# Hydrogeological characterization of the Barton Springs segment of the Edwards Aquifer

## Texas, United States of America

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## INDEX

## LIST OF FIGURES



## APPENDIX

# 1 ABSTRACT

Understanding the sources of surface water, the processes that control groundwater compositions and the timing and magnitude of groundwater vulnerability to potential surface-water contamination under different meteorological conditions is critical to protect water resources thru regulations and good practices, specially in karst systems where infiltrating surface water can rapidly affect groundwater quality. The objective of this study is to improve the understanding of the Barton Springs segment of the Edwards Aquifer, its flow paths and their relationship with the surface environment,) during the transition from extreme drought to wet conditions. To this end, several methods of study have been carried out during the summer of 2014, like statistical analysis of discharge, analysis of the evolution of groundwater compositions (major ions and Sr isotopes) from wet to dry conditions, a dye tracer test and analysis of the intrinsic fluorescence with the TOC.

# 2 INTRODUCTION

A karst aquifer could be described as a body of soluble rock that can conducts water principally via enhanced porosity formed by the dissolution of the rock. They are commonly structured as a branching network of tributary conduits connected together to drain a groundwater basin and discharge to a perennial spring.

The studies of karst systems have always concentrated on analyzing the natural responses of springs to recharge events (Goldsceider & Drew 2007), like variations in temperature (Ghenton *et al.* 2005), chemical composition (Hess and White, 1993), and hydrodynamic parameters (Mangin 1975; Bonacci 1993).

The joint use of artificial tracers with strontium isotopes and intrinsic fluorescence can contribute to the knowledge of the sources of the water, the underground flow paths and the processes suffered during the infiltration (Christian et al., 2011, Mudarra et al., 2014). In addition to this, data of discharge, rainfall and surface flow had been interpreted as well as water samples had been chemically analyzed to reinforce the information obtained.

As a result of this, a combined use of different technics had been used to improve the comprehension of the Barton Springs segment of the Edwards Aquifer, its flow paths and their relationship with the surface like infiltration processes, all established by previous studies.

The Edwards (Balcones Fault Zone) Aquifer is a major aquifer in the south-central part of the state of Texas in the United States of America (Fig. 1). The aquifer feeds several well-known springs, including Comal Springs in Comal County, which is the largest spring in the state, and San Marcos Springs in Hays County, which is the second, and Barton Springs in Travis County.

The Edwards Aquifer consists primarily of partially dissolved limestone that creates a highly permeable aquifer. The thickness of the aquifer ranges from 60 to 180 m, and freshwater saturated thickness averages 170 m in the southern part of the aquifer (Rose, 1972). The strata of the Edwards Group have been buried, suffered diagenetic processes and exposed to the surface again (Rose, 1972), making it a telogenetic karst system (characterized by secondary porosity, mainly conduits and fractures) as defined by Vacher and Mylroie (2002). Due to these characteristics, the aquifer presents a highly permeable nature, making the water levels and spring flows respond quickly to rainfall, drought, and pumping.


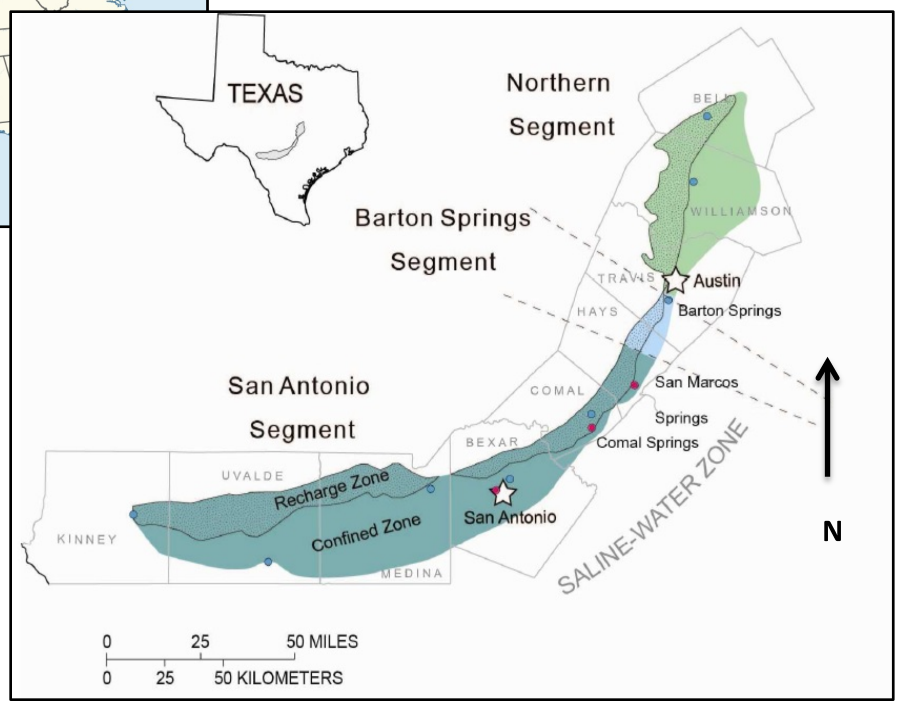


*Figure 1: Location of the Edwards Aquifer in Central Texas and its segments. Modified from the US Geological Survey Hydrologic Atlas 730-E (Ryder, 1996)*

## 3 OBJECTIVES

This hydrogeological research has been carried out to contribute to expand the understanding of the Barton Spring Segment of the Edwards Aquifer, to enhance the knowledge of its underground flow paths and their relationship with the surface water and to characterize the influence zone of Antioch Cave, which is located within Onion Creek, near the town of Buda.

Through these objectives it will be possible to improve systems and regulations that avoid contamination to the aquifer, and consequently make its water quality better.

# 4 METHODS

## 4.1 SAMPLING METHODS

To investigate the evolution of groundwater compositions during the project interval, groundwater from different parts of the aquifer and surface water was sampled. Groundwater samples were collected from four wells:

- 5858128: Ben Wright well at Old Black Colony road.
- 5858121: Public Supply well at Leisurewoods.
- 5858431: Multiport well at Antioch Cave.
- 5858427: David Demint well at Cole Springs road.

Water collected from wells 5858121, 5858128 and 5858427 was pumped from similar depths in the aquifer and from similar stratigraphic units. Water collected from the multiport well was taken from different units and depths (fig. 6).

Spring water was collected from several points:

- Main spring orifice, also known as Parthenia, Eliza and Old Mill springs of Barton Springs, being Parthenia the principal discharge point of the BSE (Slade et al., 1986).
- Pleasant Valley, Park and Little Park Springs in Blanco River and Jacob Well in Cypress Creek.
- Crater Bottom, Weiss Mueler, Diversion and Deep Hole springs at San Marcos Springs.
- Huaco and Comal Springs in New Braunfels.

Wells and springs coordinates shown in appendix: Table 1.

Routine collections of discrete samples were collected from spring stream sites by submerging bottles beneath the water surface at the centroid of flow (Wilde and others, 1999). Samples at wells were collected prior to any filtration, chlorination, or other treatment. Wells were purged prior to sample collection, as determined by stable readings of water temperature, pH, conductivity, dissolved oxygen, and turbidity measured by a multi-parameter sonde (Wilde and others, 1999).

All samples for anions, cations and Sr isotope analysis were filtered using a 0.45-lm disc filter. Samples for analysis of TOC were taken in a container with a preservative of $H_2SO_4$.

## 4.2 DATA ANALYSIS OF DISCHARGE

Data of discharge from the Mains Spring at Barton Springs and surface flow (15-min and daily mean) was obtained from the Lower Colorado River Authority (LCRA) and from the United States Geological Service (USGS) National Water Information System (U.S. Geological Survey, 2012), and interpreted in different intervals of time with the objective of using that information to compare major ions and Sr isotopes in wet versus dry conditions.

