of uranium concentrations in the Brazos River and Yegua Creek show that uranium concentrations in Yegua Creek occur over a greater range than the Brazos River, with uranium concentrations higher and much lower in Yegua Creek compared to the Brazos River (Figure 6). This corroborates that tributaries or lower-discharge streams are more susceptible to dilution by rainwater than main-branch rivers (Camacho et al., 2010; Saari et al., 2008; Schmidt, 2004).

The groundwater samples exhibited the greatest range of $^{234}U/^{238}U$ activity ratios and concentrations (Figure 6). In general, the shallow groundwater samples showed lower $^{234}U/^{238}U$ activity ratios and higher uranium concentrations whereas the deeper groundwater showed higher $^{234}U/^{238}U$ activity ratios and lower uranium concentrations. Many studies have reported high $^{234}U/^{238}U$ activity ratios and low uranium concentrations in groundwater which is attributed to the increased time groundwater is in contact with geologic materials that causes a build-up of displaced ^{234}U as well as a more reducing environment that causes precipitation of the dissolved uranium in groundwater (Chabaux et al., 2003; Kumar et al., 2016). Both processes appear to control the uranium in the Brazos River Alluvial Aquifer based on the observed $^{234}U/^{238}U$ activity ratios and uranium concentrations. Previous studies on the interactions between the Brazos River and the Brazos River Alluvial Aquifer agree that there is a good hydraulic connection between them (Alden and Munster, 1997; Cronin and Wilson, 1967; Turco et al., 2007; Wrobleski, 1996). Comparison between $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River and in shallow groundwater of the Brazos River Alluvial Aquifer show that $^{234}U/^{238}U$ activity ratios are similar. This provides more evidence of a good hydraulic connection between the river and its alluvial aquifer. Further, monitoring wells in row C exhibited less temporal variability in uranium concentrations than in the monitoring wells closer to the river in rows A and B. This is most likely due to water exchange between the Brazos River and the Brazos River Alluvial Aquifer which causes larger variations in the uranium in groundwater close to the river.

Regarding the variability of $^{234}U/^{238}U$ activity ratios and uranium concentrations observed within the surficial water samples along this stretch of the Brazos River, the highest $^{234}U/^{238}U$ activity ratios and uranium concentrations were consistently measured at the furthest upstream sampling site, Lake Whitney. The lowest $^{234}U/^{238}U$ activity ratios and uranium concentrations were measured in the tributary samples while intermediate values were measured in the Brazos River at sampling sites Hwy 21, Hwy 60, and Hwy 105. This is most likely due to the change in lithology from carbonate to siliciclastic rock units south of Waco city limits, located between Lake Whitney and Hwy 21. Higher $^{234}U/^{238}U$ activity ratios are generated in waters in contact with rocks that are fine-grained and have high uranium content (Chabaux et al., 2003; Kraemer and Brabets, 2012; Porcelli and Swarzenski, 2003). Additionally, many previous studies have documented higher $^{234}U/^{238}U$ activity ratios in rivers within a carbonate region and lower $^{234}U/^{238}U$ activity ratios in rivers within a siliciclastic or igneous region (Palmer and Edmond, 1993; Riotte and Chabaux, 1999; Ryu et al., 2009). In this respect, lithology could at least partly explain the higher $^{234}U/^{238}U$ activity ratios observed upstream at Lake Whitney where it is composed of mostly carbonate rocks; and the lower $^{234}U/^{238}U$ activity ratios measured in the tributaries as the lithology through which they flow is siliciclastic. The higher uranium concentrations consistently measured in Lake Whitney may also be attributed to the carbonate lithology as higher uranium concentrations are expected in watersheds that drain rocks that weather quickly (Amiotte Suchet et al., 2003; Bluth and Kump, 1994; Grzymko et al., 2007). Hence, two factors likely explain the lower uranium concentrations in the tributary samples, the fact that siliciclastic rocks weather more slowly than carbonate rocks and the enhanced effect of dilution on lower-discharge streams by rainwater. Notably, however, two samples from Yegua Creek on the dates of 10/31/16 and 11/14/16 had high uranium concentrations when discharge was almost zero. These higher uranium concentrations are probably the result of stagnant water in Yegua Creek, as water that is in contact with rocks for extended time has been shown to result in higher uranium concentrations (Chabaux et al., 2003). The intermediate values of $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River at Hwy 21, Hwy 60, and Hwy 105 are the result of mixing between Lake Whitney's water and tributary water with an additional contribution from groundwater, which has been shown to have a significant hydraulic connection with the river.

