First Dye Tracer Tests in Sutton County

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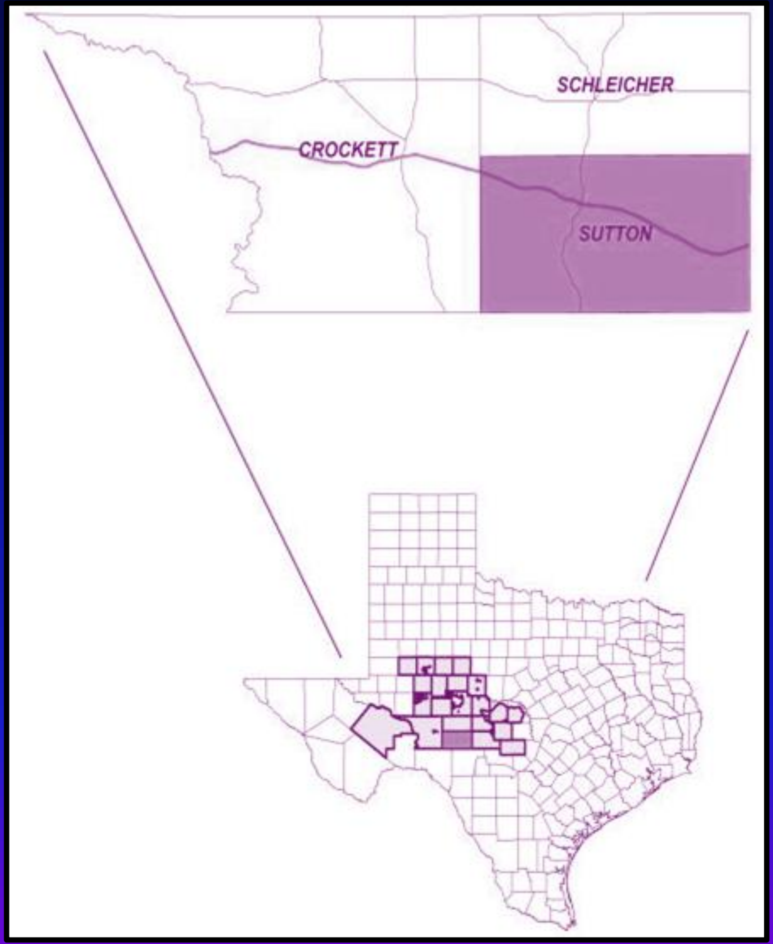
Introduction

- Sutton County Underground Water Conservation District
  - Local government agency that provides for the conservation, preservation, protection, recharge and prevention of waste of the underground water reservoir, Edwards-Trinity (Plateau) Aquifer
  - Consistently adheres to Chapter 36 of the Texas Water Code (TWC)
- Location
  - Sutton County covers approximately 1453 square miles or 929,920 acres over the Edwards- Trinity Aquifer in West Central Texas



Edwards-Trinity Aquifer System

- Edwards-Trinity Aquifer
  - This aquifer system underlies west-central Texas nearly flat-lying Lower Cretaceous and Upper Cretaceous strata, thin northwestward atop generally massive pre-Cretaceous rocks that are comparatively impermeable and structurally complex