### 4.3 ANALYTICAL METHODS

Groundwater samples were analyzed for major ions, total dissolved solids and alkalinity at LCRA Environmental Laboratory Services in Austin, Texas, conform to the National Environmental Laboratory Accreditation Program (NELAP) standards. Major ion and alkalinity analyses were performed using ion-exchange chromatography and inductively coupled plasma-mass spectrometry, respectively (Fishman, 1993).

Groundwater samples and charcoal receptors were analyzed for dye tracers (pyranine) at Orzak Underground Laboratory (OUL) in Protem, Missouri, upon standards used at the OUL.

Groundwater samples were analyzed for Sr 87/86 at the Jackson School of Geosciences, The University of Texas at Austin. Sr was isolated using ion exchange chemistry, and Sr isotope values were measured using a Finnigan-MAT 261 thermal ionization mass spectrometer at the Department of Geological Sciences.

Groundwater and surface water samples were analyzed for total organic carbon (TOC) at LCRA Environmental Laboratory Services conform to the NELAP standards. The analysis method used was SM5310D, Wet oxidation method, in which the reagent used is granular potassium persulphate and heat is used for it activation.

### 4.4 GROUNDWATER DYE TRACING

Groundwater dye tracing was carried out to better understand the groundwater flow paths. Groundwater tracing involves the introduction of non-toxic materials (tracers) into the aquifer through surface drainages or the subsurface (injection points) and monitoring the movement of these materials at wells and springs (receptor sites). The general methodology of tracing and an evaluation of various tracers are described by Aley (1999).

The Edwards aquifer was sampled through activated charcoal bags placed in two wells and grab samples taken from springs, wells and using the multiport well located near to Antioch Cave, in Onion Creek, Hays County, in the confined zone of the aquifer.

The multiport well allows the sampling of various hydrostratigraphic units at one site. It has 21 monitor zones separated by packers that isolate the space between the casing and the walls. Each zone consists of a packer at the top and the bottom of the zone, one measurement port, one pumping port, and a magnetic collar placed two feet below the measurement port. The ports allow sampling, water-level measurements and aquifer tests. Groundwater collected and measurements are representatives of the aquifer zones between the packers (Fig. 2) (Smith and Hunt, 2011).

The pressure transducer allows to take the water samples and also to measure the temperature and the pressure inside and outside the casing, which allows to knows water-levels of each zone of the aquifer.

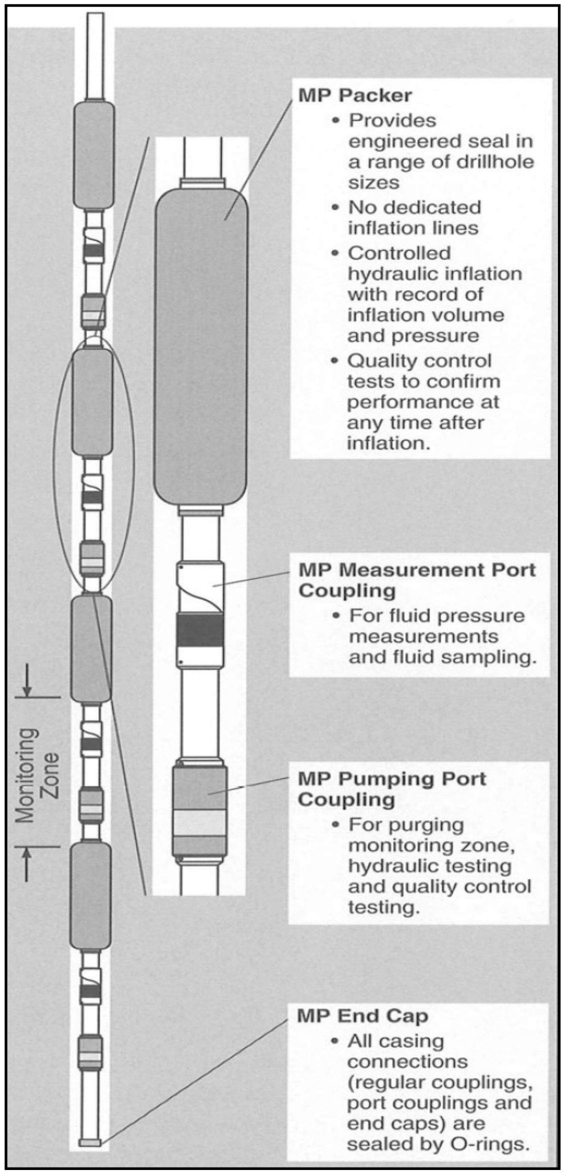


*Figure 2: Schematic diagram of multiport monitor well components and construction. Courtesy of Schlumberger Water Services, Inc.*

## 4.5 NATURAL TRACERS

### *Sr isotopes*

Groundwater Sr isotope ($^{87}Sr/^{86}Sr$) values in the Barton Springs Segment generally are lower than those measured in surface water (Oetting et al., 1996; Garner, 2005; Christian et al., 2011), and can potentially be used to quantify mixing between surface and groundwater. Water acquires its initial Sr isotope signature (~0.7090) from interaction with silicate minerals in soils overlying the BSE (Musgrove and Banner, 2004; Wong et al., 2011).

As water interacts with the underlying carbonate bedrock, $^{87}Sr/^{86}Sr$ progressively decreases, becoming more similar to that of the Cretaceous limestone bedrock ($^{87}Sr/^{86}Sr$ ~ 0.7076) (Musgrove and Banner, 2004; Christian et al., 2011).

Longer groundwater residence times and more extensive water–rock interaction with aquifer host rocks result in lower $^{87}Sr/^{86}Sr$ values (Oetting et al., 1996; Garner, 2005). Mixing of municipal water from leaking infrastructure and irrigation runoff with stream water also can result in higher surface water $^{87}Sr/^{86}Sr$ values relative to those in groundwater, because municipal water has a higher Sr isotope signature ($^{87}Sr/^{86}Sr$ ~ 0.7090) than does the Cretaceous limestone; mixing of municipal and natural water has been demonstrated to control $^{87}Sr/^{86}Sr$ values in some Austin area streams (Christian et al., 2011).

*Intrinsic fluorescence*

Intrinsic fluorescence in water is produced by the dissolved organic matter (DOM) existing in water. DOM is an aggregation of heterogeneous organic molecules that is omnipresent in aquatic systems (Findlay and Sinsabaugh, 2003).

The main tool used to characterize DOM in natural waters is the fluorescence spectroscopy which is based on the scanning of emission and excitation wavelengths using a beam of light to generate emission-excitation matrix (EMM) (Mudarra et al., 2011).

DOM is derived from decomposing organisms like plants, and is often classified into humic substances (mainly humic acids) and fulvic acids (humic acids of lower molecular weight and higher oxygen content) (Chen et al., 2010). Each compound will generate it own wavelength so it is possible to determine the source of the organic matter.

The intrinsic fluorescence from humic and fulvic acids (peaks A: $\lambda_{ex}/\lambda_{em}$ 220−260/400−450 nm, and C: $\lambda_{ex}/\lambda_{em}$ 300−350/400−460 nm) (Mudarra et al. 2014; Baker and Genty 1999; Senesi et al. 1991; Coble 1996) were obtained using a Perkin Elmer LS50-B Luminiscence Spectrofluorometer. The samples were analyzed in a 10 mm quartz cuvette at room temperature. Samples were scanned of excitation and emission wavelengths from 200-375 and from 275-575 nm with intervals of 5 nm.

According to Lawaetz and Stedmon (2009), a 5 nm slit was used for excitation and emission and the stability of the instrument was regulated using the position and the maximum intensity of the Raman peak of deionized water measured at 348 nm of excitation and 390-395 nm of emission. The maximum fluorescence intensity of each peak was recorded as Raman Units (R.U.), normalized to 29.5 ± 2.3 intensity units (Mudarra et al. 2011).