Climate may also have effective influence on the $^{234}U/^{238}U$ activity ratios observed in this study. The Salt Fork Brazos River, Double Mountain Fork Brazos River, and Clear Fork Brazos River are tributaries that feed into the main-stem Brazos River. These tributaries originate at the Brazos River's headwaters near the Texas-New Mexico border where the climate is classified as semi-arid savanna (TWDB, 2012). Rivers in regions with arid climates generally have higher $^{234}U/^{238}U$ activity ratios compared to rivers in regions with humid climates (Kronfeld et al., 2004; Kronfeld and Vogel, 1991). This has been attributed to the dominance of physical weathering in arid climates which break down rock into smaller pieces, exposing greater surface area. This means more radiogenic-induced damage sites are exposed, mobilizing ^{234}U at a greater rate. These three tributary sub-basins within the Brazos River watershed could affect the uranium signature downstream at Lake Whitney, similar to how the lithology and climate of tributaries in the Mississippi River's watershed controlled the uranium concentrations and $^{234}U/^{238}U$ activity ratios in the Mississippi River downstream (Grzymko et al., 2007). Since these tributary sub-basins were not sampled, their exact effects on the Brazos River downstream is unknown.

A more detailed look at the spatiotemporal variability of $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River at Hwy 21, Hwy 60, and Hwy 105 is shown in Figures 7 and 8. In these figures, relevant discharge data is shown along with $^{234}U/^{238}U$ activity ratios and uranium concentrations (Figure 7 describes the stretch