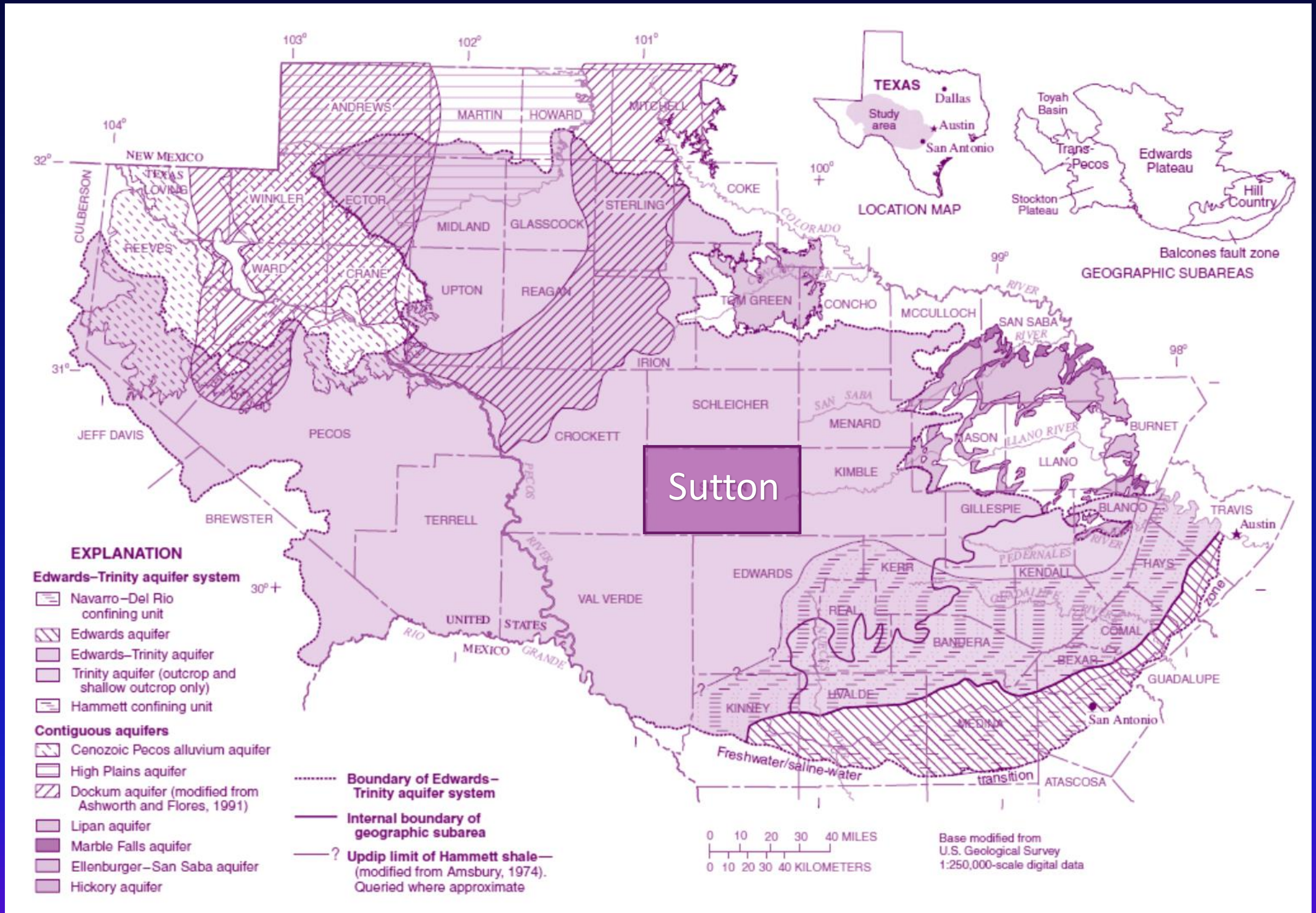
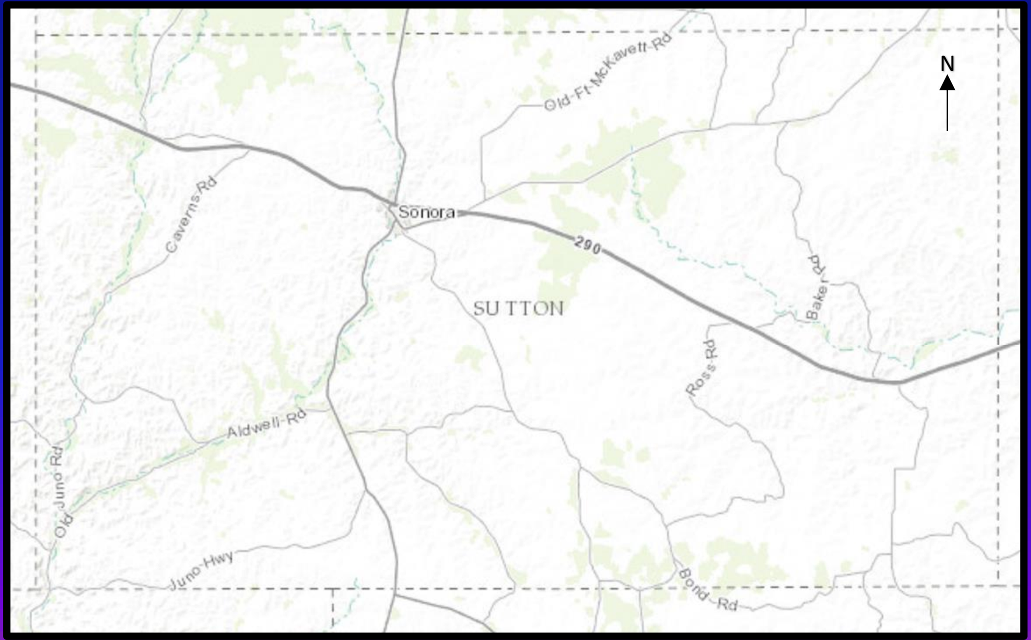


Figure 1. Study area and major and minor aquifers, west-central Texas (modified from Barker and Ardis, 1996).

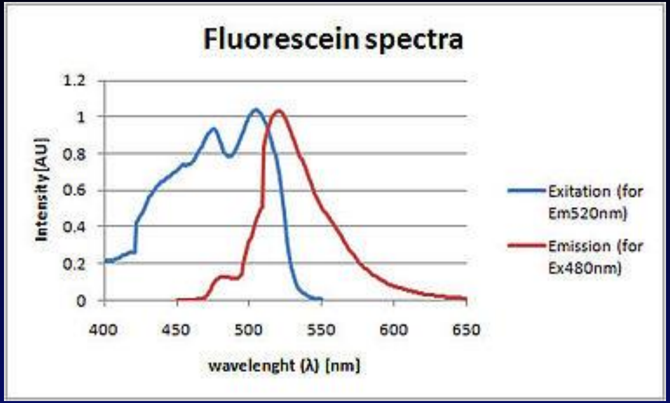
Planning the Dye Test, Phase I

- Goals for the test
  - What direction does the water come from?
  - How fast does it flow –transmissivity?
  - Where does it go?
  - What volume of water flows through this area?
  - What is the storage capability of the aquifer at this point?
- Map of the dye test area
  - No caves are in contact with the aquifer within the district
  - Must inject into DIW
  - Must collect samples from wells located along anticipated path for the dye