# 5 DESCRIPTION OF THE STUDY AREA

## 5.1. THE EDWARDS (BALCONES FAULT ZONE) AQUIFER

The Edwards Aquifer consists of highly faulted and fractured carbonate rocks of Cretaceous age located in the Balcones Fault Zone (BFZ) of central Texas. From northeast to southwest, it spans over the counties of Bell, Williamson, Travis, Hays, Comal, Bexar, Medina, Uvalde and Kinney with an area of approximately 10360 $km^2$ (Fig. 1 and 3)

It provides water for two million people for personal, irrigation and recreational uses (Ryder, 1996) and also supplies several springs, like Comal, which is the biggest spring in the state, and San Marcos and Barton Springs. The springs and the aquifer are also the habitat for unique species like the endangered Barton Springs salamander (*Eurycea sosorum*).

The aquifer is divided into three segments, the Northern Segment, which lies from the north of the Colorado River to the county of Bell, the Barton Springs Segment, occupying from the south of the Colorado River to it boundary with the San Antonio Segment, located between the cities of Kyle and Buda, although the data from dye tracer suggest that the boundary may shift until Onion Creek in high spring flow conditions (Smith et al., 2012) and the San Antonio segment that lies toward the southwest of the Edwards Aquifer (Fig.1).

The aquifer is composed of the Edwards Group and the Georgetown formation. The Edwards Group was deposited in shallow-marine, tidal, and supratidal environments and it is composed of two members, Person and Kainer (Rose, 1972) while the Georgetown Limestone was deposited in a more openly circulated shallow-marine environment (Smith et al., 2004).

It is confined by the Upper Cretaceous lithologies, the Taylor clay, Austin chalk, Eagle Ford shale, Buda Limestone and the Del Rio Clay.

The increase of the porosity and the development of the Edwards as an aquifer were determined by fracturing and faulting associated to the Balcones Fault and preferential dissolution through these fractures by meteoric water (Hovorka et al., 1995; Hovorka et al., 1998; Small et al., 1996). In addition, development of the aquifer is also thought to have been influenced by deep dissolution processes along the saline-fresh water interface known as hypogene speleogenesis at the eastern margin of the aquifer (Klimchouk, 2007; Schindel et al., 2008).

## 5.2. BARTON SPRINGS SEGMENT

The Barton Springs segment of the Edwards Aquifer is an important groundwater resource for Central Texas providing drinking water to more than 60000 people and whose iconic springs are a important recreational features for the Austin zone citizens and habitat for endangered species. Groundwater use is characterized as 80% public-supply, 13% industrial, and 7% irrigation. The various spring outlets at Barton Springs are the only known habitat for the endangered Barton Springs salamander (*Eurycea sosorum*). To protect users of the aquifer and the endangered species, pumping from the Barton Springs aquifer has been capped at 14.3 $hm^3/yr$ under non-drought conditions. During periods of drought, users must reduce pumping.

The Barton Springs zone occupies an area of 401.45 $km^2$ (155 $mi^2$), with about 80% of unconfined aquifer conditions, although the percentage fluctuates according to hydrologic conditions.

The primary discharge point is Barton Springs, located close to the confluence of the Barton Creek with the Colorado River. The main spring discharges an average flow of 180,000 $m^3$ per day. The three other springs are Eliza, Old Mill, and Upper Barton Spring, discharging an average 11,000 $m^3$ per day (USGS 08155500).

The Barton Springs aquifer is delimited to the north by the Colorado River and by the Edwards Group to the west (Fig. 1).

To the east is bounded by the interface fresh-brackish water known as the saline or bad-water zone. It is a hydrodynamically controlled boundary instead of a hydrologic barrier although local fault control was found (Hovorka et al. 1998, LBG-Guyton Associates, 2003).

The southern boundary between the Barton Springs aquifer and the San Antonio segment is located between Onion Creek and the Blanco River near the City of Kyle and it fluctuates depending on the hydrologic conditions (Hunt et al., 2005, Smith et al. 2012, LBG-Guyton Associates, 1994).

Faults in the Barton Springs zone trends from NE to SW and downthrown to the southeast. Due to the faults and its erosion and dissolution the aquifer has a thickness of about 140 m thru the east side until disappear along the west side of the recharge zone (Slade et al., 1986).

### 5.3. TRINITY GROUP AQUIFER

The Trinity Group is composed of units deposited in a variety of marine depositional environments brought about by cyclical sea transgressions and regressions. They are Cretaceous-age limestones, shales, marls, and sandstones. The major formations in the group are the Sycamore/Hosston, Sligo, Hammett, Cow Creek, and the Upper and Lower Glen Rose formations.

These formations make the up the Trinity Aquifer which is the primary source of water in the Texas Hill Country, to the west of the Edwards formations outcrop. Stratigraphically, the Trinity Aquifer underlies the Edwards Aquifer. However, along the Balcones Fault Zone (BFZ), normal faulting has juxtaposed the two aquifers laterally, with Trinity units exposed west of the Edwards outcrop in the study area (Fig. 3).

Within the units making up the Trinity group there are three distinct regional aquifers, the Lower, Middle and Upper Trinity aquifers. Due to its discontinuous nature the Upper Trinity is not heavily exploited. The Middle Trinity aquifer is the most utilized portion of the Trinity aquifer for domestic and agricultural uses due to the relatively high quality of the water from the lower Glen

Rose and Cow Creek Members. The lower Trinity aquifer traditionally was not exploited due to the high cost of drilling deep enough to reach it and the poor quality of water obtained from it.

Groundwater quality of the Trinity Aquifer is generally poorer and more variable than the Edwards Aquifer, containing higher total dissolved solids (TDS). Generally, water-supply wells were not drilled into the Trinity aquifer, although in the western part of the District, where the Edwards aquifer is thin, some water-supply wells penetrate to the Upper Trinity.