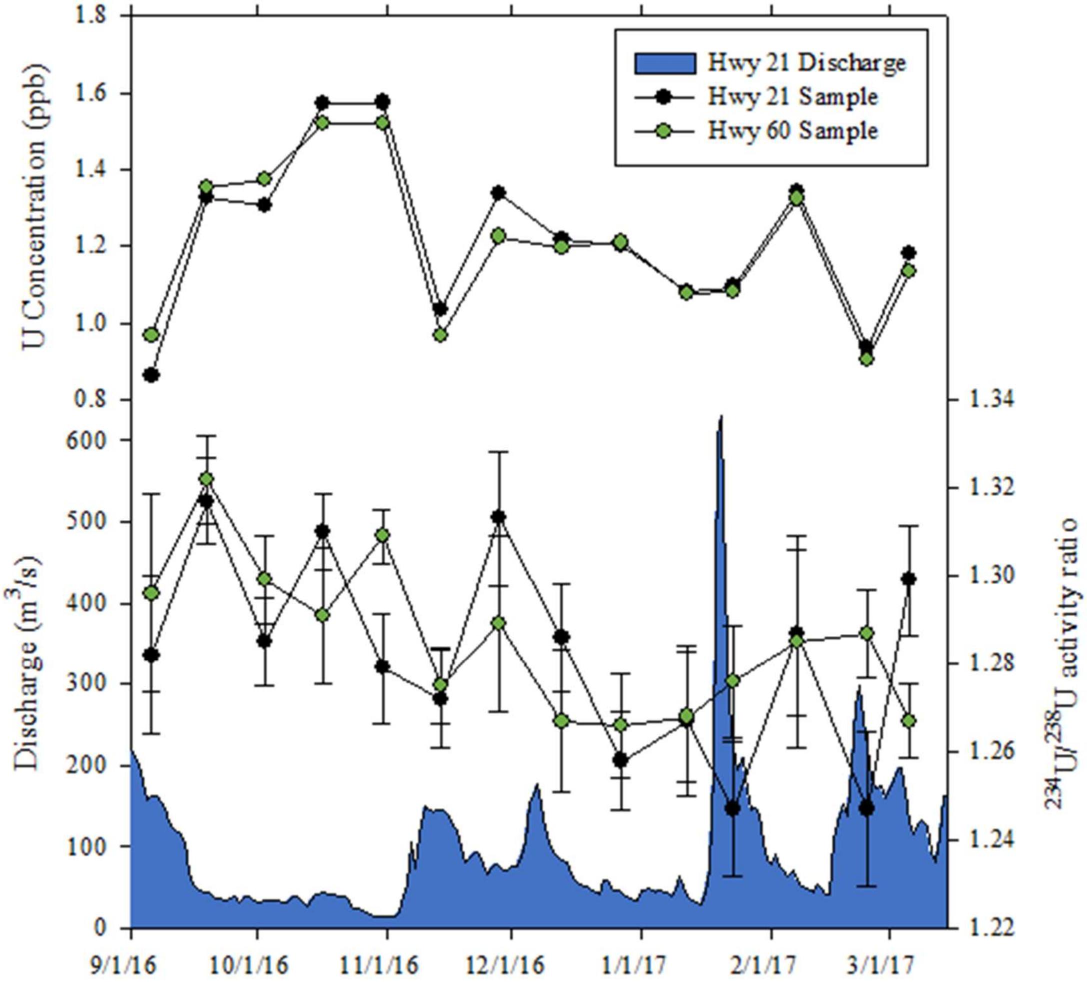

Figure 7. *Spatiotemporal variations of uranium concentrations and* $^{234}U/^{238}U$ *activity ratios between Hwy 21 and Hwy 60.*

between Hwy 21 and Hwy 60 and Figure 8 shows the stretch between Hwy 60 and Hwy 105). Since groundwater generally has higher $^{234}U/^{238}U$ activity ratios and tributary water has lower ratios, it is expected that when groundwater is the main source supplying water along a stretch of the river that the $^{234}U/^{238}U$ activity ratio will increase at the downstream sampling site. Likewise, the $^{234}U/^{238}U$ activity ratio will decrease at the downstream site if tributary inflow or runoff is the main source of water. However, both stretches had $^{234}U/^{238}U$ activity ratios that were within error for most of the sampling dates. It is expected that uranium concentrations will drop when there is significant input from tributaries because uranium concentrations were low when discharge was high in a tributary (Figure 5). The effect groundwater will have on uranium concentrations downstream may be variable depending on whether groundwater discharge to the river is coming from a shallow groundwater source or deep groundwater source. Specifically, uranium concentrations would be expected to increase downstream if a shallow groundwater source is being supplied to the river, while the reverse would happen if a deep groundwater source is supplied. Uranium concentrations exhibited minor changes between Hwy 21 and Hwy 60 (Figure 7) and slightly greater changes between Hwy 60 and Hwy 105 (Figure 8). The cause for insignificant changes observed in $^{234}U/^{238}U$ activity ratios and uranium concentrations between Hwy 21 and Hwy 60 (Figure 7) is most likely due to similar $^{234}U/^{238}U$ activity ratios between shallow/intermediate groundwater and Brazos River water and insignificant input from the Little Brazos River. On the other hand, the slightly greater changes seen in uranium concentrations and isotopic ratios between Hwy 60 and Hwy 105 is due to flow from Yegua Creek (Figure 8). Specifically, $^{234}U/^{238}U$ activity ratios dropped significantly on 9/19/16, 10/3/16, and 2/24/16 at sampling site Hwy 105 because discharge at Yegua Creek was relatively high compared to the discharge at Hwy 21 and water sourced from Yegua Creek has a low $^{234}U/^{238}U$ activity ratio.

