

# **Tracer Test Work Plan Kinney and Uvalde Counties**

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## **1.0 INTRODUCTION**

Groundwater movement in the Edwards Aquifer has been characterized primarily by well data, potentiometric surface mapping, and computer modeling. While each of these techniques provides useful information, tracer testing has long been demonstrated as one of the most effective tools in quantifying groundwater movement in karst aquifers. Tracer testing provides empirical data on groundwater behavior that can be used to delineate drainage basins, identify groundwater flowpaths, and measure groundwater velocities, dilution, dispersion, and storage. The results are far more meaningful and accurate when compared to similar results produced by computer groundwater modeling.

The focus of this test is to investigate the sources of water for the principal springs in Kinney and Uvalde counties. Included in the study will be Pinto, Mud, and Las Moras springs in Kinney County and Leona Springs in Uvalde County.

This test will be conducted under the auspices of the Edwards Aquifer Authority (Authority) and its contractor, George Veni and Associates.

This work plan describes the procedures that the Authority typically implements for tracer tests in the Edwards Aquifer. It is based on the Authority's knowledge of the groundwater conditions and the objective of obtaining scientifically valid results. Each activity within the work plan is affected by the results of the preceding work. For example, the results of the initial tracer injections will form the basis for planning subsequent injections. Consequently, some activities described in this work plan may be changed or omitted during the course of the tracer test. The Authority will prepare a report at the conclusion of the test to describe the actual methodology and findings.

## **2.0 OBJECTIVES**

The report by Green and Others (2006) on groundwater resources in Uvalde and Kinney counties recommended a series of tracer tests to test the conclusions in the report. The objective of this tracer test study is to test the conclusions of the SWRI study by:

- Evaluating the groundwater flowpaths in the Kinney/Uvalde County area.
- Evaluating the hydraulic characteristics of the Edwards Aquifer.

## **3.0 SCOPE OF WORK**

This work plan outlines a tracer test methodology for evaluation of the time-of-travel, direction, and destination of groundwater movement in a portion of the Kinney and Uvalde portions of Edwards Aquifer recharge and artesian zones. This section outlines the tasks and strategy to be implemented. Appendix A provides the project quality assurance and quality control (QA/QC) sampling protocols, as prepared by the Authority. Appendix B is a glossary of terms for this work plan. Appendix C is a conversion index from the International System of Units used in this report, to English units. Appendix D is a legend of cave map symbols.

### 3.1 LOCATION OF THE TEST AREA

The test area is located in Kinney and Uvalde counties, Texas, as shown in Figure 1. The terrain of the study area is comprised of rolling karst uplands and valleys that drain surface water to the south. In general, groundwater flow will be traced from upgradient areas in the northern parts of the counties that include the Edwards Aquifer recharge zone to wells and springs in the artesian zone. This area is largely rangeland with some irrigated fields. The tracer tests will be conducted in an area that is bounded by Grass Valley on the northeast, recharge areas for Pinto Springs on the north, Mud Springs on the west, and Las Moras Springs on the south, and Leona Springs to the southeast.

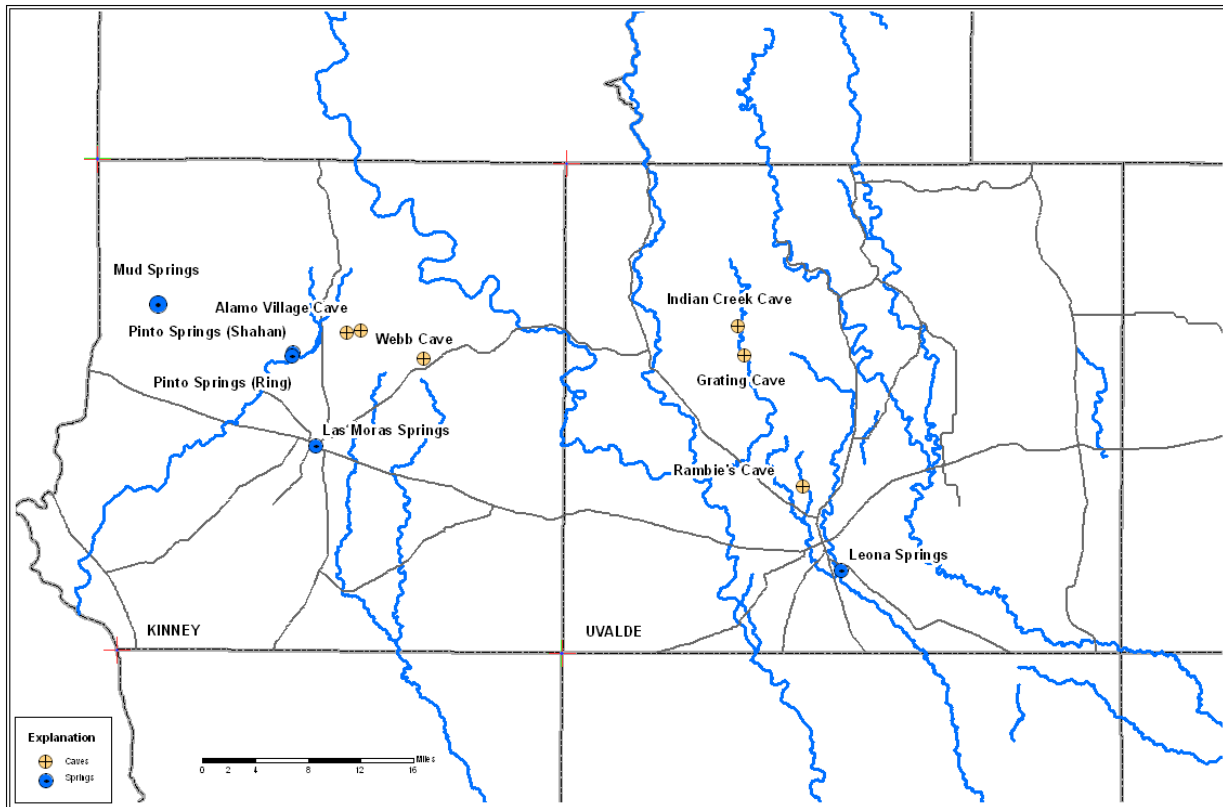


Figure 1. Location map of Kinney and Uvalde counties.

### 3.2 GEOLOGIC SETTING OF THE TEST AREA

The site is located in the recharge and confined zones of the Edwards Aquifer in Kinney and Uvalde counties. Figure 2 shows a geologic map of the area from the Geologic Atlas of Texas.

The geologic setting of the test area was described by the following paragraphs by Green and others (2006):

“Geologic units of Cretaceous to Holocene age underlie the study area. Of particular interest in this study are those units that have the greatest influence on groundwater recharge, discharge, and flow. Significant aquifers include the Cretaceous Edwards-Trinity, Trinity, Edwards, Austin Chalk, Buda Limestone, and the Quaternary Leona Formation. Localized groundwater is occasionally found in igneous intrusions and the Anacacho Formation. The Edwards Aquifer is directly overlain by the Del Rio Clay and underlain by the Glen Rose

Formation, both of which act as confining layers to the Edwards Aquifer in the study area. The stratigraphic column is illustrated in Figure [3] (Hovorka et al., 1996). The Edwards Aquifer or Group is represented by two regionally distinct facies in the study area. To the west, in the Maverick Basin, it consists of (from youngest to oldest) the Salmon Peak, McKnight, and West Nueces Formations. To the east, as part of the Devil’s River Trend, the Edwards Aquifer comprises a single formation, the Devil’s River Formation (Rose, 1972; Smith et al., 2000). The Trinity Aquifer consists of three parts: (i) the upper part consists of the Upper Member of the Glen Rose Formation, (ii) the middle part consists of the Lower Member of the Glen Rose Formation and the Cow Creek Limestone, which are separated by the Hensell Sand or Bexar Shale, and (iii) the lower part consists of the Hosston Formation and overlying Sligo Formation, and is separated from the Cow Creek Limestone by the intervening Hammett Shale (Mace et al., 2000).”

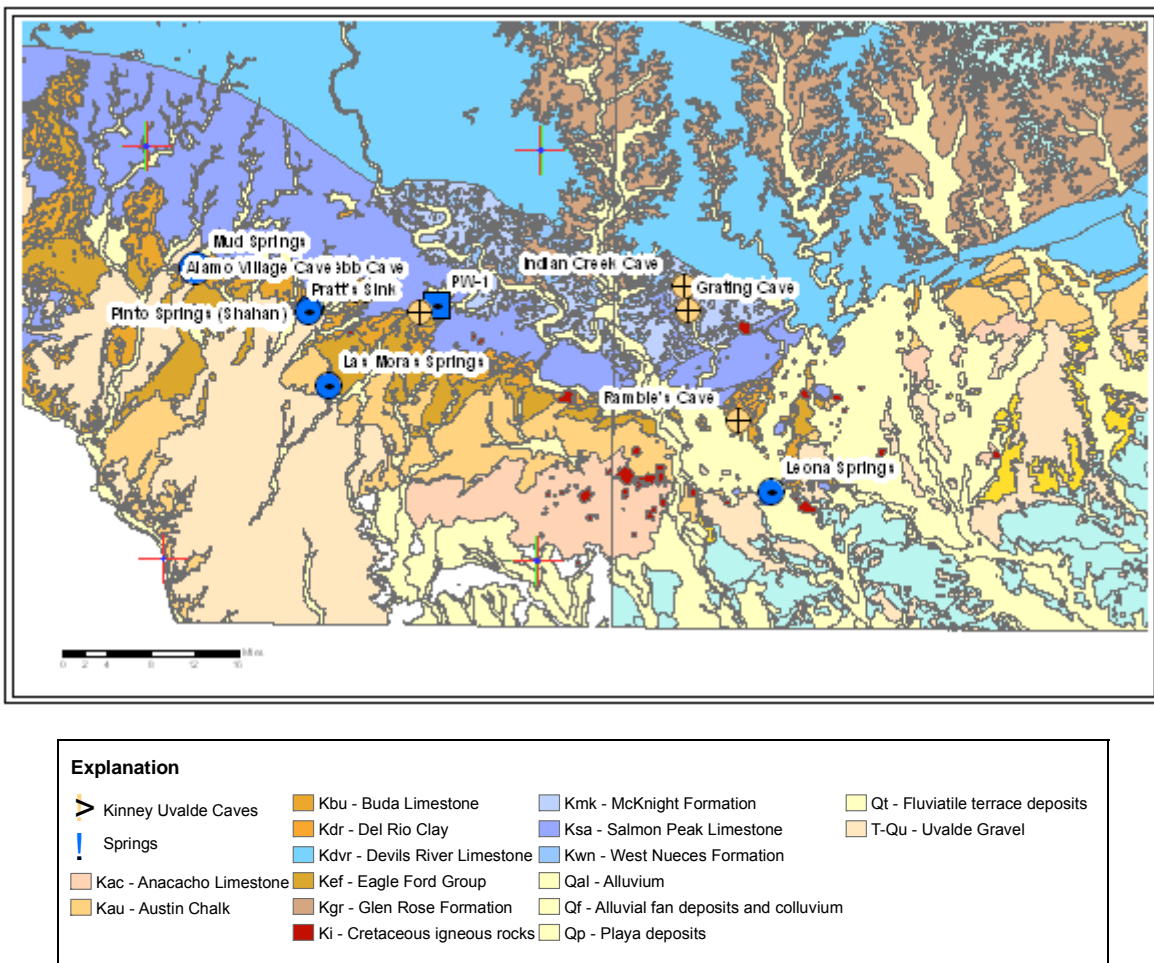


Figure 2. Geologic map of the test area.