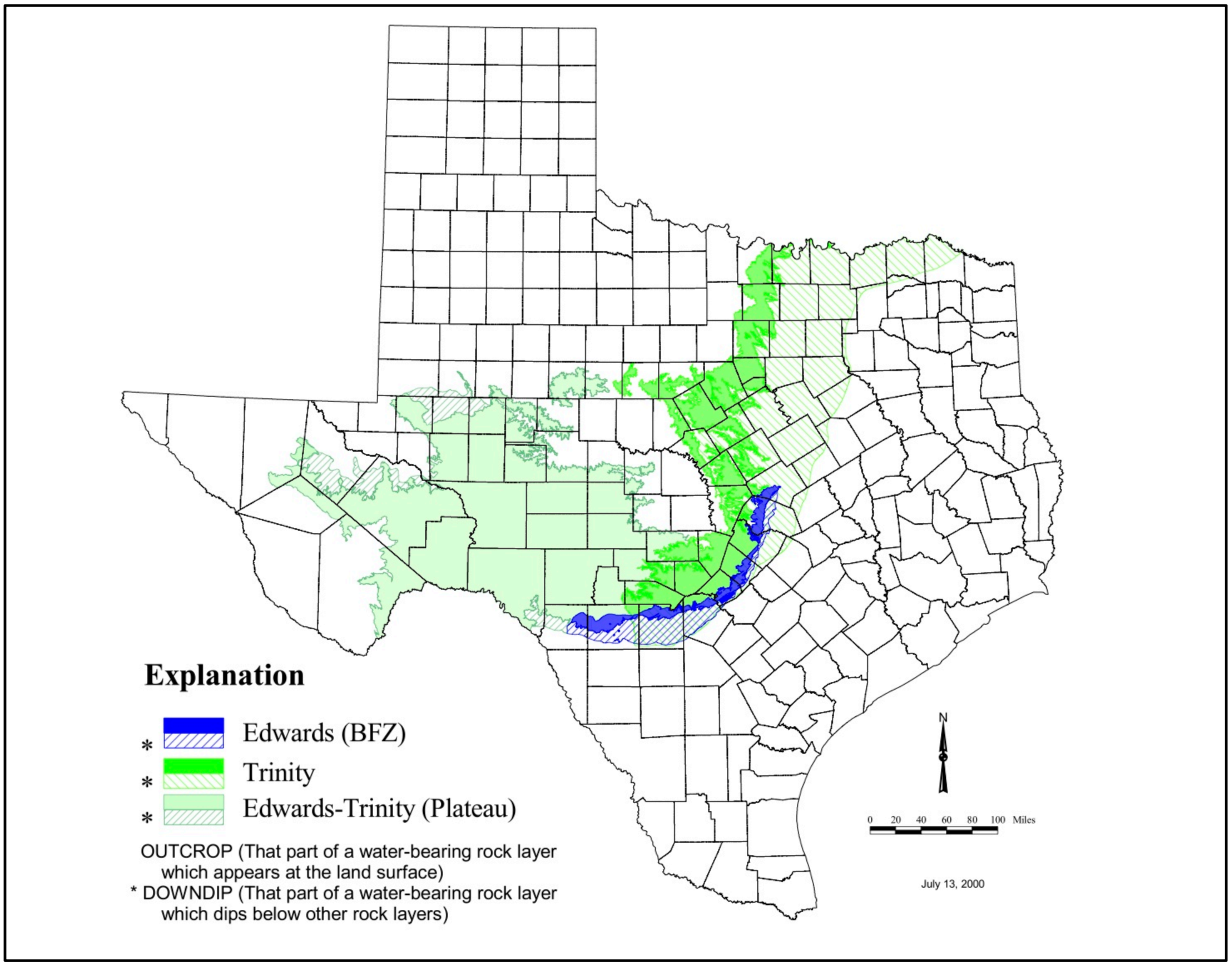


*Figure 3: Location of the Edwards (Balcones Fault Zone), the Trinity and the Edwards-Trinity Plateau aquifers in Central Texas. Courtesy of Brian Hunt (BSEACD).*

The Upper Trinity aquifer consists of the units making up the Upper Glen Rose member. The member consists primarily of interbedded, peloid packestone and grainstone limestone with fossiliferous sandy marl and an evaporitic interval. The Upper Glen Rose does not constitute a regional water source due to poor water quality characterized by high TDS values on the order of 3000 mg/l.

The Middle Trinity aquifer is made up by the Lower Glen Rose member, the Hensel formation, and the Cow Creek formation. It is separated from the underlying Lower Trinity aquifer by the confining Hammett formation, composed predominantly of shale. The Lower Glen Rose member has similar composition as the Upper Glen Rose, packestone and grainstone, limestones, interbedded with fossiliferous marly limestone, however the Lower Glen Rose member has large sections of rudist reef boundstone,capable of yielding very high quality water, which are used as regional sources. The Hensel formation consists predominantly of cemented calcareous sandstone.

The lowest formation in the Middle Trinity aquifer is the Cow Creek limestone which has very high hydraulic conductivity and produces water of relatively high quality.

The Lower Trinity aquifer is composed by the Sligo and Sycamore formations. These units are not part of this study.

### 5.4. GEOLOGICAL SETTING

The aquifer is cretaceous-age karst limestone composed of the Edwards Group and the Georgetown formation. The Edwards Group, composed of the Kainer and Person formations, was deposited in shallow-marine, tidal, and supratidal environments (Rose, 1972).

Matrix compositions vary from fossiliferous limestone, miliolid grainstone, wackestone, and mudstone classifications in the various members that make up the Person and Kainer formations (Small et al., 1996).

These varying lithologies were the basis for informal subdivisions of the Edwards created by Rose et al., 1972 and the hydrogeological subdivisions suggested by Maclay and Small, 1976 (Fig. 4). The Georgetown Limestone was deposited in a more openly circulated shallow-marine environment (Smith et al., 2004) and consists of marly limestone. The Edwards aquifer is confined by the Taylor clay, Austin chalk, Eagle Ford shale, Buda Limestone and the Del Rio Clay.

Where the aquifer is not truncated by faults, its thickness reaches up to 168 meters. The presence of these regional faults has important implications for groundwater flow direction and travel speed. The faulting has also allowed for dissolutionand the development of karst features and preferential flow paths (Smith et al., 2004). These karst features constitute extremely efficient means for recharge to occur in the aquifer.

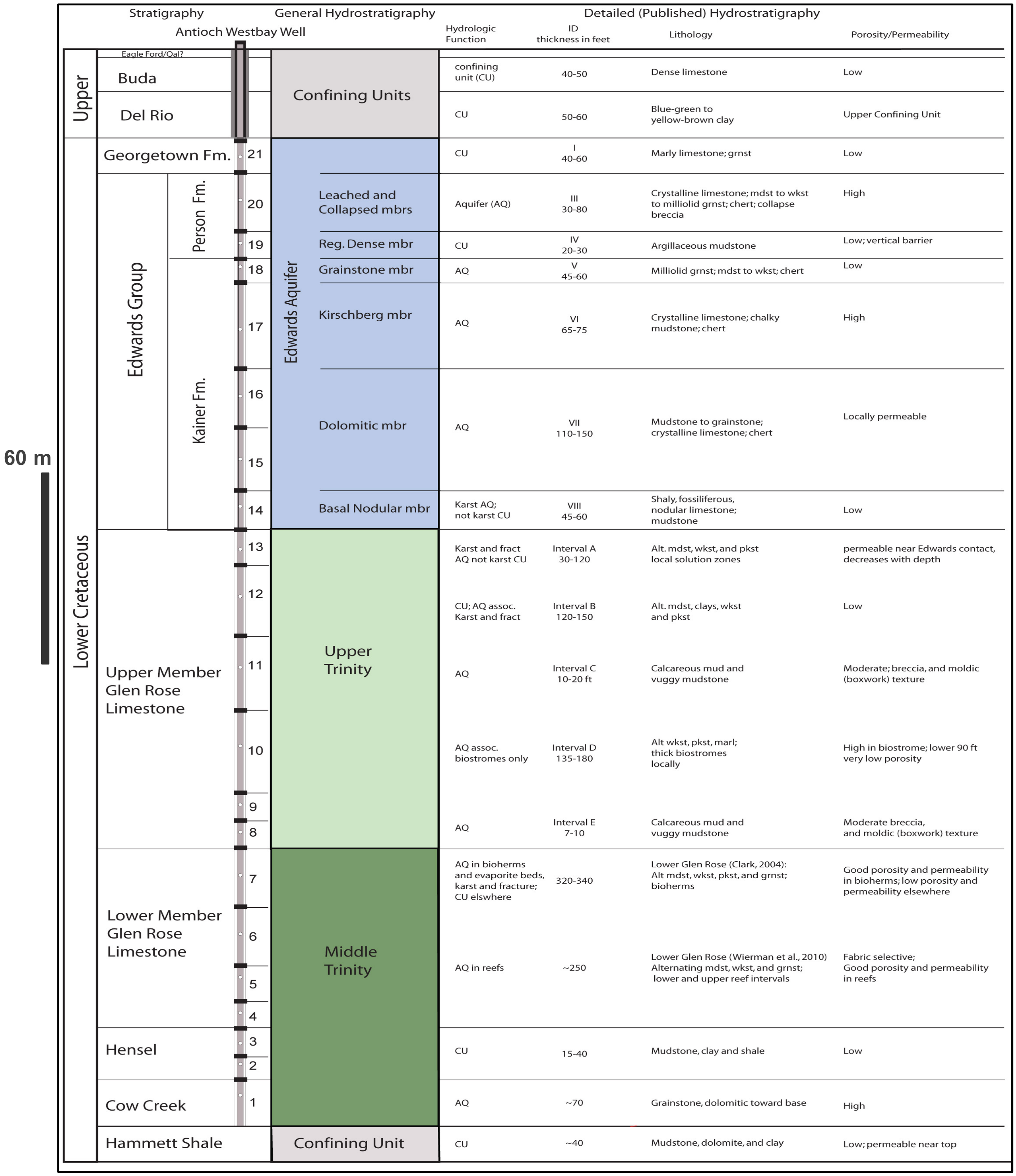


*Figure 4: Stratigraphic column with informal hydrostratigraphic information established by Small et al., 1996; Clark, 2004 and Wierman et al., 2010 for the study area and their correspondant zone in the multiport well.*

## 5.5. GROUNDWATER MOVEMMENT, RECHARGE AND DISCHARGE

Groundwater movement is generally downdip amongst the Edwards but in the San Antonio area, flow in the confined zone is toward the east and northeast through numerous northeast-ward trending faults (Fig. 5). Some of these faults may place bedrocks of different permeability ranges facing each other, creating hydrological barriers to the normal flow.