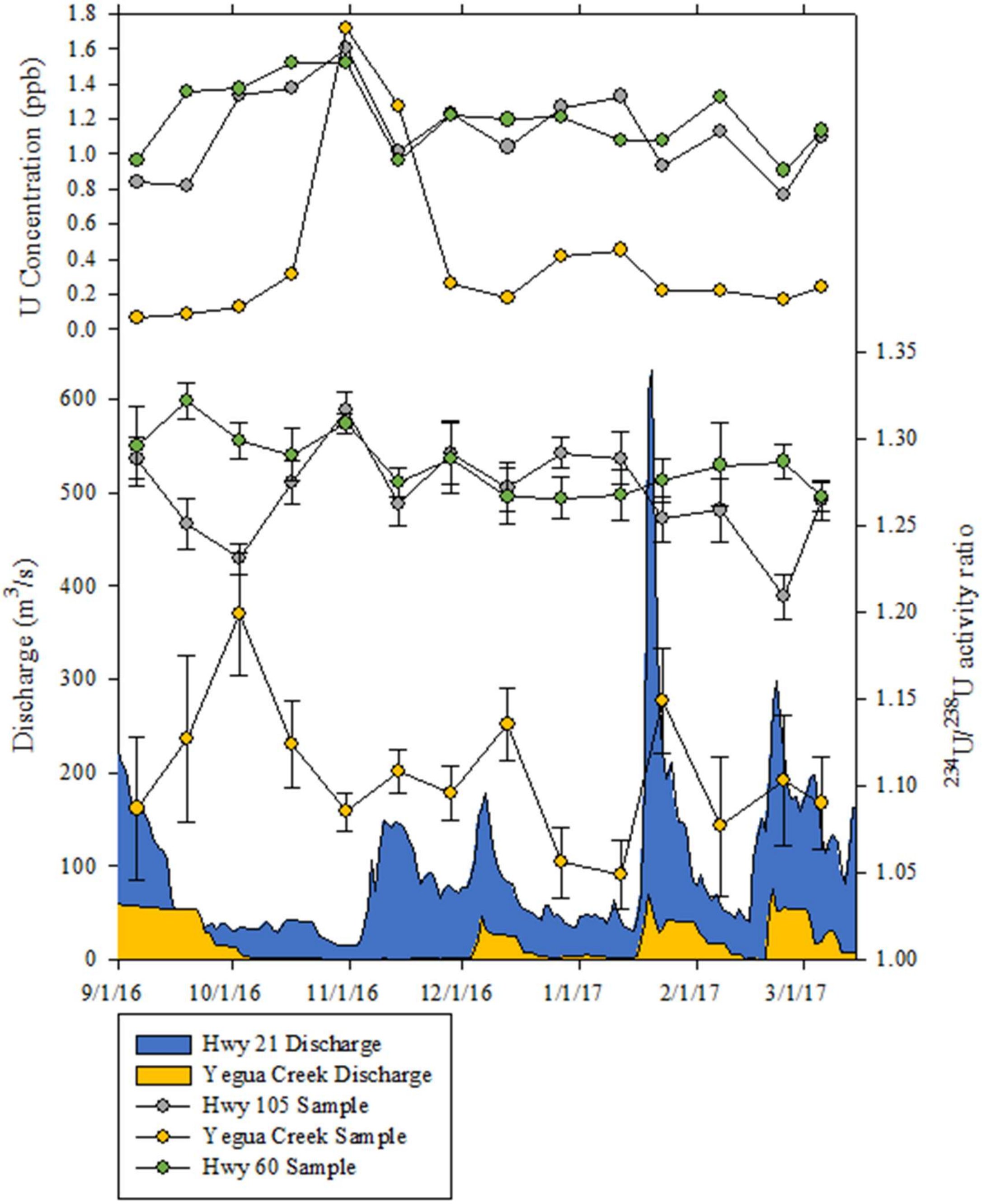

Figure 8. *Spatiotemporal variations of uranium concentrations and* $^{234}U/^{238}U$ *activity ratios between Hwy 60, Hwy 105, and Yegua Creek.*

5.2 Groundwater discharge estimates to the Brazos River

It is likely that the uranium concentration and isotopic signature in the Brazos River (Figure 6) could be produced from mixing between a Lake Whitney source and a tributary source. However, previous studies and results from this study point towards a good hydraulic connection between the Brazos River and BRAA. Under these circumstances, temporal changes observed in $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River are the result from changes in relative inputs from Lake Whitney, groundwater, and tributaries.

To evaluate the relative proportion of each source in the Brazos River at a given time, we perform mixing calculations for sampling site Hwy 21. Such calculations were not possible at Hwy 60 and Hwy 105 as there was no discharge data available at these sites. The following equations can be used to calculate the relative proportions from any number of sources (Faure and Mensing, 2005):

$$f_1, f_2, \cdots, f_n = \frac{D_1}{\sum D_T}, \frac{D_2}{\sum D_T}, \cdots, \frac{D_n}{\sum D_T} \quad (1)$$

$$U_M = U_1 f_1 + U_2 f_2 + \cdots + U_n f_n \quad (2)$$

$$\left(\frac{^{234}U}{^{238}U}\right)_M = \left(\frac{^{234}U}{^{238}U}\right)_1 \frac{U_1}{U_M} f_1 + \left(\frac{^{234}U}{^{238}U}\right)_2 \frac{U_2}{U_M} f_2 + \cdots + \left(\frac{^{234}U}{^{238}U}\right)_n \frac{U_n}{U_M} f_n \quad (3)$$

where f is the fraction or relative proportion of each source (subscripts 1, 2, n) which can be rewritten in terms of its discharge (D) divided by the total discharge, U is the uranium concentration, ($^{234}U/^{238}U$) is the $^{234}U/^{238}U$ activity ratio, and subscript M denotes the resulting mixture which in this case is river water. These three equations can be used to solve for any unknown values in a mixture of water sources.