“The Edwards and Trinity aquifers are complex karst limestone aquifer systems that have permeability architectures that include a combination of host rock permeability, fractures and fault zones, and dissolution features (Maclay et al., 1981; Maclay and Small, 1983; Edwards Aquifer Authority, 2005). Although the strata that make up the Edwards Aquifer are

younger and stratigraphically overlie the strata that comprise the Trinity Aquifer (Figure 5.2.1), displacement along faults of the Balcones fault system has placed the Edwards Aquifer laterally against (side-by-side with) the Trinity Aquifer in parts of the study area. The location and amount of fault juxtaposition are sensitive to the location, geometry, and displacement on faults (Ferrill et al., 2005). Along faults that define the structural interface between the Edwards and Trinity Aquifers, caves and some fault zones provide conduits for groundwater flow and potential pathways for interaquifer communication. The occurrence of and degree to which interaquifer communication occurs is not well defined, although various hydrologic and hydrochemical studies have attempted to place constraints on the amount of water that the Trinity Aquifer contributes to the Edwards Aquifer (e.g., LBG-Guyton Associates, 1995).”

The complete report by Green et al (2006) is available at the Authority web site ([www.edwardsaquifer.org](http://www.edwardsaquifer.org)) under publications/reports and plans/aquifer research and optimization program plans/Flowpath and Modeling Studies/Evaluation of the Edwards Aquifer in Kinney and Uvalde counties.

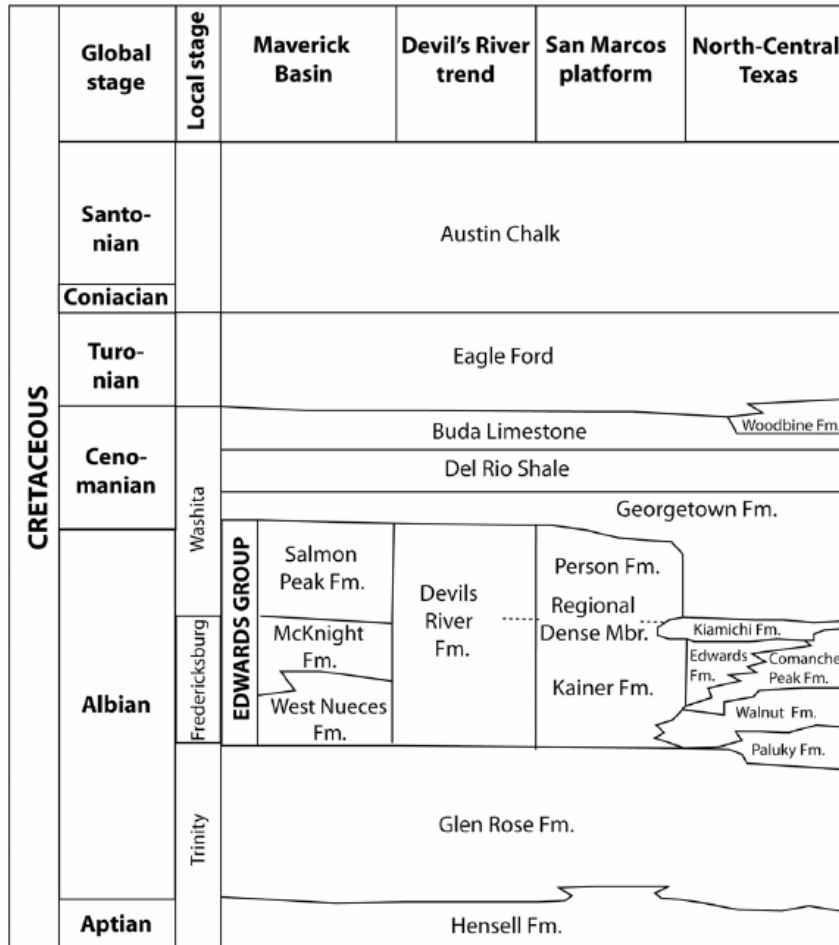


Figure 3. Cretaceous Stratigraphy for Kinney and Uvalde counties (from Hovorka et al, 1996).



### 3.2.1 Groundwater Conditions in the Test Area

The Edwards Aquifer is the principal water-bearing formation in the test area, but there are other water-bearing formations, including the Trinity Aquifer, Buda Limestone, Austin Chalk, and the Leona Formation, that may be involved in the tracer tests. Groundwater generally flows from north to south in all of these aquifers.

Green and others (2006) concluded that a transition zone between the Devil’s River Trend on the east and the Maverick Basin on the west limits groundwater flow from Kinney County eastward to Uvalde County. The transition zone consists of a depositional facies change in the Edwards Group that is characterized by low-yielding sediments. Figure 4 shows the location of the transition zone beneath the Kinney-Uvalde county line. It separates the Uvalde pool established by the Authority’s regulations from groundwater beneath Kinney County, named the Kinney County pool by Green and others (2006).

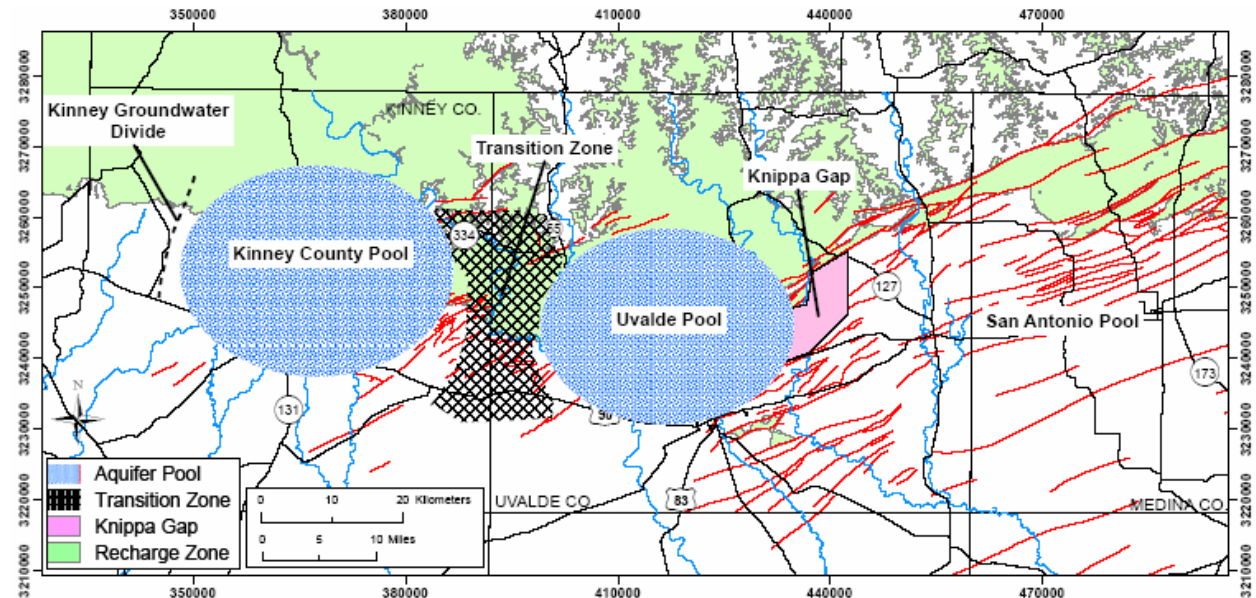


Figure 4. Location of the transition zone between Uvalde and Kinney counties (Green and others, 2006).

Based on this interpretation, recharge from the upper reaches of the West Nueces River basin goes to the Kinney County pool, and recharge from the lower reaches goes to the Uvalde pool. Instead of a groundwater divide, the low permeability limestone of the Edwards Aquifer in the bed of the West Nueces River in the transition zone limits recharge to the Kinney County pool. Water upstream of the transition zone infiltrates into the Kinney County pool, and water downstream of the transition zone infiltrates into the Uvalde pool. The recharge boundary between the two pools may be located with borings, tracer tests, aquifer tests, water level measurements, and other techniques, which is beyond the scope of this investigation.

Groundwater flows from north to south in the test area. The potentiometric contours in Figure 5 from Green and others (2006) is based on the most comprehensive set of groundwater levels available. They indicate that the groundwater surface generally parallels the topographic contours.

In the Edwards Aquifer, groundwater conditions may vary considerably between wells. Groundwater flows in discrete flowpaths, and the water elevation may represent the level only in a particular flowpath. Groundwater will carry tracers southward, but the exact route is not reliably predicted by regional groundwater elevation contour lines.

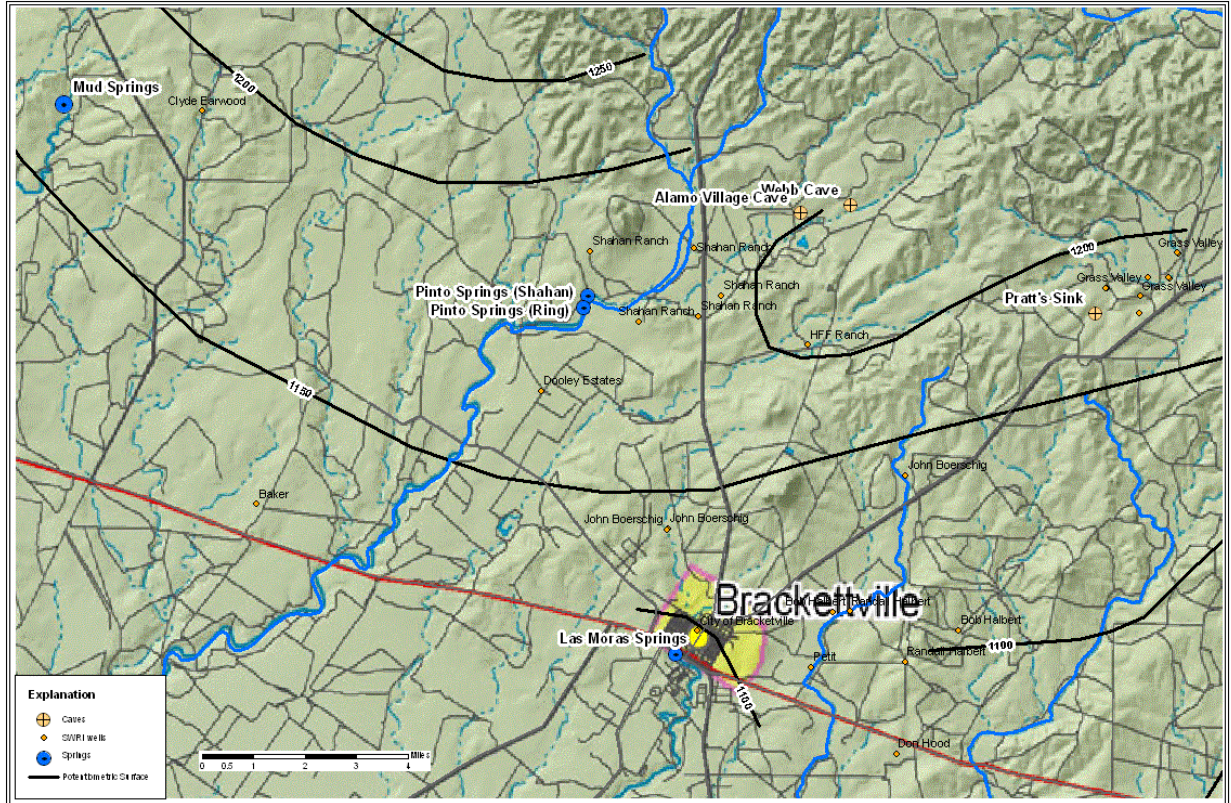


Figure 5. Location of potential tracer test monitoring and dye injection locations.

Groundwater elevations are approximately 200 feet higher in Kinney County compared to Uvalde County due to the low transmissivity of the transition zone. Although a relatively steep gradient exists across the transition zone, Green and others (2006) concluded that little groundwater flows through this area because of the lack of karstification and the low permeability of the sediments.

Groundwater discharge points in the test area consist of Mud Springs, Pinto Springs, and Las Moras Springs. Figures 6, 7, and 8 show discharge hydrographs for Mud Springs, Pinto Springs, and Las Moras Springs, respectively, from measurements made by the International Boundary Waters Commission (IBWC). The hydrographs indicate that discharge from the springs is highly variable. The steep curves of the hydrographs suggest that there is limited storage in the recharge areas, and they drain relatively quickly over a period of several months.