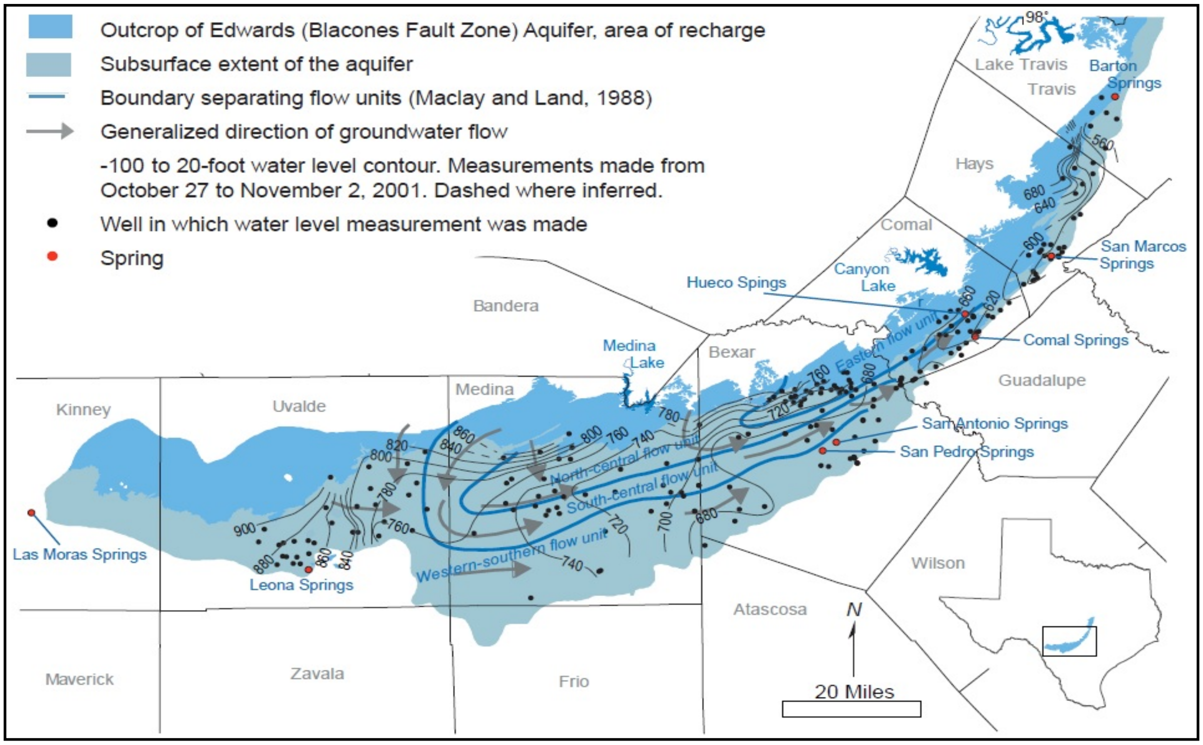


*Figure 4: Potentiometric surface and inferred groundwater flow in the Edwards Aquifer, Central Texas. Modified from Lindgren et al., 2004.*

The majority (~70–85%) of recharge to the Barton Springs segement is surface water from losing streams (Barton, Williamson, Slaughter, Bear, and Onion) that cross the recharge zone (Figures 6 and 7), where the Edwards formation outcrops at the surface and is heavily faulted and fractured (Slade et al., 1986; Barrett and Charbeneau, 1997; Hauwert, 2009).

Other sources of recharge include diffuse recharge through the soil zone and direct recharge into karst features. These have been estimated to account for 15–30% of total recharge (Hauwert, 2009). Surface water recharge along conduit flow routes has been deduced by correlations between groundwater specific conductance values and Barton Spring discharge and between groundwater specific conductance values and estimated stream-loss recharge to the BSE (Garner and Mahler, 2007). Dye traces have delineated major conduit flow routes that allow rapid (up to 12 km/day) transport of surface water to Barton Springs (Hauwert, 2009).

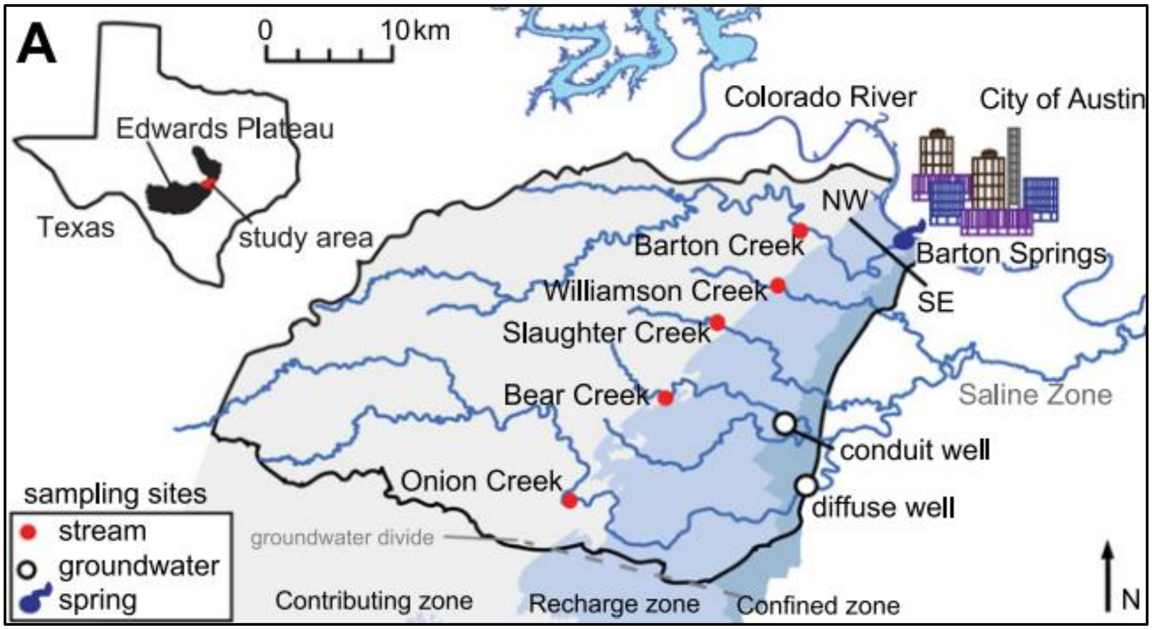


*Figure 5: Conceptual map of Barton Springs segment with it main surface losing streams. Modified from Wong, C. I. et al., 2012.*