The $^{234}U/^{238}U$ activity ratio and uranium concentration measured at Hwy 21 at any given time is the result from interactions between Lake Whitney, tributaries, and groundwater. The relative contribution can be constrained from Lake Whitney as there is an USGS stream gage near Aquilla, Texas directly downstream from Lake Whitney Dam. Relative contributions from groundwater and tributaries are unknown. If $^{234}U/^{238}U$ activity ratios and uranium concentrations are set for each of these three sources, then a unique solution can be obtained for the relative contributions from groundwater and tributary water in the Brazos River. Based on the results from this study, a good approximation for Lake Whitney is represented by a $^{234}U/^{238}U$ activity ratio of 1.35 and uranium concentration of 1.30 ppb. A good estimation of the $^{234}U/^{238}U$ activity ratio and uranium concentration is harder to obtain for groundwater in the Brazos River Alluvial Aquifer and tributary water. Heterogeneity within the alluvial aquifer will cause large variability in the dissolved uranium within groundwater. As for the tributary water, originally Yegua Creek was to be used as a proxy for tributaries along this stretch of the Brazos River. However, it became apparent upon completing preliminary calculations that Yegua Creek is not a good representation of tributary waters between Lake Whitney and Hwy 21.

To compensate for this, the relative contribution Lake Whitney has on the $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River at Hwy 21 can be removed from those values of the river to yield the uranium concentration and isotopic signature of the missing source composed of groundwater and tributary water. First, the relative contribution of Lake Whitney is calculated by dividing discharge measured near Aquilla, Texas by discharge at Hwy 21. A four-day lag time is used between these discharge measurements to account for the time it takes for the water at Lake Whitney to flow downstream to Hwy 21. It follows that the remaining fraction of water missing is composed of the missing water source. The uranium concentration of the missing source is obtained from the following relationship:

$$U_{MS} = \frac{(U_{21} - U_{LW} f_{LW})}{f_{MS}} \qquad (4)$$

where subscripts MS, 21, and LW refer to the missing source, Hwy 21, and Lake Whitney, respectively. The $^{234}U/^{238}U$ activity ratio of the missing source is obtained using the uranium concentration calculated for the missing source:

$$\left(\frac{^{234}U}{^{238}U}\right)_{MS} = \frac{\left[\left(\frac{^{234}U}{^{238}U}\right)_{21} - \left(\frac{^{234}U}{^{238}U}\right)_{LW} \frac{U_{LW}}{U_{21}} f_{LW}\right]}{\left[\frac{U_{MS}}{U_{21}} f_{MS}\right]} \qquad (5)$$

Plotting the calculated $^{234}U/^{238}U$ activity ratios against the reciprocal of uranium concentrations for the missing source at Hwy 21 shows there is a weak negative trend (Figure 9). The trend most likely represents mixing between a more consistent groundwater source which has a higher $^{234}U/^{238}U$ activity ratio and uranium concentration with a tributary source which has a lower $^{234}U/^{238}U$ activity ratio and a variable uranium concentration (i.e., note the greater scatter of the data in the lower right than that in the upper left). Now, to estimate the relative proportions of the groundwater and tributary sources, we assume a groundwater source represented by a $^{234}U/^{238}U$ activity ratio of 1.35 and uranium concentration of 2.00 ppb. As for the tributary source, we constrain the $^{234}U/^{238}U$ activity at 1.10 based on results from the tributaries Yegua Creek and Little Brazos River. The uranium concentration of the tributary endmember