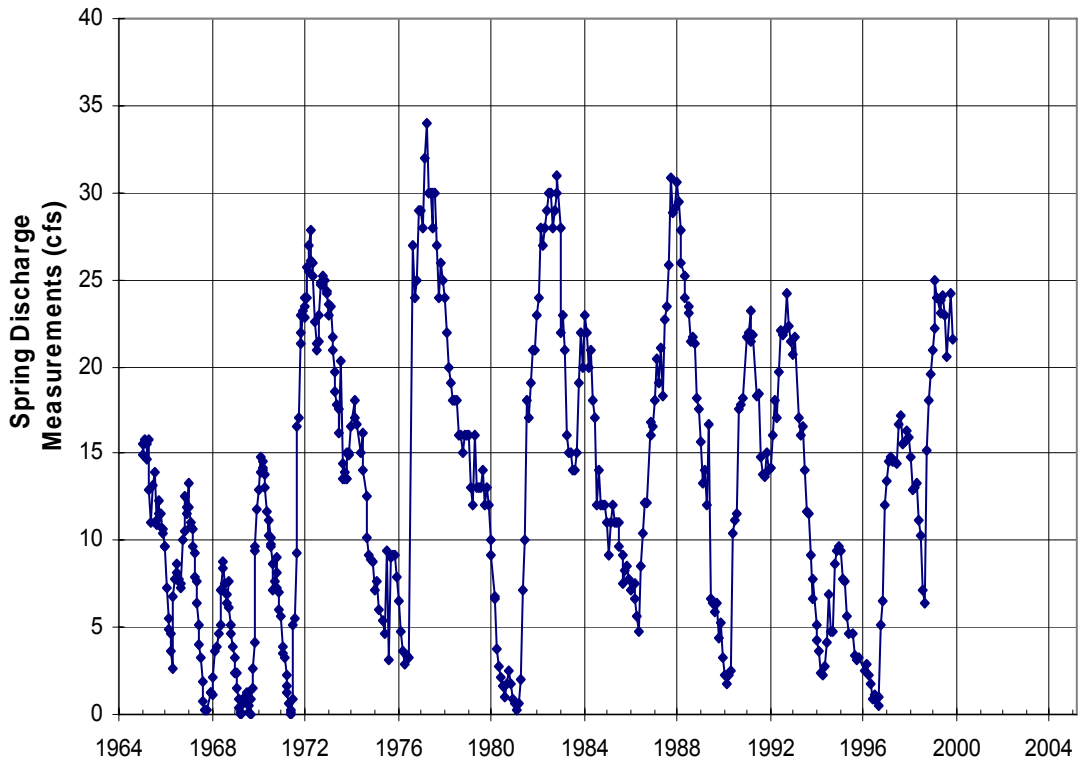


Figure 6. Mud Springs Discharge Measured by the IBWC.

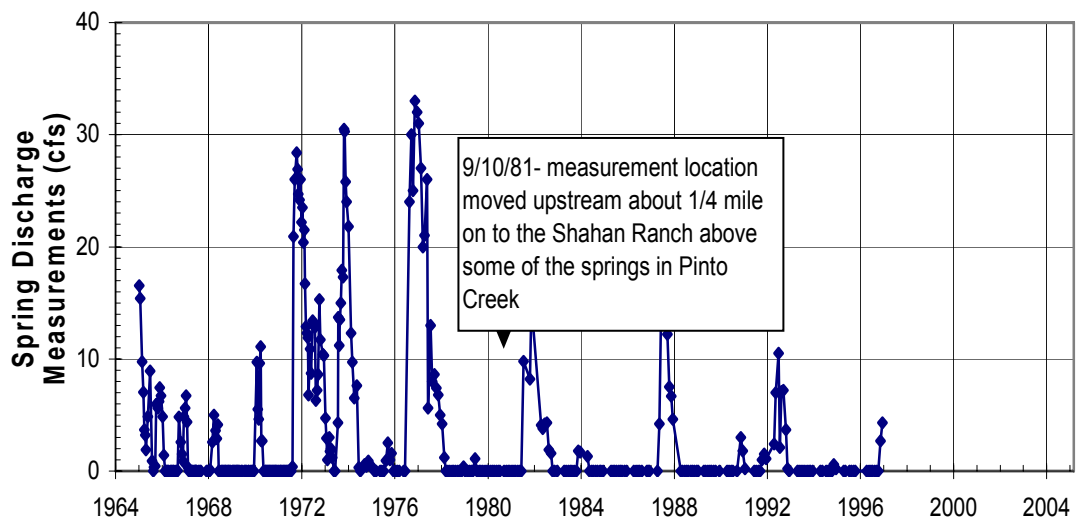


Figure 7. Pinto Springs Discharge Measured by the IBWC.

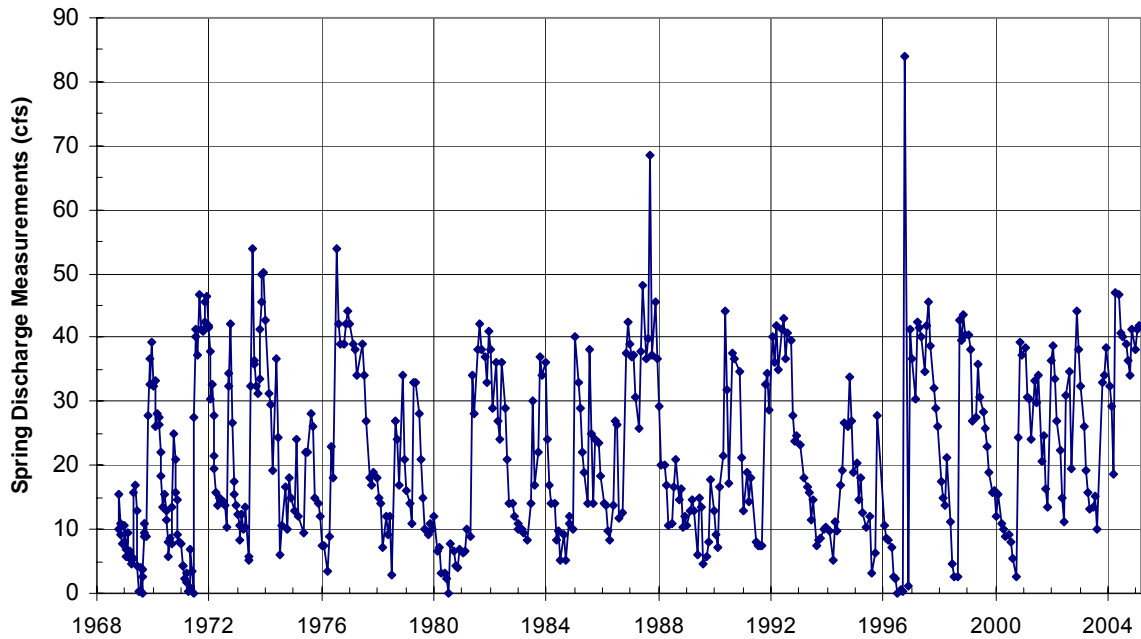


Figure 8. Las Moras Springs Discharge Measured by the IBWC.

Figure 9 shows the response of Las Moras Springs and the Tularosa well (7038902) to storm events in March and April 2004. Both the well and the spring responded quickly to the precipitation, which is typical of karst aquifers.

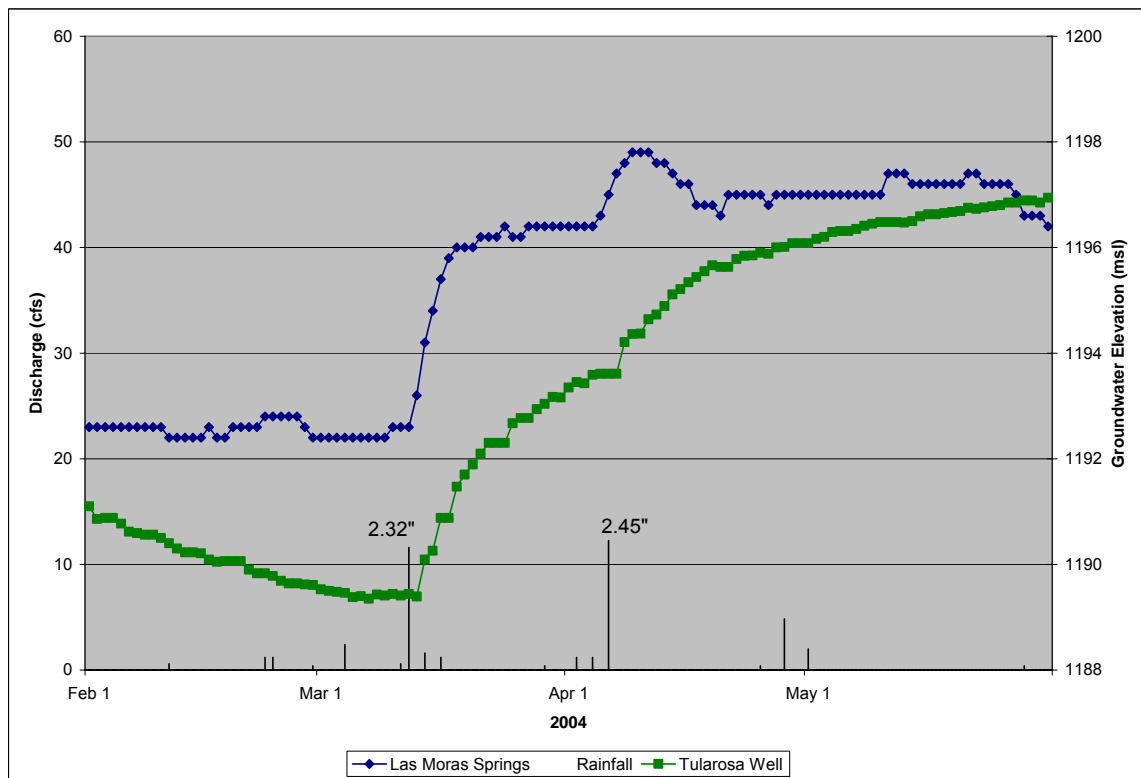


Figure 9. Response to Storm Events in 2004 measured by the Authority.



### **3.3 DESIGN OF THE TRACER TEST IN KINNEY COUNTY**

The objective of the tracer testing project is to test the conclusions of Green and others (2006) by evaluating the groundwater flowpaths in the Kinney County area and evaluate the hydraulic characteristics of the Edwards Aquifer.

#### **3.3.1 Potential Injection and Monitoring Points in Kinney County**

Green and others (2006) concluded that groundwater flows from recharge areas in the northern part of the county to Las Moras, Pinto, Mud springs, and other discharge points. Consequently, the tracer test will be designed to inject dye into one or more groundwater flowpaths between the recharge area and the springs. The Authority will monitor as many wells as possible between the injection points and the springs to determine the route that the dye follows. However, wells on other flowpaths also will be monitored because it is not unusual for groundwater in the Edwards Aquifer to flow in unexpected directions.

Caves are typically the best injection points because they are probably integrated with the local and regional groundwater systems. They were formed by infiltrating water and are probably hydraulically connected to the present groundwater system. Three caves have been identified in the suspected recharge area for the springs: Webb Cave, Pratt's Sink, and Alamo Village Cave as shown on Figure 5. Webb Cave is in a deep sinkhole and contains approximately 2,000 feet of passages. It is a former bat cave, and an ephemeral stream flows through part of it. Pratt's Sink is a 12-foot deep elongate sinkhole measuring about 200 feet long and 75 feet wide. There is a low room off the northeast side of the sinkhole that collects water. Alamo Village Cave can be traversed about 60 feet downward to a perched water table. The cave receives floodwater from a small channel and is clean-washed, which suggests that it drains water rapidly into the aquifer.