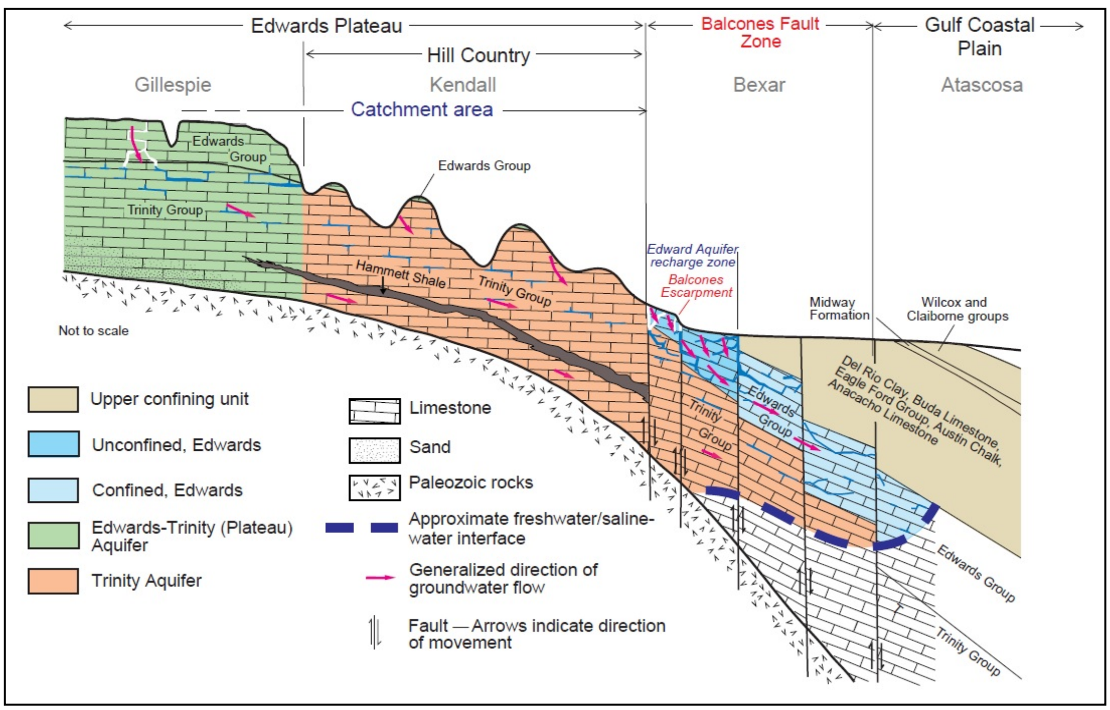


*Figure 6: Diagrammatic cross section showing hydrogeologic framework and groundwater flow through the Edwards Aquifer, Central Texas. Modified from Barker and Ardis, 1996 and Lingren et al., 2004*

The main discharge points of the Edwards Aquifer are Comal Springs located in Comal County and San Marcos Springs in Hays County. Barton Springs is the lowest point of discharge of the Edwards Aquifer and also the main discharge point of the Barton Spring segment.

Previous studies have demonstrated that Edwards aquifer ground- water compositions also can be affected by mixing with water from the adjacent and underlying Trinity aquifer (Senger and Kreitler, 1984) and from the saline zone (Oetting et al., 1996).

### 5.6. CLIMATE SETTING

Central Texas is characterized by a sub-humid to semi-arid climate with cool winters and hot summers (Larkin and Bomar 1983). During winter, the area is alternately influenced by a continental regime, with winds from the north and west, and by a modified maritime regime, with south and southeast winds from the Gulf of Mexico. Daytime temperatures in summer are hot, with highs over 33°C (90°F) more of the time (NOAA, Climate Narratives 2012).

It has an average annual rainfall of 860 mm and a range of 390 to 1370 mm (1856 to 2010; National Climate Data Center 2012). Groundwater in the Barton Springs segment of the Edwards is sensitive to changes in meteorological conditions, which often cycle between wet and dry intervals (Wong et al. 2012).

Precipitation is fairly evenly distributed throughout the year with heaviest amounts occurring in April-May and September. In a single year the region can receive up to 48 inches (1,200 mm) of rain, and flooding is common near rivers and in low-lying areas.

Its many rivers and hills shape the Texas Hill Country, at central Texas. The vegetation is both deciduous in the valleys and coniferous where there is greater elevation. The rivers and lakes in this area help to regulate the temperature. In addition there are large areas of forest where tends to inhibit the development of thunderstorms.

In addition, the El Niño–Southern Oscillation (ENSO) cycle has a huge impact on the weather in Texas. During the El Niño phase, the jet stream is located west-to-east across the southern portion of the United States. Therefore, winters in Texas are colder and receive more snowfall than normal. Texas is also less likely to get impacted by hurricanes due to the increased wind shear across the Atlantic. During the opposite phase, La Niña, the jet stream is much further north, therefore winter is milder and drier than normal. Hurricanes are more likely to impact Texas during La Niña due to decreased wind shear in the Atlantic. Droughts in Texas are much more likely during La Niña (NOAA, El Niño Portal)

# 6 RESULTS

## 6.1. DATA ANALYSIS

Discharge data can be used to determine wet against dry conditions using the covariation between discharge at Barton Springs and the Palmer Drought Severity Index (PDSI) (National Climate Data Center, 2012; Wong et al., 2012), in which when discharge is lower of 2 $m^3/s$ the system is under dry conditions. A discharge of 1 $m^3/s$ has a rate of -4 in the PDSI while a discharge of 3 $m^3/s$ has a rate of 4 (fig. 8).

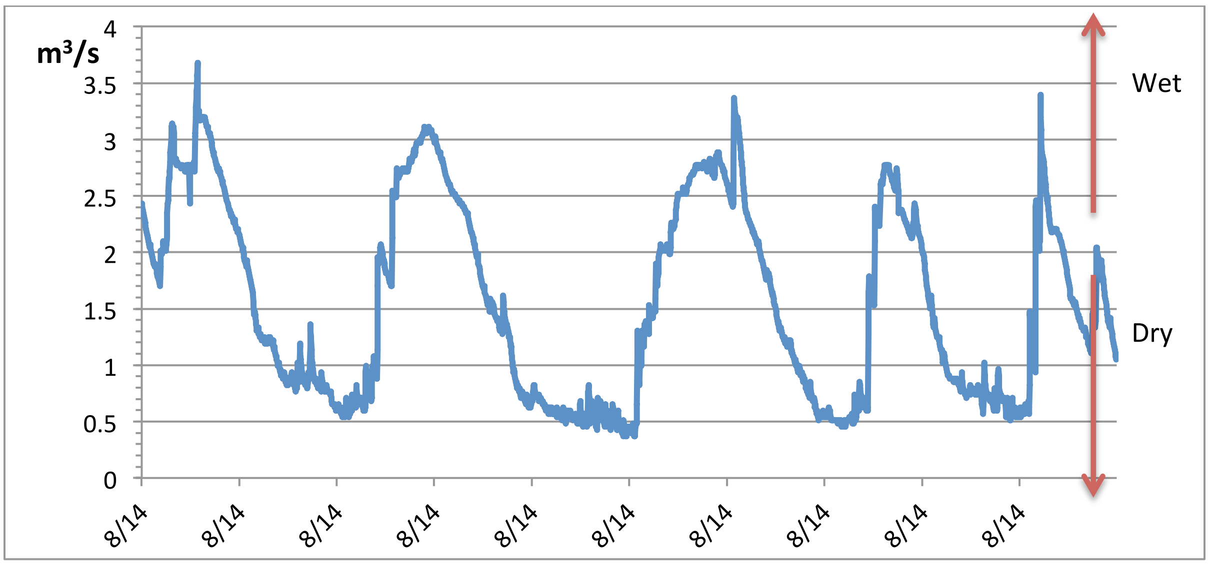


*Figure 8: monthly average discharge at Barton Springs from 2004 to 2014.*

## 6.2. MAJOR ION COMPOSITIONS

Surface water, spring and groundwater samples were Ca-$CHO_3$ (Fig. 9) type waters with pH values ranging from 6.3 to 8.0. Stream water composite samples generally had higher concentrations of $Ca^{2+}$, $Cl^-$, $Na^+$, and $SO_4^{2-}$ and low concentrations of $Mg^{2+}$ and $Sr^{2+}$ relative to groundwater.