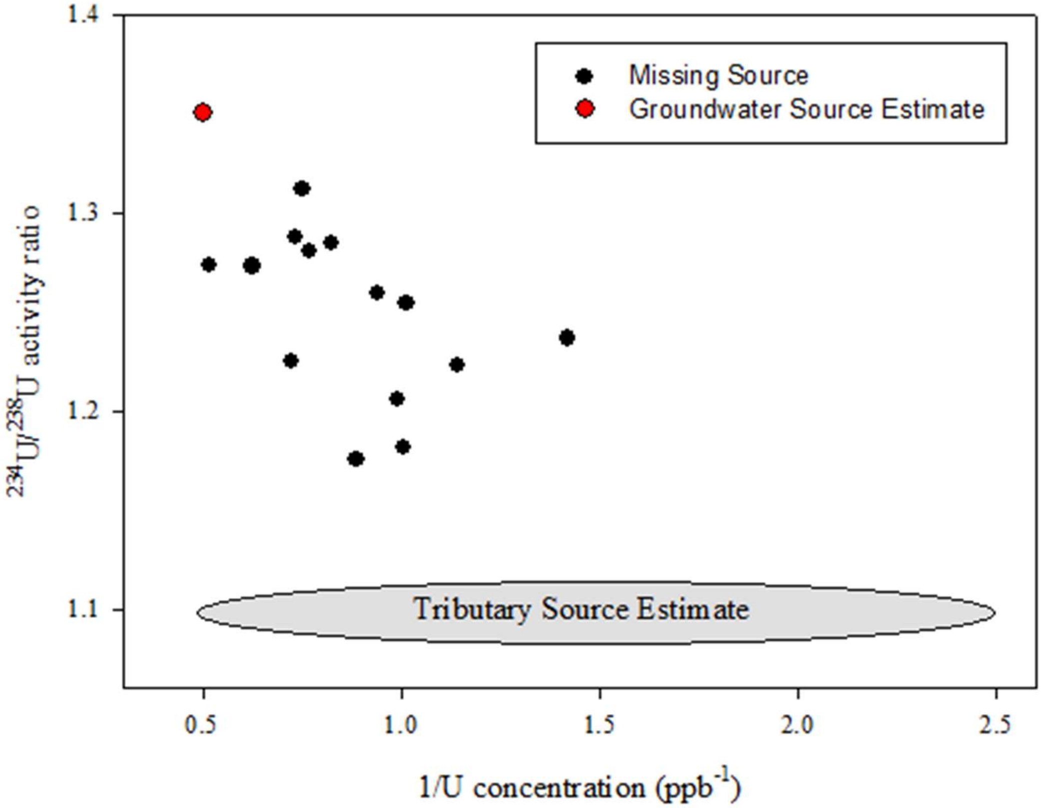

Figure 9. *^{234}U/^{238}U activity ratios plotted against the reciprocal of the uranium concentration for the missing source at Hwy 21. The groundwater source estimate fixed at a ratio of 1.350 and concentration of 2 ppb is shown in addition to the tributary source estimate which is fixed at a ratio of 1.100 and has a variable uranium concentration.*

can be estimated for each sampling period by drawing a straight line from the groundwater source to the missing tributary source, which is set to a ^{234}U/^{238}U activity ratio of 1.100. In this way, we are able to estimate what we believe to be the most appropriate ^{234}U/^{238}U activity ratios and uranium concentrations for the three sources of Brazos River water: Lake Whitney water, tributary water, and groundwater. The relative proportions of each source can be obtained by using equation number 3 above.