Dye may also be injected into either production or monitoring wells in the Grass Valley area, which is located on FM 334 about 12 miles northeast of Brackettville.

Monitoring points will consist of the springs, and private and public wells along the anticipated flowpaths and other potential travel directions. Table 1 lists private wells downgradient of the injection sites that were identified by Green and others (2006). Several of these well owners have been approached to participate in the tracer test. As described in Section 3.5, selected wells will be monitored with automatic water samplers, grab sample, charcoal detectors, or a combination of these techniques. Monitoring wells will be selected south and southwest of the injection points. With the steep hydraulic gradient across the transition zone, a small amount of groundwater may flow southeastward from the injection points. Consequently, wells in the transition zone and at the City of Uvalde also will be monitored.

As the dye travels from the injection points to the monitoring points, it will be influenced by many factors, including depth to groundwater, groundwater flow velocities, pumping, and the hydraulic gradient. One or more of the dyes may have multiple arrival times at any of the monitoring points due to these influences. The initial injections will consist of small volumes of dye to avoid either saturating the aquifer which would limit the ability to use the dye again during the project or causing a visible detection of dye in a public water supply well or spring. Subsequent injections will involve additional volumes of dye if there is no visible detection in public water supplies or springs.

Tracers will be flushed into the aquifer by pouring water into the cave or well following the injections. Water will be transported to the injection sites with tank trucks and either stored until the injection or pumped into the injection point immediately. The amount of water that is used to flush dyes into the groundwater system is usually limited by the logistics of bringing water to the injection site. The Authority will attempt to flush the dyes with 5,000 to 10,000 gallons of water. At Webb Cave and Alamo Village Cave, the injection point will be flushed with water prior to introducing dye to reduce the absorption of dye on the unsaturated surfaces of the sediments. If flowing water is present in any of the injection sinkholes or caves, additional flush water will not be added to the site.

### **3.4 DESIGN OF THE TRACER TEST IN UVALDE COUNTY**

The objective of the tracer testing project is to test the conclusions of Green and others (2006) by evaluating the groundwater flowpaths in the Uvalde County area and evaluate the hydraulic characteristics of the Edwards Aquifer.

#### **3.4.1 Potential Injection and Monitoring Points in Uvalde County**

Groundwater generally flows from the northern part of the county to the south and east and issues from several orifices in the Leona River channel. Most of the water conveyed by the Leona River is through the alluvium in the channel, and it appears typically as seeps at a few locations.

There are several caves in Uvalde County that may be used as injection points: Rambie's Cave, Indian Creek Cave, and Grating Cave.

### **3.5 TRACER TEST PROTOCOL**

#### **3.5.1 Selection of tracing agents**

Five fluorescent dyes have been selected for use in this study (Table 2) on the basis of non-toxicity, availability, analytical detectability, low cost, and ease of use. The tracers that are the most easily detected are assigned to the injection sites furthest from the downgradient monitoring points. This is especially important in keeping concentrations low to minimize the risk of a tracer's visual appearance at nearby wells, while maintaining sufficient concentration for detection upon analysis.

All of these dyes have been previously used as groundwater tracers at other sites within the Edwards Aquifer or in other karst settings and their properties have been extensively documented in the karst-related literature. None of the dyes contain toxic ingredients. Material Safety Data Sheets are available upon request.

**Table 1 – Potential Tracer Test Dyes**

<b>Color Index Generic Name</b>	<b>Food and Drug Administration Name</b>	<b>Common Name</b>
Acid Yellow 73	D&C Yellow No. 8	uranine (sodium fluorescein)
Acid Red 87	D&C Red No. 22	eosine (eosin)
Acid Red 92	D&C Red No. 28	phloxine B
Acid Red 52	None	sulforhodamine B
C.I. Acid Red 388	None	rhodamine WT

The quantities of dyes to be used in this study will be based on the experience gained from tracer testing in similar situations. Factors evaluated in determining these quantities include: detection limit of the analytical method to be used for dye analysis, a desire not to induce visible coloration to spring waters, wells, or streams, and a desire not to use excessive amounts of dye which may persist in the aquifer. All of the dyes used are non-toxic (non-carcinogenic, non-mutagenic, non-tumorogenic, non-poisonous, etc.), in the concentrations to which they will be diluted and discharged at springs and wells (Smart, 1984) and pose no threat to the quality of private or public water supplies.

The mass of dye needed and the peak recovery concentrations for individual traces will be calculated using the relationships derived from 185 tracer tests in carbonate aquifers (Worthington and Smart, 2003). The following empirical regression equations were calculated from the data by Worthington.

$$m = 0.73 (tQc)^{0.97} \quad (1)$$

$$m = 19 (LQc)^{0.95} \quad (2)$$

where:

m is the mass of dye injected in grams,

t is the time elapsed between injection and peak recovery in seconds,

Q is the output discharge in m<sup>3</sup>/s,

c is the peak recovery dye concentration in g/m<sup>3</sup>, and

L is the distance in meters between injection and recovery points.

The volume of dye to be injected will be determined at the time of injection based on calculations derived from the Worthington equations.

### **3.5.2 Tracer Injection**

Prior to the injection of tracer at each site, the working surfaces where dye may be accidentally released will be covered with sheets of heavy-gauge, 6-mil thick plastic. All equipment needed for the injection will be placed on those sheets before the tracer is released. Personnel working in those areas will wear hooded disposable coveralls, disposable plastic gloves, and disposable shoe covers. Seams between the garments will be taped shut. The personnel will not leave the area of the plastic sheeting and any needed supplies, if any, will be brought and passed to them at the edge of the sheeting. When the injection is complete, any soiled or dyed supplies or materials will be carefully

placed into plastic trash bags to avoid soiling the bags' exteriors and then sealed in additional bags for disposal. Personnel will then remove the disposable garments by folding the outsides inward and stepping out of the sheeted area with each foot as each shoe cover is removed. The garments will be bagged in the same manner as the soiled supplies. Once all personnel are outside of the sheeting, the sheets will be folded inward and sealed in plastic trash bags for disposal. A clean set of clothing will be available if dye is found on clothes worn under the coveralls, and the soiled clothes will be carefully placed and sealed in a plastic bag. If dye is found or potentially occurs on equipment or a person's skin, the affected area will be washed in a bleach solution at least 20 m from the injection site. Bleach will neutralize the dye. Plastic bags with tracer on their exteriors will be bagged in successive bags until all visible or suspected tracers are contained.

### 3.5.3 Tracer Recovery

Monitoring for tracers at the wells will use three complementary methods to maximize information and minimize cost. The methods are outlined in Table 2. Prior to tracer injection, at least one of these methods will have been used at each monitoring site to measure the background fluorescence.

**Table 2 – Description of Three Sampling Methods**

<b>Sample Method</b>	<b>Goal</b>	<b>Sample Interval</b>	<b>Analytical Method</b>
Autosampler	Collect water samples at timed intervals from selected wells or springs	4 to 8 hours initially, increasing the interval as the test progresses	Water samples will be analyzed with luminescence spectrometer
Water samples collected by hand	Grab samples from sites to verify results of other sampling methods and/or should the other methods not function during a given sampling period.	During each collection of automatic water samplers and charcoal detectors	Water samples will be analyzed with luminescence spectrometer
Charcoal detectors	Determine presence of tracer in each spring or well	4 to 8 days	Charcoal will be eluted and samples will be analyzed with a luminescence spectrometer

The strategy is to make periodic visits to the wells to collect water samples, change automatic water sampler bottles, change charcoal detectors, and conduct any field maintenance on the sites as needed. The interval of the visits will vary according to the characteristics of each site and the expected time of tracer arrival. In general, the automatic samplers will collect samples every 4 to 8 hours at the beginning of the test and sample intervals may be lengthened if the test extends more than two weeks. The charcoal detectors will be changed every four to eight days, with a fresh detector. It is likely that groundwater velocities will be about 600 m/day or greater after the dye reaches the saturated zone, especially with the influence of pumping. Consequently, the sampling intervals will be short to obtain sufficient samples for a well-defined breakthrough curve.

In the event that there are visible concentrations of dye in a public or private water supply, well



owners are instructed to call the Edwards Aquifer Authority at 210-222-2204. Additionally, if it is after business hours, individuals are instructed to call George Veni and Associates (GVA) at one of the following numbers until reaching someone: Dr. George Veni at 210.558.4403 (24-hour office number) or 210.863.5919 (mobile phone); Mr. Lew Schnitz at 210.698.2077 (24-hour office number) or 210.416.7248 (mobile phone); or Ms. Bev Shade at 512.826.5027 (mobile phone). That person will notify other GVA staff and the Authority, then immediately proceed to the site for sampling and analysis of water. The GVA call list is arranged in order of personnel closest to the study site and most likely to provide the fastest response in the field. All of the above telephone numbers will be accessible for calls 24 hours a day and seven days a week.

### **3.5.4 Duration of monitoring**

The Authority will continue to collect samples from the springs and monitoring wells until the staff is satisfied that the dyes have traveled out of the groundwater system. If the injection points and the springs are connected by highly transmissive flowpaths, then the dyes may appear in a matter of hours or days. However, relatively low groundwater levels due to the current drought and the length of the actual flowpath will slow the dye velocity significantly. If the test proceeds as planned, the dye concentrations at one or more monitoring points will be detectable. Uranine is the most detectable of the five dyes with an instrument detection limit of about 12 parts per trillion (ppt) when using a luminescence spectrometer.

The volume of dye discharged from the springs will be estimated during the test to calculate what percent of the original volume has passed through the system. However, it is not unusual to recover only a small percentage of the volume of dye that was injected.

### **3.5.5 Monitoring tracer concentrations with automatic water samplers**

Automatic water samplers will be deployed at Las Moras and Pinto springs and at the selected monitoring wells shown in Figure 5. The purposes for each site vary. Most of the automatic water samplers are placed where tracer is believed likely to discharge in significant (but non-visible) concentrations. Accurately measuring the tracer flowing from or past a site will be important to calculating total tracer recovery, which has practical benefits such as determining when to stop sampling, as well as uses in assessing groundwater volume and movement. Water sampling will start before tracer injection to measure background fluorescence.

Upon removal of the sample bottles from an automatic water sampler, each bottle will be decanted into a 13-mL glass screw-top bottle and marked with an identification number written in non-fluorescent permanent ink. The bottles will be placed in a rack, and the date, time, location of the sample set will be recorded. A duplicate sample will be taken at this time for each batch of samples. The samples will be stored in a light-proof box to avoid photodecomposition. Each set of bottles will be handled following standard chain-of-custody protocols as outlined in Appendix A.

After all samples have been decanted into 13-mL bottles and securely placed into light-proof boxes, the remaining water will be discarded. Care will be taken to pour out the sample away from the sampling location, so that it cannot be accidentally resampled. The empty bottles will be rinsed three times with water from the Edwards Aquifer Authority's water treatment system. The rinse

stock water will be sampled with each batch of samples, as will rinsate from one of the automatic water sampler bottles.

### **3.5.6 Monitoring tracer concentrations with manual collection of water samples**

There will be manual sampling at all monitoring sites to verify the results of automatic water samplers and charcoal detectors and to supplement those methods should samples become lost or possibly compromised. In wells not equipped with a pump, a PVC bailer will be used at the well. After each use, the bailer will be rinsed three times with water from the Edwards Aquifer Authority's water treatment system and stored in a new, clean plastic bag. All string that entered the well will be removed for proper disposal. Water from the bailer will be poured into glass, 13-mL screw-top bottles. The sample site and time will be written with non-fluorescent permanent ink near the top of the bottle. Grab water samples from surface streams and springs will be collected directly in the 13-mL screw-top bottles. The opening of the bottle will be oriented upstream to assure a representative sample has been collected. The bottles will be placed in a rack, and the date, time, location of the sample set will be recorded. A new clean set of disposable vinyl gloves will be used in the collection of each sample. Each set of bottles will be handled following standard chain-of-custody protocols as outlined in Appendix A.