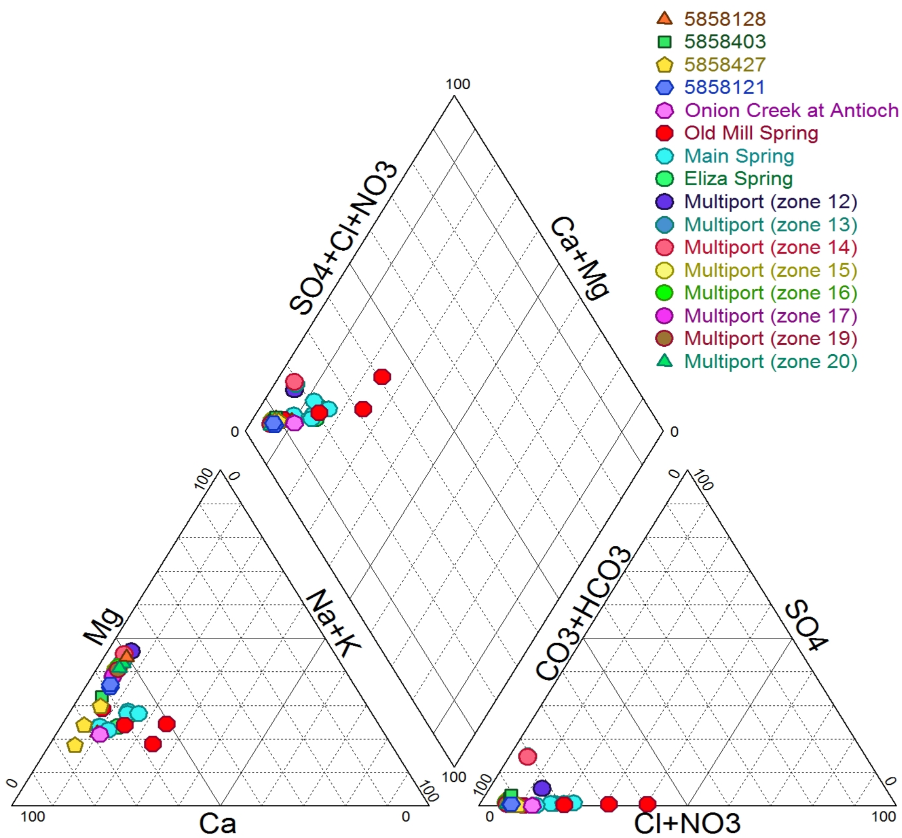


*Figure 9: Piper diagram to show the hydrochemical facies of the 16 samples taken during the summer of 2014.*

### 6.3. GROUNDWATER DYE TRACING

The dye used in this study was 4.5 kilograms of pyranine and it was injected on May the 30th at Antioch Cave in Onion Creek. In order to monitor the movement of the tracer, seven adsorbent activated charcoal receptors were placed in the 5858121 public-supply well at Leisurewoods and in the 5858128 domestic well in Old Black Colony (also referred as Ben Wright well), from the 30th of May to the 18th of June.

Furthermore, several grab samples were taken at the multiport well in Antioch, at the domestic wells in Old Black Colony numbers 5858427 and 5858128, and at Barton Springs (Eliza, Old Mill and Main springs) between the 30th of May and the 18th of June.

The grab samples as well as the charcoal receptors were collected every two days during the first week of project and then once a week.

Pyranine was found in one charcoal receptor placed in the public-supply well at Leisurewoods (5858121) between the 4th and the 6th of June and in the five receptors placed at the domestic well 5858121 between the 30th of May and the 9th of June (Fig. 10) (Appendix: Table 2).

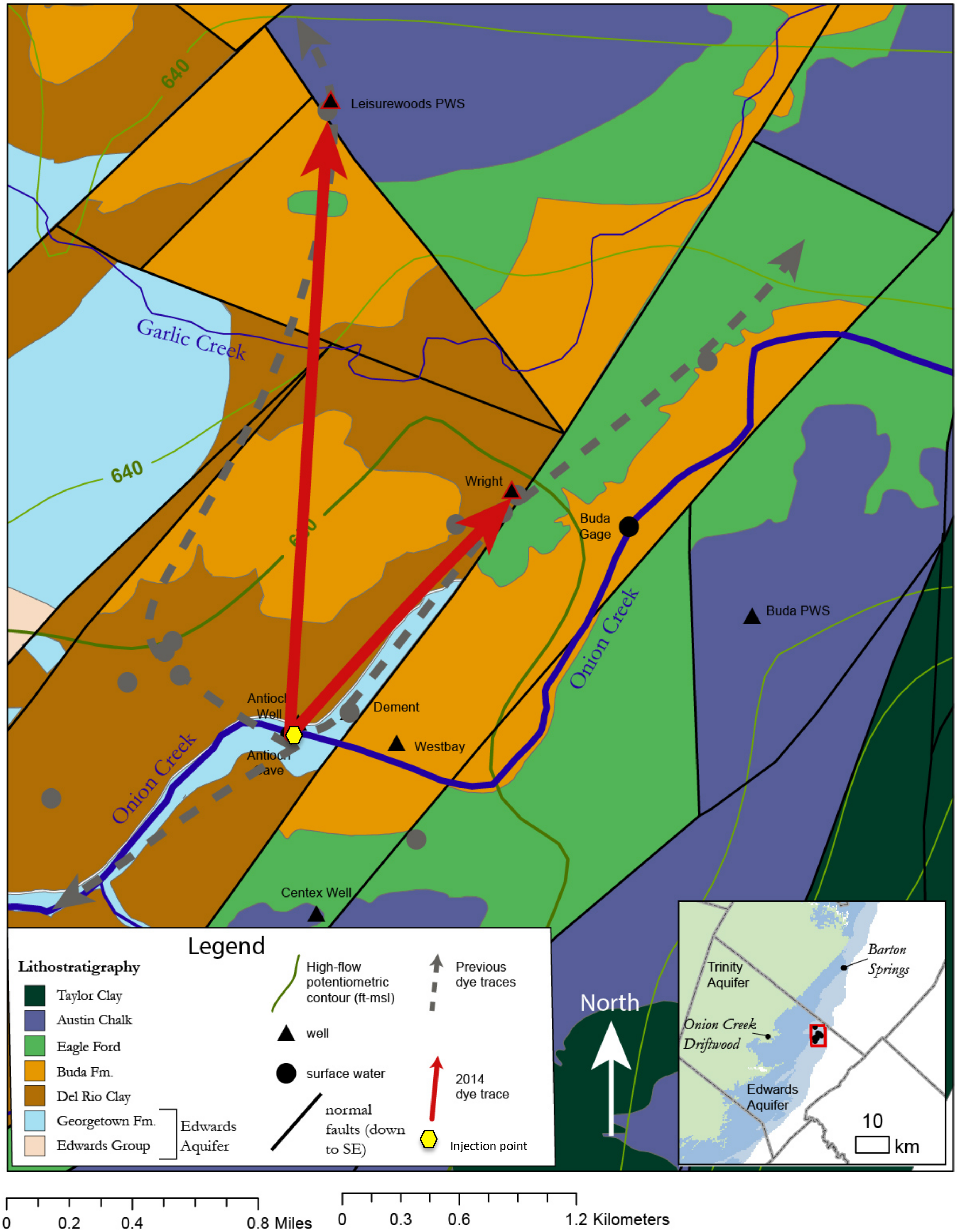


*Figure 10: Geological map of the study area with the dye traces from the 2014 study and previous ones.*

## 6.4. Sr ISOTOPES

A total of 19 grab samples for Sr isotopes analyses were taken from the zones 18 and 20 of the multiport well at Antioch, from Onion Creek at Antioch Cave and at the domestic wells in Old Black Colony numbers 5858427 and 5858128 between the 30th of May and the 18th of June.

Samples were analyzed at the UT including four standard measures to prove the stability of the equipment and the precision of the analysis.

$^{87}Sr/^{86}Sr$ values in groundwater ranged from 0.707650 and 0.708047, which are between values measured for the Edwards Group (0.7075–0.7080; Koepnick et al., 1985; Christian et al., 2011) and surface water from 0.707919 to 0.707936.

The results were considered together with previous data of Sr isotopes.

## 6.5. INTRINSIC FLUORESCENCE AND TOC

Grab samples for intrinsic fluorescence were taken in different days at various spots. Blanco River was sampled at Halifax Ranch on the 23rd and at Pleasant Valley Springs, Park Spring and Little Park Spring on the 24th of July. Cypress Creek at Jacobs Well was also sampled this day. This seven water grabs were analyzed on the 29th.