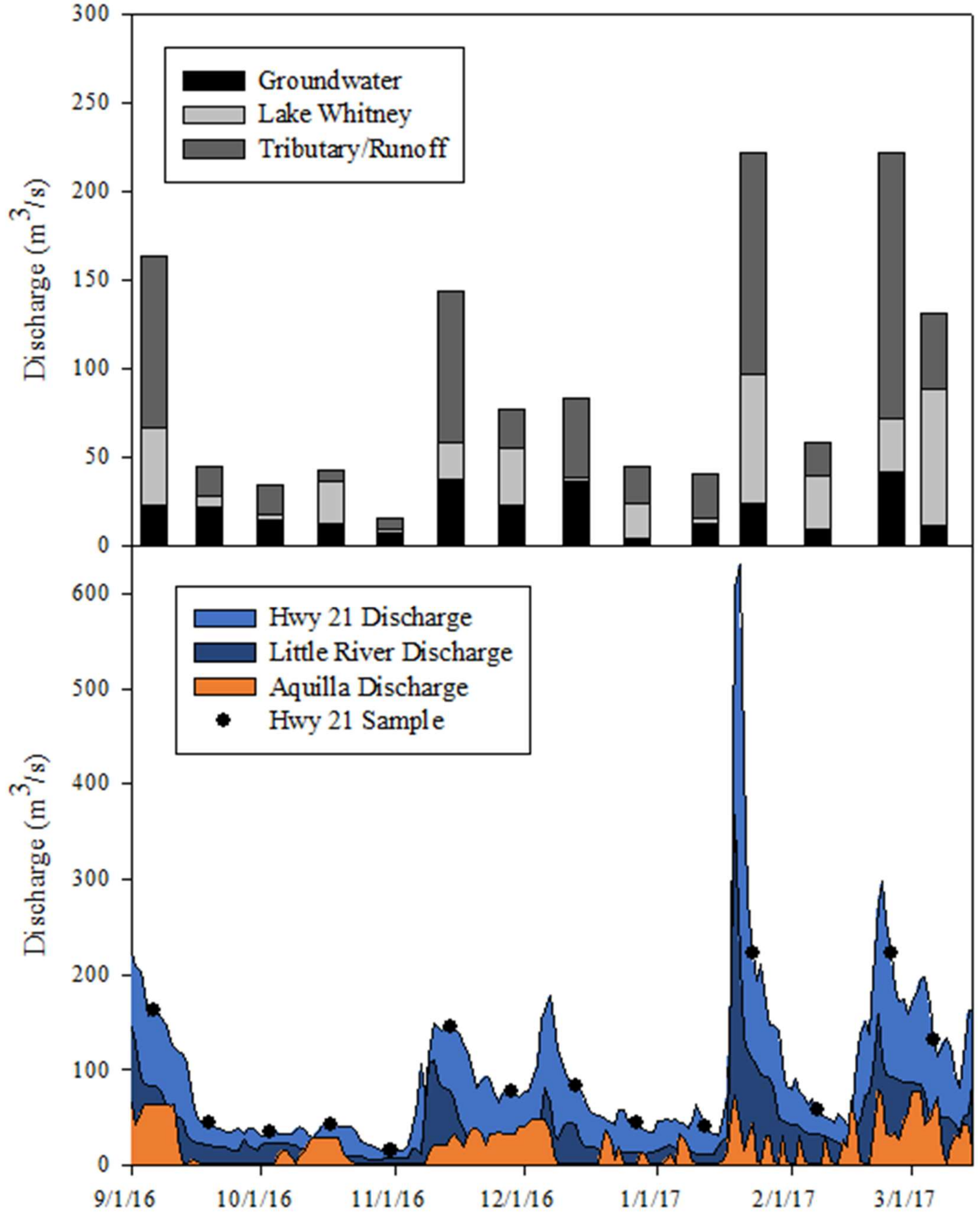

Figure 10. *Source discharge estimates for Lake Whitney, groundwater, and tributary water at Hwy 21 for each of the 14 sampling periods (top). Daily discharge measurements are shown for Hwy 21, the Little River, and Aquilla (bottom).*

Results indicate that net groundwater discharged to the river upstream of Hwy 21 ranged from 4 m^3/s to 42 m^3/s while tributary discharge to the river ranged from 6 m^3/s to 151 m^3/s (Table 4). There was a positive correlation between both groundwater discharge and tributary discharge against total discharge at Hwy 21 ($r^2=0.43$ and $r^2=0.93$, respectively; Figure 10). However, the positive correlation was stronger with respect to tributary discharge (r^2 of 0.93) indicating appreciable increases in discharge at Hwy 21 is due to higher flow in tributaries because of increased runoff within the Brazos River watershed. The positive correlation (r^2 of 0.43) between groundwater discharge to the Brazos River and total discharge agrees with previous studies that have found increases in the groundwater contribution to rivers as discharge increases (Unland et al., 2013; Yu et al., 2013). Significantly, our tributary discharge estimates agree remarkably well with those measured for the Little River ($r^2=0.91$; Figure 11). The Little River is the only major tributary that flows into the Brazos River between the sampling sites at Lake Whitney and Hwy 21 (Figure 1). This provides a check on the accuracy of our tributary source estimates for $^{234}U/^{238}U$ activity ratios and uranium concentrations within the area of this study. The variability observed among $^{234}U/^{238}U$ activity ratios and uranium concentrations in the Brazos River highlights the importance of adequate spatial and temporal measurements of uranium within a watershed if uranium isotopes and concentrations are to be used to trace sources of water to a river.