### **3.5.7 Monitoring tracer concentrations with charcoal detectors**

Charcoal detectors will be used to determine if dye is present at sites not monitored by automatic water samplers and as back-up for all automatic sampling sites should a sampler fail. Charcoal adsorbs dye from the water that passes through the detector. It yields an integrated sample that, barring interference from other organic compounds, is a product of continual sorption of dye, whenever dye is present in water. The tracer detectors will consist of small nylon screen mesh packets containing activated coconut charcoal. Where employed, these packets will be placed in wells or in their discharge stream. See Table 1 for a list of potential sites and Figure 5 for their locations.

During the initial placement of the charcoal packets and during each replacement, a water sample will also be collected for confirmation as described in the previous section. An engravable aluminum tag will be attached with the site identification number, site name, date, time, and initials of the persons collecting the detector. The detector will be submitted for laboratory analysis. Two charcoal detectors will be set at each site and replaced daily on eight-day intervals, staggered four days apart to give a 4-day resolution to the data.

Alexander and Quinlan (1996) discuss the rationale and the techniques for using charcoal detectors and methods for the analysis of dyes. They are summarized briefly below.

Charcoal detectors will be used to monitor dye concentrations in selected wells, either in the well or in the discharge line from the pump. For in-well applications, the detector will be constructed from a thin mesh bag containing charcoal with a weight (glass marbles) attached and suspended in the well. In discharge lines, the charcoal detector will be placed to maximize the flow through the packet. A tee fitting may be attached to the discharge line to conduct water to the detector. During placement/retrieval of each detector, a 13-mL bottle of water will be collected as a backup for the

detectors. All detectors will be placed and retrieved using new disposable vinyl gloves. Upon removal/replacement, each charcoal detector will be placed in a clear plastic bag for transport. Each charcoal detector will be handled following standard chain-of-custody protocols as outlined in Appendix A.

### **3.6 ANALYSIS OF SAMPLES**

#### **3.6.1 Water samples**

Water samples will be collected in 13-ml glass bottles. These bottles will be stored in a lightproof container until they can be analyzed using the Perkin Elmer Model LS50B luminescence spectrometer. The samples will either be placed in a 4 ml cuvette for analysis or will be analyzed in the 13-ml glass sample bottles. The samples will be analyzed using the Perkin Elmer LS50B luminescence spectrometer owned by the Authority. The laboratory will perform a series of synchronous scans exposing the samples to a known wavelength of light and monitoring for emissions of light from the dye. Laboratory standards for the tracer dyes will be used to calibrate the instrument and for comparison of samples. Each of the dyes fluoresce at a known wavelength. The instrument detection limit for the dyes in this test using the LS50B instrument approaches 12 parts per trillion.

#### **3.6.2 Laboratory analysis of charcoal detectors**

Each charcoal detector with its identification tag will be placed in an individually marked bag in the field and shipped for analysis to the Edwards Aquifer Authority's laboratory in San Antonio. All detectors will be thoroughly washed with tap water to remove sediment before being analyzed. The results of detector evaluation will be recorded on a tracer test form by date that conforms to standards in Appendix A.

Charcoal detectors will be evaluated by eluting them for one hour in a solution containing 95 percent of a 70 percent solution of 2-propanol in water and 5 percent sodium hydroxide. The elutant is then decanted for storage in a closed, labeled glass vial until analyzed.

Laboratory analyses for uranine, phloxine B, rhodamine WT, sulforhodamine B and eosine elutants from charcoal will be conducted with the Perkin Elmer LS50B luminescence spectrometer.

### **3.6.3 Conversion of Fluorescence to Concentration**

The Perkin Elmer LS50B measures fluorescence in intensity units, across the range of sampled wavelengths. The intensity of fluorescence in a sample is linearly related to the concentration of dye in water. However, simply using maximum peak height is not sufficient, as all other fluorescent compounds in the sample will add to the peak height. To calculate the concentration of dye in a sample, we will create a correlation between intensity and concentration.

Standards are made for each tracer at known concentrations by serial dilution, based on mass. A set of standards will be analyzed with each set of samples, and when the standards have degenerated to 80% of their original fluorescence, a new set of standards will be made.

The standards are analyzed on the luminescence spectrometer. Mathematical curves are then fit to the spectra using Systat PeakFit software, with a Pearson VII curve model. This software will calculate the area under each dye peak curve. Using all analyzable standards in the series, regressions will be determined for the data to establish an equation that relates peak area to concentration.

Generally, the coefficients of determination ( $r^2$ ) on the regression equation for our standards are between 0.9998 and 0.9999.

### **3.6.4 Project Quality Control/Quality Assurance and Data Quality Objectives**

Project quality control/quality assurance procedures are included in Appendix A and below in Table 4. Trip Blanks, field blanks, control blanks, field duplicates, method blanks, laboratory control standards, and matrix spikes and matrix spike duplicates will be prepared and analyzed for this study with the other samples. Approximately 10 percent of the total number of analyses will be quality control/quality assurance samples.

### **3.6.5 Photodegradation**

Generally, many of the tracers used in this project will degrade from long exposures to sunlight. Thus, all samples will be placed in light-proof containers as quickly as possible in the field, and will remain in these containers until analyzed.

## **4.0 DATA MANAGEMENT**

For this trace, each ISCO automatic water sampler has been assigned a sequential number starting with number 1. In addition, each sampler will be assigned a name based on its location. When a tray of samples is removed from one of the machines, the data will be logged on a form. These data will include the location, ID number, name of crew, date of maintenance, beginning and end dates of sampling interval, information about QC samples, and date and time of each sample (Appendix A). There are 24 bottles per tray, so the samples will be given a number based on the bottle from which they were collected. The sampling will start at 1 and proceed sequentially. The samples are then placed into 13-ml bottles in plastic trays and stored in light-proof containers. The field form is

placed into the box with the samples. The samples will be delivered to the Authority’s laboratory under chain of custody procedures. When samples change custody, a signature and date is recorded for both parties. If samples have to be stored before delivery, they will be kept in a secure location, and remain in the light-proof containers. Table 3 describes the Authority’s quality control sampling program.

**Table 3 – Quality Control Samples**

<b>Sample Type</b>	<b>Common Name</b>	<b>Quality Control Samples: Duplicates, Splits, Blanks</b>	<b>Data Quality Objectives</b>	<b>Corrective Action</b>
ISCO Automatic Water Sampler	ISCO	2 duplicate samples/tray 1 sample of stock from rinse water 1 sample of rinsate with deionized water 1 prepared trip blank/crew/day 1 field blank/sampling event	1) No unusual fluorescence in rinse and rinsate samples. 2) Duplicate sample analyses with same number of peaks, peak areas within 20% of sample.	If duplicates, rinse or rinsate samples yield unexpected results, these bottles will be pulled from field use and inspected.
Passive Charcoal Detectors	Bugs	1 blank bug/set 1 grab sample collected with every bug 1 replicate bug/20 collected	1) No unusual fluorescence in blank bug. 2) Grab samples conform to bug sample analysis.	If bugs yield unusual, unexpected or inexplicable results, grab samples will be analyzed.
Direct Water Samples	Grab Samples	1 grab sample/bug as backup 1 grab sample/ISCO site when possible	1) No unusual fluorescence in grab samples. 2) Grab samples conform to other sample analysis.	Grab samples are backup to ISCO and bug samples.
Perkin-Elmer luminescence spectrometer	Scans	1) Full set of standards and blanks run at start and end of every session 2) Partial set of standards and blanks run every batch (about 20 samples). 3) For water samples, analyze 1 method blank (distilled water)/20 samples, and 1 matrix spike and matrix spike duplicate/full set of samples. 4) For bugs, 1 preparation blank/elutant batch, and 1 matrix spike and matrix spike duplicate/full set of samples.	1) Standards and blanks analyze within 20% to confirm machine stability. 2) Calibration on standards will be carried out on at least every tenth run of complete standards. 3) Matrix spike is within 30% and 170% of calculated concentration. RPD between matrix spike and duplicate on water will be less than 50%.	When standards have photodegraded more than 20%, due to use, new standards will be mixed. If both standards and blanks are off by more than 20%, machine may need to be recalibrated. If matrix spike and matrix spike duplicate data are outside of RPD, then matrix will be evaluated to determine compatibility with dye.

Charcoal detectors will be placed into individual plastic bags which will be labeled with location, date, and time of collection. These samples will be listed on a field form (Appendix A), which will

be stored with the detectors. The procedure for custody of detectors will be the same as described above for the automatic water samplers.

Direct water samples may be collected from a range of locations, and will be labeled on the sample bottle with time, date and location, and logged onto the appropriate field form.

Sample management in the laboratory will include the following protocols.

- 1) Water and charcoal samples will be collected in the field, labeled with the site name, date, time, and type, and stored in a light-proof container.
- 2) Samples are transported to facilities for elution and/or analysis by the Perkin Elmer luminescence spectrometer. Water samples are sent directly for scanning and charcoal samples are sent for scanning after elution.
- 3) Samples are analyzed on the luminescence spectrometer and results are recorded to a hard drive on a dedicated computer for future interpretation. The sample name, date collected, time collected, and type (“w” for water or “b” for bug/charcoal detector) are added to the data file separated by a space. The file names generated by the luminescence spectrometer will have “KC07” for a prefix followed by the number of the analysis, e.g., “KC07#255.sp.” KC designated Kinney County, 07 designates the year.
- 4) Files may be copied from the laboratory computer using a USB drive for evaluation or offsite storage. In addition, the laboratory computer files are backed up onto a storage media after each day of analyses.
- 5) Data will be processed with Systat PeakFit 4.0 analytical software. Separate baseline files will be developed for each site for each dye to facilitate quantification of peaks.
- 6) PeakFit data are written out in ASCII format. Two files will be exported from PeakFit in “.txt” format for each analysis: fitted peak data and numeric. The fitted peak data will be named with the Perkin Elmer prefix and number followed by a “p,” and the numeric data will be named with the Perkin Elmer prefix and number followed by an “n.”
- 7) Text files will be imported into Microsoft Access for evaluation and reporting.

## **5.0 PROJECT SCHEDULE**

Work on the tracer testing study is expected to follow the following schedule:

December 2006 – Mid January 2007

Identify monitoring and injection locations, collect background samples

Mid January 2007

Operate monitoring system and inject dyes

January 2007 – April 2007

Continue monitoring and injection of dyes in subsequent phases based on results of initial injections.

The Authority will produce a final report after the tracer tests are complete. It will describe the objectives, methodologies, and findings of the tests.

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## **APPENDIX A**

### **EDWARDS AQUIFER AUTHORITY QUALITY CONTROL/QUALITY ASSURANCE MANUAL FOR TRACER TESTING**

**December 2006**

These Quality Control/Quality Assurance (QC/QA) protocols were prepared to define field and laboratory operations and methods for the performance of tracer testing of groundwater in karst terranes using fluorescent dyes. The operations and procedures contained in this manual define a very high standard of data collection. However, depending upon the data quality objectives of the project, the user may determine that some of the QC/QA methods are not necessary.

#### **A 1.0 SAMPLING PROCEDURES**

The initial field investigation for tracer test studies will be conducted by an Edwards Aquifer Authority hydrogeologist or a representative of George Veni and Associates, contractor to the Authority. The hydrogeologist will be experienced in the identification of karst features. Work will be supervised by the Authority's Chief Technical Officer. The hydrogeologist doing the initial field investigation will also place the background charcoal detectors and oversee other personnel in the collection and replacement of charcoal detectors.

#### **A 1.1 PROCEDURES FOR SAMPLING GROUNDWATER AND SURFACE WATER FOR DYE**

Water samples may be collected for direct analysis of dye or in support of data from passive charcoal detectors. Water samples from springs and surface streams will be collected by submerging a laboratory supplied container directly into the water. The clean sample bottle will be rinsed with sample water before being used to collect a sample for analysis. When a sample is collected from a spring or stream, the container will be held upstream of the sampler and oriented in an upstream direction during sample collection.