The 30th of July were taken three samples at Barton Springs, in the Old Mill, Eliza and Main Springs. The Glen Rose formation of the Trinity group and the lower, middle and upper Edward formation were sampled at Antioch with the multiport well (zones 12, 14, 17 and 20) as well as three leakage grabs from the soil and one from the domestic well in Old Black Colony number 5858128 were taken on the 31st of July and analyzed on the 1st of August.

San Marcos, Comal and Huaco, Springs samples were taken on the 6th of August and analyzed on the 13th.

Several problems with the equipment and the storage of samples happened, furthermore, the maximum precision of the analysis of total organic carbon was 0,5 mg/L and most of the samples present smaller quantities making almost impossible to compare TOC with Peak A of the samples.

Only two of the samples (from a total of 27) are exempt of any problem, Huaco and Comal A (figures 11 and 12). Both of the matrixes show a higher peak A (between 400-450 NM of emission and 230-250 NM of excitation) than peak C (between 400-450 NM of emission and 310-330 NM of excitation) (figures 12 and 13). They don't present a defined pattern, but both contain one or more of $T_1$, $T_2$ and B Peaks, with a lesser fluorescence intensity compared with A and C peaks. Even though the problems with the natural fluorescence analysis, some information can be taken.

Most of the organic compounds present in the water are associated with the fulvic acid-like substances (A and C peaks) produced as a consequence of the decomposition of organic matter in the soil. However, a small proportion of organic matter (T and B peaks) may be originated in situ as a result of microbiological activity. This second type of organic matter could be indicative of a certain degree of contamination associated with livestock farming activities that can be found in the area

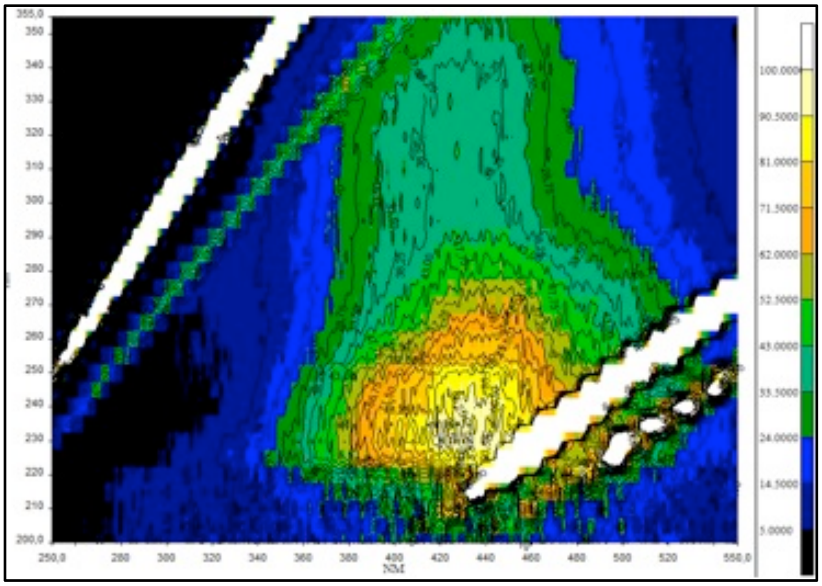

*Figure 11: Huaco Spring matrix of fluorescence. Courtesy of M. Mudarra*

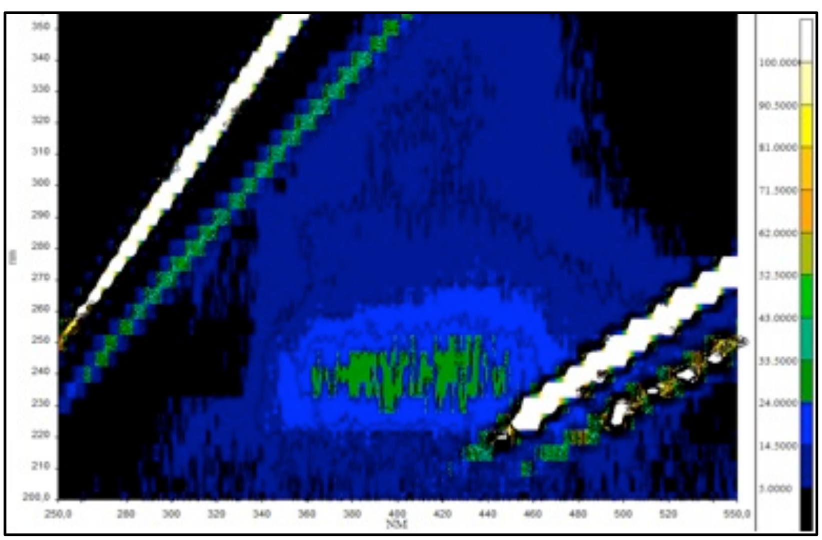

*Figure 12: Comal Spring matrix of fluorescence. Courtesy of M. Mudarra.*

# 7 DISSCUSSION AND INTERPRETATION

Water analyzed from springs and from the underground show a light mineralization and has a chemical composition in accordance with water drained from carbonate rocks. Alkalinity and the contents of $Ca^{2+}$ and $Mg^{2+}$ are derived from the dissolution of carbonate rocks, mainly limestone which constitutes the epikarst and unsaturated zone.

During the dry interval, the geochemistry of groundwater was consistent with mineral solution reactions with carbonate minerals. Concentrations of constituents measured in samples collected from wells varied little throughout the dry and wet intervals and were similar or slightly higher than the sample collected at the spring site (Appendix: Table 3).

Analysis of the data provided by artificial fluorescent tracers and natural organic tracers, allow to make an approximate determination of the hydrogeological functioning of the Barton Springs segment of the Edwards Aquifer

Each method carried out in the study provides different information of about the aquifer behavior:

Piranine found in the public water supply well at Leisurewoods and at the domestic well at Old Black Colony (wells 5858128 and 5858121) reflect the response of the aquifer to concentrated recharge in a specific point over the surface (Antioch Cave).

Natural tracers as $^{87}Sr/^{86}Sr$, TOC and intrinsic fluorescence show the global response of the entire recharge area and the reactions that occurs in the water when it goes thru the soil and the karst environment. Values of $^{87}Sr/^{86}Sr$ varied little throughout the transition from dry to wet conditions (Appendix: Table 3) and gradually increased during the wet interval in both surface and underground water. These values are consistent with extensive and relatively uniform interaction with Edwards aquifer bedrock. This supports the hypothesis that, during the dry interval, water was draining from the aquifer matrix to its conduits (Wong et al., 2012).

## 8 CONCLUSIONS

Combined use of natural and artificial tracers, with water compositions and the characteristics of the environment in a karst system under dry and wet conditions highlights the value and complementarity of these techniques in karst hydrogeology and enhances understanding of the hydrogeological functioning of the aquifer. Analysis of natural responses recorded at Barton Springs and the divergence of geochemical compositions in response to different meteorological conditions in groundwater provides a small idea of the dual nature of groundwater flow in this karst system. A better quantification of the contribution of surface water to spring discharge must be done to demonstrate that the majority of spring water is composed of surface water.

Dye tracer tests mapped (figure 6) provides more information about the groundwater flow in the vicinity of Antioch Cave. Flow-paths comes from southwest to northeast thru the faults proving again that dual nature of the karst system, with main conduits empowered by the faults in the area where the water flows fast and slow movement thru the diffuse zone.

Environmental tracers are helpful to investigate infiltration processes and to evaluate the response time of carbonate aquifers infiltration.

Finally, results presented permit to better understand the mineralization of the water during the infiltration and inside of the Barton Springs segment, its flow-paths in the Antioch Cave zone and the degradation processes of organic matter inside of the aquifer, as well as the hydrogeological functioning of Barton Spring.

Furthermore this outcome could be useful to improve the knowledge of the vulnerability to contamination in the area.

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# APPENDIX

- **TABLE 1: Water samples sites coordinates.**
- **TABLE 2: Results for charcoal and water samples analyzed for the presence of pyranine dye at Orzak Underground Laboratory.**
- **TABLE 3: Major ions and values of $^{87}Sr/^{86}Sr$ compared from dry to wet conditions, showing the difference in the concentration of any ion.**