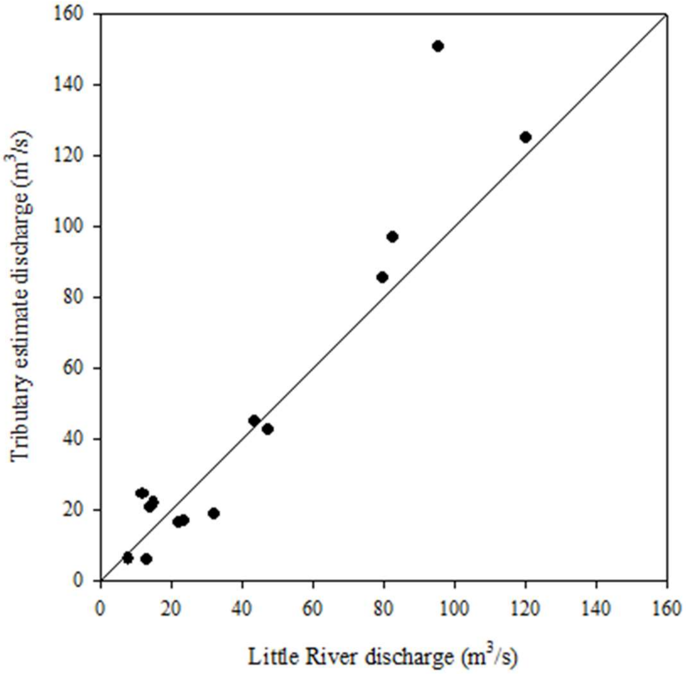

Figure 11. *Comparison of discharge between our tributary source estimate and the Little River. Line drawn in figure is a 1:1 line.*

Table 4. *Source discharge estimates from Lake Whitney, groundwater, and tributary water at Hwy 21.*

Hwy 21 Source Estimates

Date	**Hwy 21**		**Discharge (m^3/s)**				
	$^{234}U/^{238}U$ activity ratios	U concentration (ppb)	Hwy 21 Total Flow	Aquilla Lake Whitney	Groundwater	Tributary	Little River
9/6/2016	1.28 ± 0.02	0.86	163	43	23	97	83
9/19/2016	1.32 ± 0.01	1.33	44	6	22	17	22
10/3/2016	1.29 ± 0.01	1.30	34	2	15	17	24
10/17/2016	1.31 ± 0.01	1.57	43	25	12	6	13
10/31/2016	1.28 ± 0.01	1.57	15	1	8	6	8
11/14/2016	1.27 ± 0.01	1.03	144	21	37	86	80
11/28/2016	1.31 ± 0.02	1.34	77	32	23	22	15
12/13/2016	1.29 ± 0.01	1.22	84	2	37	45	44
12/27/2016	1.26 ± 0.01	1.20	45	20	4	21	14
1/12/2017	1.27 ± 0.02	1.08	40	3	13	25	12
1/23/2017	1.25 ± 0.02	1.09	222	73	24	125	120
2/7/2017	1.29 ± 0.02	1.34	59	30	10	19	32
2/24/2017	1.25 ± 0.02	0.93	222	30	42	151	95
3/6/2017	1.30 ± 0.01	1.18	131	77	12	43	47

6. CONCLUSION

Uranium concentrations and $^{234}U/^{238}U$ activity ratios were measured over a 6-month period within the Brazos River's watershed along the Brazos River Alluvial Aquifer to expand on previous work completed on the interactions between the Brazos River and its alluvial aquifer. Previous studies agree that the Brazos River is a gaining stream near College Station, Texas. $^{234}U/^{238}U$ activity ratios and uranium concentrations appear to suggest the same result at Hwy 21. Specifically, the water at Hwy 21 is sourced from Lake Whitney, groundwater, and tributary water. Contributions from Lake Whitney are controlled by releases from Lake Whitney Dam whereas water from a tributary-like source appears to come solely from the Little River. Groundwater flows into the Brazos River at a steady rate and increases slightly as discharge increases.

Additionally, low concentrations of uranium in rain water suggest water within a hydrological system obtains almost all its dissolved uranium from the rocks it comes into contact with. Further, rain will not affect $^{234}U/^{238}U$ activity ratios of source waters within a hydrological system but will dilute the uranium concentration of these sources. The extent of dilution depends on how much rain falls within the watershed and the size of the river, where smaller streams will be more susceptible to dilution from rainfall. Spatiotemporal variations in $^{234}U/^{238}U$ activity ratios and uranium concentrations from this study indicate lithology and climate may control the uranium signature of water within the Brazos River as has been previously suggested. Higher $^{234}U/^{238}U$ activity ratios and uranium concentrations were observed in Lake Whitney compared to sampling sites along the Brazos River and tributaries. The former ratios are controlled by a primarily carbonate lithology near Lake Whitney, while the latter ratios are controlled by a siliciclastic lithology further downstream. The semi-arid climate of tributaries further upstream may also have some control on uranium isotope ratios and concentrations in Lake Whitney but their effect, if any, was not able to be determined since we did not sample water upstream from Lake Whitney. In groundwater, higher $^{234}U/^{238}U$ activity ratios and lower uranium concentrations were observed in deeper groundwaters. This was attributed to the increased time groundwater is in contact with geologic materials that causes a build-up of displaced ^{234}U.

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