Samples from groundwater monitoring wells will be collected with pre-cleaned dedicated PVC or Teflon bailers or dedicated submersible pump. Prior to sampling, the water level in the well will be determined with an electronic water level meter, fiberglass tape, or steel tape and recorded in a field book. Date, time, location, tracing project name, and other relevant field data will be recorded in a field book. Groundwater will not be purged from the well before the sample is collected.

Table A-1 lists the sample containers, preservatives, holding times and conditions for groundwater and elutant samples. Only new sample containers will be used for sample collection. For each shipment of containers received, blanks will be taken from the lot and analyzed for the presence of dye. The results will be reviewed before any containers from the lot are used.

All sample containers will be stored in an area isolated from the extraction laboratory. Trip blanks for dye will also be prepared in this area.

**TABLE A-1  
REQUIRED CONTAINERS, SAMPLE STORAGE TECHNIQUES AND  
RECOMMENDED HOLDING TIMES WATER**

<b>Parameter</b>	<b>Sample Container</b>	<b>Sample Storage/Preservation</b>	<b>Recommended Maximum Holding Times</b>
Uranine (Sodium Fluorescein) (Acid Yellow 73)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months
Rhodamine WT (Acid Red 388)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months
Sulforhodamine B (Acid Red 52)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months
Eosin (Acid Red 87)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months
Phloxine B (Acid Red 92)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months
Optical Brightener Solophenyl (Direct yellow 96) Blankophor (F.B.A. 28) Tinopal CBSX (F.B.A. 35)	13-ml glass bottle with screw top lid or 50-ml plastic culture tube with screw top lid	Store in dark at 4° C.	6 months

### **A 1.2 PROCEDURES FOR USE OF CHARCOAL DETECTORS**

Dye receptors (detectors) consisting of granular activated coconut carbon (charcoal) will be used to adsorb dye present in surface or groundwater. Approximately 20 grams of charcoal will be placed into a nylon screen mesh packet and placed in springs, cave streams, surface streams, and monitoring wells. Charcoal is used to adsorb uranine, rhodamine WT, sulforhodamine B, phloxine B, and eosin.

Charcoal detectors will be suspended in a surface stream, spring, or cave stream using a wire, string, pins, and/or weight. The detectors will be placed so that they are exposed to any flow that may be present. A rock, brick, or concrete weight (gum drop) will be used to help maximize the volume of water flowing through the packet and secured with dark colored nylon string to a nearby tree, tree root, rock or pin. The dark colored string is used to blend with the surroundings and help to minimize tampering.

The placement of charcoal detectors in monitor wells will also utilize the nylon screen packet but will be weighted using new glass marbles to submerge the charcoal detectors below the surface water.

For sampling water wells, a PVC pipe will be fitted with a hose attachment for attachment to a faucet. The PVC pipe will be constructed such that it will allow the placement of a nylon screen packet within the pipe that will channel flow through the packet.

### **A 1.3 PROCEDURES FOR USE OF UNBRIGHTENED COTTON**

Charcoal detectors consisting of unbrightened cotton, polyethersulfone (PES) film, or other absorbent media will be used to absorb dyes and brightening agents; specifically Direct Yellow 96, and F.B.A. 28 and F.B.A. 351. A piece of cotton or filter media will be placed into a nylon screen mesh packet and suspended in water as described in Section A1.2.

### **A 2.0 SAMPLE CUSTODY**

#### **A 2.1 FIELD COLLECTION AND SHIPMENT**

When samples are transferred/or shipped from the field, they will be accompanied by chain-of-custody records. The records will include the signatures of the relinquisher and the receiver, the date and time of the exchange, and any pertinent remarks. Sample chain-of-custody forms are shown in Figures A-1 and A-2 at the end of this QA/QC document.

During sample collection, the following procedures will be observed:

- To maintain the validity of the sample, on-site procedures will be reviewed prior to arrival in the field.
- Sample handling will be minimized in order to reduce the chance of error, confusion, and damage.
- Sample bags will be marked in the field with water proof ink to prevent misidentification due to illegible labels.
- The shipping container will be either padlocked or secured with a tamperproof seal.

Samples will be shipped in one of the following ways so that safeguards in chain-of-custody can be observed.

- Hand carried and delivered
- Registered mail, so that a return receipt is requested and available for documentation,
- Common carrier, so that a bill of lading can serve this purpose,
- Air freight collect, for complete documentation.

Samples collected in the field under the supervision of the Authority's staff for field analysis will contain a sample identification form but does not requires a chain-of-custody form. All samples determined to be hazardous, according to the U.S. Department of Transportation (U.S. DOT) (49 CFR Section 172.1 or 49 CFR 173.3), will be shipped in strict accordance with U.S. DOT regulations.

## A 2.2 DOCUMENT AND SAMPLE CONTROL

A field log book will be maintained by the sampler as a permanent record of all activities relating to the collection of a sample. Information included in the log book will include: list of those responsible for a sample, date collected, description of location and sample number and the testing objective. The log book will also include data on the weather at the sampling time and location and other related field conditions. If the field book is lost or damaged, it will promptly be reported to the Authority's Chief Technical Officer. This procedure will also be used for field data records and in-house records. Table A-2 presents a list of specific information which will be recorded at the time a sample is collected.

A sample log book will also be maintained by the sample custodian as a permanent record of all activities relating to receipt and disposition of the sample. Information included in the log book are: initials of sampler, sample number and location, date collected, date received, project, and testing parameters.

Identification of samples will be serialized in an alpha-numeric system consistent with the procedures of the study. If a sample is contaminated, it is to be disposed of properly and noted in the log book. Similarly, if a sample is lost, the sampler will document it and promptly notify the Authority's Chief Technical Officer. Tags or labels affixed to the sample will include all of the information listed above and the sample number.

## A 2.3 PACKAGING

Sample packaging for shipment is done such that under normal handling, there is no release or damage of charcoal detectors, the effectiveness of the packing is not reduced, and there is no internal mixing of substances. The procedures which are followed to achieve these objectives are listed below:

- The volume of the sample will be limited to the quantity needed for analysis.
- Plastic containers will be used whenever possible. The plastic container will be protected from puncture. If glass containers are used, the glass will be well cushioned.
- Screw lids will be used whenever possible.
- Charcoal and cotton detectors will be placed in sealed plastic bags with minimal volume of air.

**TABLE A-1  
SAMPLE INFORMATION**

<b>IN-SITU SAMPLES, if collected (e.g., temperature, conductivity)</b>	
Data in Log book	project name or code
	identification number
	location name
	date
	time
	sampler(s) initials
	field observations - weather, problems, etc.
	remarks
	value of parameters measured

<b>IN-SITU SAMPLES, if collected (e.g., temperature, conductivity)</b>	
TRANSPORTED SAMPLES	
DATA on TAGS or LABELS:	all above information
	split sample/duplicate
	sample/blank

## A 2.4 SAMPLE RECEIPT

Upon receipt, the Sample Custodian will follow the procedures listed below:

- If samples have been damaged during shipment, the remaining samples will be carefully examined to determine whether they were affected. Any affected samples will also be considered damaged. It will be noted on the chain-of-custody record that specific samples were damaged and that the samples will be removed from the analytical schedule.
- Samples received will be compared against those listed on the chain-of-custody.
- The chain-of-custody form will be signed and dated and attached to the waybill.
- The samples will be entered in the sample log book which will contain the following information:
  - Project identification
    - Sample numbers
    - Sample location name
    - Type of samples
    - Date and time sampled
    - Date and time received
- The samples will be placed in adequate storage.
- The appropriate Project Manager will be notified of sample arrival.
- The completed chain-of-custody records will be placed in the project file.

If samples arrive either without a chain-of-custody record or an incorrect chain-of-custody record, the following procedure will be undertaken by the sample custodian:

- If the chain-of-custody is incorrect or incomplete, a memorandum to the Project Manager and field personnel will be prepared stating the inaccuracy and necessary correction. The memorandum must be signed and dated by the person originating the chain-of-custody. The memorandum serves as an amendment to the chain-of-custody. If the information on the chain-of-custody form cannot be corrected by the Project Manager or the field personnel, the affected samples will be removed from the analytical schedule.
- If the chain-of-custody record is not shipped with the samples, the field personnel will be contacted and a memorandum prepared which lists the persons involved in collection, shipment, receipt and the times, dates, and events of such. Each person involved must sign and date this memorandum. The completed memorandum will be maintained in lieu of the chain-of-custody record.

## **A 2.5 SAMPLE STORAGE**

Water samples will be stored in a secure area in the dark at 4° C unless signed out for analysis by analytical personnel.

## **A 2.6 CUSTODY DURING TESTING PROGRAM**

When chain-of-custody samples are being analyzed or processed, they will be signed out by the appropriate analyst. The individual performing the tests becomes responsible for the samples at that point. The samples will be maintained within sight or in the secure possession of the individual performing the test. When the work is completed, the samples will be returned and logged in to secure them in the proper storage location. During processing, the sample may be split into several fractions, depending upon the analysis required. The chain-of-custody record remains intact, however, for all sample fractions with the corresponding sample number.

After the analytical results have been reported, the chain-of-custody samples remain secured in storage. Restricted access to these samples is maintained.

## **A 3.0 CALIBRATION PROCEDURES**

### **A 3.1 LABORATORY INSTRUMENTS**

The following procedures will be followed for calibration of laboratory instruments:

#### **A 3.1.1 Filter Fluorometer**

The filter fluorometer is standardized for the parameter of interest by the analysis of calibration standards prepared by diluting a stock solution of known concentration. Five working standards are prepared from the stock solution with concentrations that cover the working range of the instrument. Subsequently, all measurements are made within this range. After the working standards are prepared, instrument response is calibrated to provide a direct readout. The calibration curve is completed by plotting instrument response versus concentration (in µg/L) of the parameter being analyzed. Verification of the calibration curve is accomplished by analyzing a midpoint standard. For the filter fluorometer, the accuracy checks must conform to within 20 percent.

Once the filter fluorometer has been initially calibrated, check standards are analyzed every twentieth sample to confirm the initial calibration curve. A typical analysis sequence is presented below:

- Working standards are prepared by dilution of a stock standard solution of the parameter of interest.
- A calibration curve is established within the working range of the instrument by the analysis of five calibration standards.
- Samples are analyzed for the parameter of interest.
- During sample analysis, a calibration check standard is analyzed every twentieth sample to monitor instrument stability. If the analysis indicates that instrument calibration is not within 20 percent, the instrument is recalibrated and the analysis is repeated.

- Following the completion of the sample analysis the calibration check standard is reanalyzed to confirm instrument calibration.

If calibration is confirmed (within 20 percent), the analysis is complete. However if calibration is not confirmed, the instrument may be recalibrated and the analysis repeated.

### **A 3.1.2 Luminescence Spectrometer (Perkin Elmer LS-50B)**

The luminescence spectrometer is standardized for the parameter of interest by the analysis of calibration standards prepared by diluting a stock solution of known concentration. Five working standards are prepared from the stock solution with concentrations that cover the working range of the instrument. Subsequently, all measurements are made within this range. After the working standards are prepared, instrument response is calibrated to provide a direct readout. The calibration curve is completed by plotting instrument response versus concentration (in  $\mu\text{g/L}$ ) of the parameter being analyzed. Verification of the calibration curve is accomplished by analyzing a midpoint standard. For the luminescence spectrometer, the accuracy checks must conform to within 20 percent.

Once the luminescence spectrometer has been initially calibrated, check standards are analyzed approximately every twentieth sample to confirm the initial calibration curve. A typical analysis sequence is presented below:

- Working standards are prepared by dilution of a stock standard solution of the parameter of interest.
- A calibration curve is established within the working range of the instrument by the analysis of five calibration standards.
- Samples are analyzed for the parameter of interest.
- During sample analysis, a calibration check standard is analyzed every twentieth sample to monitor instrument stability. If the analysis indicates that instrument calibration is not within 20 percent, the instrument is recalibrated and the analysis is repeated.
- Following the completion of the sample analysis the calibration check standard is reanalyzed to confirm instrument calibration.

If calibration is confirmed (within 20 percent), the analysis is complete. However if calibration is not confirmed, the instrument may be recalibrated and the analysis repeated.

## **A 4.0 QUALITY CONTROL SAMPLES**

### **A 4.1 TRIP BLANKS**

A trip blank for water samples will consist of dye-free distilled water that is placed in a sample bottle before field work. Trip blank water will have been tested and shown to be negative for the presence of fluorescent dyes. The purpose of the trip blank is to test for the inadvertent presence of contamination by dye. A trip blank will accompany field personnel during all charcoal detector collection activities. A trip blank will not be used for activated carbon (charcoal) and unbleached



cotton detectors.

All water samples will be collected in plastic or glass containers. A prepared trip blank will utilize the same type of container as is used for sampling of media.

#### **A 4.2 FIELD BLANKS**

A field blank for water will be obtained by pouring dye-free distilled water into a sample bottle in the field at the first site sampled. One field blank will be collected for each sampling event. The field blank will be used to test for the presence of airborne dye particles as tracer injection artifacts.

#### **A 4.3 CONTROL BLANKS**

A control blank for activated charcoal will consist of an activated-charcoal detector which has been placed in a spring or well located in an area out of the influence of the tracer test. The control blank will have been placed during the previous sampling round and will be collected at the start of the current sampling round. This assures that the control blank will be handled and treated like other charcoal detectors. This protocol better replicates field conditions, thus achieving one of the purposes of using blanks and enhancing the QC/QA program. The term control blank is used because, strictly speaking, it is neither a trip blank nor a field blank. A control blank will be utilized during the entire tracer test and will be collected during each charcoal detector collection event.

#### **A 4.4 FIELD REPLICATES**

A field replicate is a second water or charcoal sample collected from a location that is monitored as part of a tracer testing program. The field replicate must be placed, collected and analyzed exactly like the original sample from the site. Replicate samples should be collected from one site in 20 that will be analyzed as for the tracer test.

#### **A 4.5 PREPARATION BLANKS**

Elutant is used in the extraction of dye from charcoal. Preparation blanks consist of elutant solution that is analyzed before the elution is performed. This ensures that dye in the elutant is not an artifact from the elutant and it makes it possible to prevent contamination before it occurs. A preparation blank will be prepared for each batch of elutant solution used.

#### **A 4.6 METHOD BLANK**

Distilled water is analyzed so that it can be shown that the dye signal indicated is not a property of water itself. This will be analyzed once for every 20 samples.

#### **A 4.7 LAB CONTROL STANDARDS**

Lab control standards consist of serial dilutions by mass of a known concentration of dye. Five working standards are prepared from a stock solution. The concentrations of the calibration standards are chosen to cover the working range of the instrument. Subsequently, all measurements are made within this range. After the working standards are prepared, instrument response is calibrated to provide a direct readout. The calibration curve is verified by plotting instrument response versus concentration (in  $\mu\text{g/L}$ ) of the parameter being analyzed. The calibration curve is verified by analyzing a midpoint standard. Lab control standards indicate that the instrument is capable of detection of at least the lowest standard concentration of dye if it were present.

Method blanks (distilled water) and lab control standards for each dye expected to possibly be in the samples are analyzed before and after a set of samples. A lab control standard for each expected dye is also analyzed after every 20 samples.

#### **A 4.8 TEMPERATURE CONTROL**

Air temperature will be recorded at the beginning and end of each dye analysis session. This is because some dyes have a thermal coefficient of fluorescence of 3 percent. Standard calibration for this particular dye can be adversely affected by ambient temperature.

#### **A 4.9 DYE ABSORPTION/ELUTION VERIFICATION**

The following protocol will be followed for one sample of activated charcoal from each batch used in this investigation. The protocol has been developed to verify that the activated charcoal is capable of absorbing and eluting dye. The proposed procedure for testing the adsorption capacity for each lot of activated charcoal consists of the following:

- Tap-water will be used to pre-wash approximately 40 grams of charcoal for 3 hours at about 0.25 gallons per minute (gpm) using a charcoal-holding device that forces all water to flow through charcoal.
- The charcoal will be split into two halves.
- Half of the charcoal will be eluted using the standard procedure, and the elutant analyzed for uranine. The elutant will be analyzed to establish that there is no dye-like fluorescence compound in the charcoal.
- The remaining 10 grams of charcoal will be placed into a nylon mesh bag and suspended in a 1,000 mL beaker containing 250 mL of a 100 ppb solution of uranine in water. The beaker will be fitted with a magnetic stirring device and stirred for one hour on a low setting.
- The remaining charcoal will be eluted using the standard procedure and analyzed for uranine.
- Concentration of uranine, if present, will be reported.

#### **A 4.10 MATRIX SPIKES FOR CHARCOAL**

The following protocol will be followed for one sample of activated charcoal for each sampling event using charcoal. The protocol has been developed to verify that the activated charcoal is

capable of adsorbing and eluting dye after placement and recovery from the field. The proposed procedure for testing the adsorption capacity after sample collection. If, after elution, and analysis no dye is detected, then the sampling event has the possibility of creating a false negative result. Testing of charcoal using the matrix spike method is as follows:

- One charcoal packet which had been placed in the field for dye monitoring will be selected for a matrix spike and matrix spike duplicate. The packet will be rinsed with tap-water for 30 to 60 seconds using a charcoal-holding device that forces water to flow through the charcoal to remove sediment.
- The charcoal will be split into two halves.
- Half of the charcoal will be eluted using the standard procedure, and analyzed for uranine.
- If analysis indicates that there are no dye-like fluorescent compounds in the charcoal, the other half of the charcoal may be used for MS/MSD testing. If uranine compounds are detected, another charcoal packet will be chosen.
- The remaining charcoal will be placed into a nylon mesh bag and suspended in a 1,000 mL beaker containing 250 mL of a 100 ppb solution of uranine in water. The beaker will be placed on a magnetic stirring device and stirred for one hour on a low setting.
- The charcoal will then be eluted using the standard procedure and analyzed for uranine.
- The concentration of uranine will be reported, if present.

#### **A 4.11 MATRIX SPIKES AND MATRIX SPIKE DUPLICATES FOR WATER**

The following protocol will be followed for each sampling event in which water is collected and analyzed for the detection of fluorescent dyes. The protocol has been developed to determine if the matrix interferes with the ability to detect fluorescent dyes in water. If the matrix interferes with the ability to detect fluorescent dyes, then the sampling event has the possibility of creating a false negative result. The procedure for testing for matrix interference of water follows:

- Two additional water samples will be collected from a spring or well during each sampling event for matrix spike and matrix spike duplicate analyses.
- Each sample will be analyzed for the presence of fluorescent dyes.
- If the analysis indicates that there are dye-like fluorescent compounds in the water samples, the concentration will be recorded.
- A known volume of each sample will be measured and placed in a separate clean glass container with an equal volume of a known standard. The known standard will be a dye that is being considered or used in the tracer test. Each sample will then be analyzed for the presence of fluorescent dyes and the concentrations recorded. If fluorescent dyes were present in the original samples, a volume-adjusted concentration will be added to the calculated concentration.
- Each sample will be analyzed for the presence of fluorescent compounds.
- The first sample will be designated the matrix spike. The matrix spike should be between 30% and 170% of the calculated concentration of the sample.
- The second sample will be designated the matrix spike duplicate. The results of the analysis of the matrix spike duplicate will be recorded. The relative percent difference (RPD) of the matrix and matrix spike duplicate will be calculated using the following formula:

$$C_1 - C_2 / \text{Average } (C_1, C_2). \text{ The RPD should be less than 50\%.}$$

**Figure A-1: Automatic Water Sampler Tracking Form**

Tracking # EAA-WS-0051

**EAA Tracer Project, 2006: Water Samples**

Segment: <input type="checkbox"/>	
Crew:	
Collection Date(MM/DD/YY)	
Location Name: ISCO Sampler ID #:	
Start time/date:	End Time/Date:
Water Level	Other comments:
Grab Sample?	Datum Type: <input type="checkbox"/> Top of Well <input type="checkbox"/> Staff Gauge

Bottle #	Sample date (MM/DD/YY)	Sample Time	Other Comments
1	//		
2	//		
3	//		
4	//		
5	//		
6	//		
7	//		
8	//		
9	//		
10	//		
11	//		
12	//		
13	//		
14	//		
15	//		
16	//		
17	//		
18	//		
19	//		
20	//		
21	//		
22	//		
23	//		
24	//		
25	//		duplicate from bottle #:
26	//		rinsate with DI water
27	//		stock (tap water used for rinsing)
28	//		Trip blank (stock DI water poured up on site)

\*Chain-of-Custody information should have signature, date and time

relinquished by:	received by:
relinquished by:	received by:
relinquished by:	received by:
relinquished by:	received by:
relinquished by:	received by:



## APPENDIX B

### Glossary of Hydrogeological and Karst Terminology

This glossary is broad in scope to assist with reviewing this report, but is not meant to cover all possible terms. Additional karst definitions and geologic terms can be found in the geologic dictionary of Jackson (1997).

**Aquiclude:** Rocks or sediments, such as shale or clay, which do not conduct water in significant quantities.

**Aquifer:** Rocks or sediments, such as cavernous limestone and unconsolidated sand, which store, conduct, and yield water in significant quantities for human use.

**Aquitard:** Rocks or sediments, such as cemented sandstone or marly limestone, that transmit water significantly more slowly than adjacent aquifers and that yield at low rates.

**Artesian:** Describes water that would rise above the top of an aquifer if intersected by a well; sometimes flows at the surface through natural openings such as fractures.

**Base level:** The level to which drainage gradients (surface and subsurface) are adjusted, usually a surface stream, relatively impermeable bedrock, or water table. Sea level is the ultimate base level.

**Baseflow:** The “normal” discharge of stream when unaffected by surface runoff; derived from groundwater flowing into the stream channel.

**Bearing:** The azimuthal direction of a linear geologic feature, such as the axis of a fold or the orientation of a fracture; commonly used to denote specific orientations rather than average or general orientations. See trend for comparison.

**Beds:** See strata.

**Bedding plane:** A plane that divides two distinct bedrock layers.

**Borehole:** A drilled hole, commonly used for fluid or mineral extraction and injection, or for the monitoring or testing of geologic parameters.

**Breakdown:** Rubble and boulders in a cave resulting from collapse of the cave ceiling.

**Breccia:** A rock composed of broken, angular fragments of a pre-existing rock that were cemented to form the present rock unit.

**Calcite:** The predominant mineral in limestone. It is relatively soluble compared to other common minerals, and allows for the dissolution of limestone and the precipitation of calcite speleothems.

**Carbonate aquifer:** An aquifer developed in predominantly carbonate rock, usually limestone or dolomite.

**Cave:** A naturally occurring, humanly enterable cavity in the earth, at least 5 m in length and/or depth, in which no dimension of the entrance exceeds the length or depth of the cavity (definition of the Texas Speleological Survey).

**Chamber:** See room.

**Conduit:** A subsurface bedrock channel formed by groundwater solution to transmit groundwater; often synonymous with cave and passage, but generally refers to channels either too small for human entry, or of explorable size but inaccessible.

When used to describe a type of cave, it refers to base level passages that were formed to transmit groundwater from the influent, upgradient end of the aquifer to the effluent, downgradient end.

**Conduit flow:** Groundwater movement along conduits; usually rapid and turbulent.

**Conduit groundwater divide:** Where the baseflow of a cave passage splits to flow downstream in two different conduits, and often to two different destinations. Divides can occur both above and below the water table.

**Cone of depression:** A sunken or funnel-shaped area of the potentiometric surface; usually associated with groundwater withdrawal through wells.

**Confined:** Pertaining to aquifers with groundwater restricted to permeable strata that are situated between impermeable strata.

**Conformable:** A contact between strata that reflects a period of continuous deposit of material, typically a smooth surface without evidence of the erosion in the underlying older strata; see *unconformity*.

**Cretaceous:** A period of the geologic time scale that began 135 million years ago and ended 65 million years ago.

**Depth:** In relation to the dimensions of a cave or karst feature, it refers to the vertical distance from the elevation of the entrance of the cave or feature to the elevation of its lowest point. See vertical extent for comparison.

**Dip:** The angle that joints, faults or beds of rock make with the horizontal; colloquially described as the “slope” of the fractures or beds. “Updip” and “downdip” refer to direction or movement relative to that slope.

**Diffuse flow:** Laminar and very slow groundwater movement within small voids of primary and secondary porosity, excluding conduit and fissure flow; “intergranular” flow.

**Discharge:** The water exiting an aquifer, usually through springs or wells; also the amount of water flowing in a stream.

**Drainage basin:** A watershed; the area from which a stream, spring, or conduit derives its water.

**Drainage divide:** Location where water diverges into different streams or watersheds. On the surface they usually occur along ridges or elevated areas. In aquifers, they occur along highs in the potentiometric surface between groundwater basins.

**En echelon:** Typically refers to faults or other structures that occur in an overlapping but collectively linear arrangement, such as to form a fault zone.

**Epikarst:** The highly solutioned zone in karst areas between the land surface and the predominantly unweathered bedrock.

**Estavelle:** A feature that either recharges or discharges groundwater, depending on the level of the water table or potentiometric surface.

**Fault:** Fracture in bedrock along which one side has moved with respect to the other.

**Fissure flow:** Groundwater movement along fractures and bedding planes that usually have been enlarged by solution. Flow is laminar to turbulent, and generally constitutes a moderate to large volume of groundwater in karst aquifers.

**Floodplain:** The flat surface that is adjacent and slightly higher in elevation to a stream channel, and which floods periodically when the stream overflows its banks.

**Fracture:** A break in bedrock that is not distinguished as to the type of break (usually a fault or joint).

**Geomorphology:** The branch of geology that studies the shape and origin of landforms.

**Grade:** The continuous descending profile of a stream; graded streams are stable and at equilibrium, allowing transport of

sediments while providing relatively equal erosion and sedimentation. A graded profile generally has a steep slope in its upper reaches and a low slope in its lower reaches.

**Groundwater trough:** A steep furrow-shaped feature in the potentiometric surface, usually indicative of high groundwater transmissivity through an underlying conduit.

**Head:** The difference in water level elevations that creates the pressure for water movement down a gradient.

**Headward:** In the direction of greater elevation; typically refers to upstream or up a hydraulic gradient.

**Heterogeneous:** Condition where an aquifer's hydraulic properties vary in different locations.

**Homoclinal hinge:** The axis of a single, uniform bend in strata.

**Homogeneous:** Condition where an aquifer's hydraulic properties are the same in all locations.

**Honeycomb:** An interconnected series of small voids in rock, commonly formed in karst by near-surface (epikarstic) solution, or by phreatic groundwater flow.

**Hydraulic gradient:** The continuous descending profile of a stream or an aquifer's water table or potentiometric surface from areas of water input to areas of discharge.

**Hydrogeology:** The study of water movement through the earth, and the geologic factors that affect it.

**Hydrograph:** A graph illustrating changes in water level or discharge over time.

**Hydrograph separation:** The division of a hydrograph into component sections, usually to show the behavior of baseflow versus quickflow; often used in karst to identify conduit flow versus diffuse flow.

**Hydrology:** The study of water and its origin and movement in atmosphere, surface, and subsurface.

**Impermeable:** Does not allow the significant transmission of fluids.

**Joint:** Fracture in bedrock exhibiting little or no relative movement of the two sides.

**Karst:** A terrain characterized by landforms and subsurface features, such as sinkholes and caves, which are produced by solution of bedrock. Karst areas commonly have few surface streams; most water moves through cavities underground.

**Karst feature:** Generally, a geologic feature formed directly or indirectly by solution, including caves; often used to describe features that are not large enough to be considered caves, but have some probable relation to subsurface drainage or groundwater movement. These features typically include but are not limited to sinkholes, enlarged fractures, noncavernous springs and seeps, soil pipes, and epikarstic solution cavities.

**Laminar flow:** Smooth water movement along relatively straight paths, parallel to the channel walls.

**Length:** In relation to the dimensions of a cave or karst feature, it refers to the summed true horizontal extent of the cave's passages or the feature's extent.

**Lithology:** The description or physical characteristics of a rock.

**Miocene:** An epoch of the Tertiary Period of the geologic time scale that occurred between 5 and 23 million years ago.

**Normal fault:** A fault where strata underlying the fault plane are higher in elevation than the same strata on the other side of the fault plane.

**Passage:** An elongate, humanly traversable, roofed portion of a cave or karst feature; usually a conduit for groundwater flow.



**Perched groundwater:** Relatively small body of groundwater at a level above the water table; downward flow is impeded within the area, usually by impermeable strata.

**Permeable:** Allows the significant transmission of fluids.

**Permeability:** Measure of the ability of rocks or sediments to transmit fluids.

**Phreatic:** The area below the water table, where all voids are normally filled with water.

**Piracy:** The natural capture of water from a watershed, stream, aquifer, or cave stream, and its transmission to a different watershed, stream, aquifer, or cave stream.

**Pit:** A vertical cavity extending down into the bedrock; usually a site for recharge, but sometimes associated with collapse.

**Porosity:** Measure of the volume of pore space in rocks or sediments as a percentage of the total rock or sediment volume.

**Potentiometric surface:** A surface representing the level to which underground water confined in pores and conduits would rise if intersected by a borehole. See water table.

**Quickflow:** The floodwater component of stream or spring discharge that persists only for a relatively short time following storm events, typically associated with water stored in and moving through conduits.

**Rating curve:** A curve on a graph based on measurements and extrapolated data, which correlates stage height to stream discharge.

**Reach:** The length of a stream or stream segment; often used to denote similar physical characteristics.

**Recharge:** Natural or artificially induced flow of surface water to an aquifer.

**Room:** An exceptionally wide portion of a cave, often at the junction of passages; commonly indicative of either the confluence of groundwater flowpaths or of slow, nearly ponded, groundwater flow. Generally synonymous with chamber, except that chamber is usually reserved for relatively large rooms.

**Shaft:** See pit.

**Sink:** See sinkhole.

**Sinkhole:** A natural indentation in the earth's surface related to solutional processes, including features formed by concave solution of the bedrock, and/or by collapse or subsidence of bedrock or soil into underlying solutionally formed cavities.

**Sinking stream:** A stream that losses all or part of its flow into aquifer. See swallet.

**Solution:** The process of dissolving; dissolution.

**Speleogenesis:** The process of cave origin and development.

**Speleothem:** A chemically precipitated secondary mineral deposit (e.g., stalactites and stalagmites) in a cave; usually calcite but can form from gypsum and other minerals.

**Spring:** Discrete point or opening from which groundwater flows to the surface; strictly speaking, a return to the surface of water that had gone underground.

**Stage:** The water level elevation or height measured in a stream or a well.

**Storativity:** The volume of water released from or taken into an aquifer for each unit of aquifer surface area per unit of change in head; usually refers to storage within confined aquifers. See specific yield.

**Strata:** Layers of sedimentary rocks; usually visually distinguishable. Often called beds. The plural of stratum.

**Stratigraphic:** Pertaining to the characteristics of a unit of rock or sediment.

**Stratigraphy:** Pertaining to or the study of rock and sediment strata, their composition and sequence of deposition.

**Strike:** The direction of a horizontal line on a fracture surface or on a bed of rock; perpendicular to dip.

**Structure:** The study of and pertaining to the attitude and deformation of rock masses. Attitude is commonly measured by strike and dip; deformational features commonly include folds, joints, and faults.

**Swallet:** A surface stream that loses all of its baseflow into a cave or sinkhole. The stream channel may extend beyond the swallet, but it would contain only overflowing floodwaters.

**Tapoff passage:** A relatively short, high-gradient cave stream passage that pirates flow from a high elevation stream to a lower elevation stream, which may also have a more hydrologically efficient or steeper channel. Tapoffs can form between any combination of surface and subsurface streams.

**Terrace:** A relatively narrow, flat topographic surface; with reference to streams it usually marks the elevation of a former, higher, water level, and is composed of and formed by the deposition of unconsolidated sand, gravel, and related alluvial material.

**Tracer test:** The injection of a non-toxic, traceable substance, often a fluorescent dye, into a groundwater system, and its recovery at a downgradient location (usually a spring). This technique is commonly used in karst areas to define groundwater flow paths and travel times.

**Transmissivity:** The rate at which water moves through a unit width of an aquifer under a unit hydraulic gradient.

**Turbulent flow:** Variable movement of water particles along very irregular paths. Typical flow regime of cave streams.

**Unconfined:** Pertaining to aquifers having no significant impermeable strata between the water table and the land surface.

**Unconformity:** A break in the sequence of stratigraphic deposition that is often recognized by an erosional surface overlain by younger strata; see *conformable*.

**Vadose:** Pertaining to the zone above the water table where all cavities are generally air-filled, except during temporary flooding.

**Vertical extent:** In relation to the dimensions of a cave, refers to the vertical distance from the highest elevation to the lowest elevation of the cave. Generally used when a portion of a cave extends above its entrance. See depth for comparison.

**Water table:** The boundary of the phreatic and vadose zones. A potentiometric surface but the term is used only in unconfined aquifers.

**Weir:** A dam with a notch or upper surface shaped to carry water such that the stream's discharge over the dam can be calculated from the stream's height behind (upstream of) the dam.


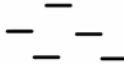


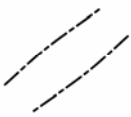







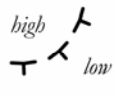






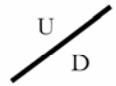

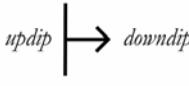


## APPENDIX C

### Conversions: International System of Units to English Units

MULTIPLY	BY	TO GET
<b>Length</b>		
centimeters (cm)	0.3937	inches (in)
meters (m)	3.281	feet (ft)
kilometers (km)	0.621	miles (mi)
<b>Area</b>		
square meters (m <sup>2</sup> )	10.76	square feet (ft <sup>2</sup> )
square kilometers (km <sup>2</sup> )	0.3861	square miles (mi <sup>2</sup> )
square kilometers (km <sup>2</sup> )	247.1	acres (ac)
<b>Volume</b>		
liters (L)	0.264	gallons (gal)
cubic meters (m <sup>3</sup> )	264.17	gallons (gal)
cubic meters (m <sup>3</sup> )	0.00081	acre-feet (a-f)
<b>Flow</b>		
liters per second (L/s)	0.0353	cubic feet per second (cfs)
liters per second (L/s)	15.85	gallons per minute (gpm)
cubic meters per second (m <sup>3</sup> /s)	35.31	cubic feet per second (cfs)
cubic meters per second (m <sup>3</sup> /s)	1,585	gallons per minute (gpm)
cubic meters per second (m <sup>3</sup> /s)	70.05	acre-feet per day (a-f/d)
<b>Temperature</b>		
degrees Celsius	multiply by 1.8 then add 32	degrees Fahrenheit

# APPENDIX D

## Cave Map Symbols

	passage walls		mud or clay
	lower level passage		stalactite
	upper level passage		stalagmite
	breakdown walls		column
	unexplored or impassable passage		flowstone
	drop in floor		water, with flow direction
	drop in ceiling		cross section, with view direction
	large breakdown		vertical joint
	small breakdown or talus		dipping joint
	bedrock floor		fault, D side moved down relative to U side
	stream cobbles		dipping fault
	sand or soil		strike and dip of bedding