Planning the Dye Test, Phase II

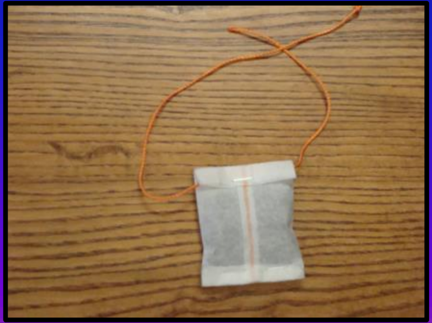
- Writing the test plan
- Choosing the “right” dye
  - The Basics of Uranine (aka Fluorescein)
  - Why Uranine?
    - High detectability in both water and elutant samples from activated charcoal samples
    - Unlike other fluorescent dyes, Uranine is not as susceptible to interference caused by certain pH levels
    - Little difference between the fluorescence magnitudes of Uranine in water compared to Uranine in the standard eluent
    - According to Smart and Laidlaw (1977), Uranine exhibits a high rate of resistance to absorption onto inorganic materials, which is very important when testing in a karst aquifer system



Dye Type and Common Name	Color Index Generic Name	Molecular Weight	CAS Number	Excitation Wavelength (nm)	Emission Wavelength (nm)	Fluorescence Intensity (%)	Detection Limit (µgL-1)	Sorption Tendency
Sodium fluorescein (Uranine)	Acid Yellow 73	376.27	518-47-8	493	520	100	0.002	Very low

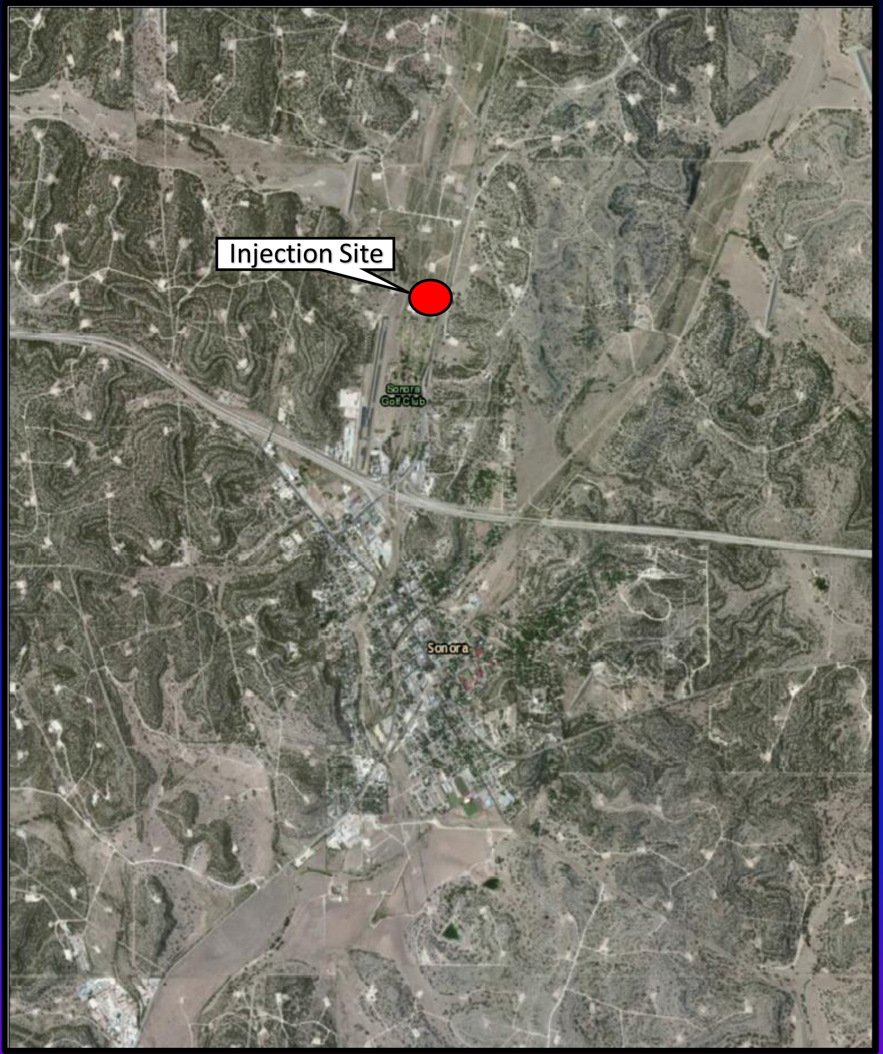
Planning the Dye Test, Phase III

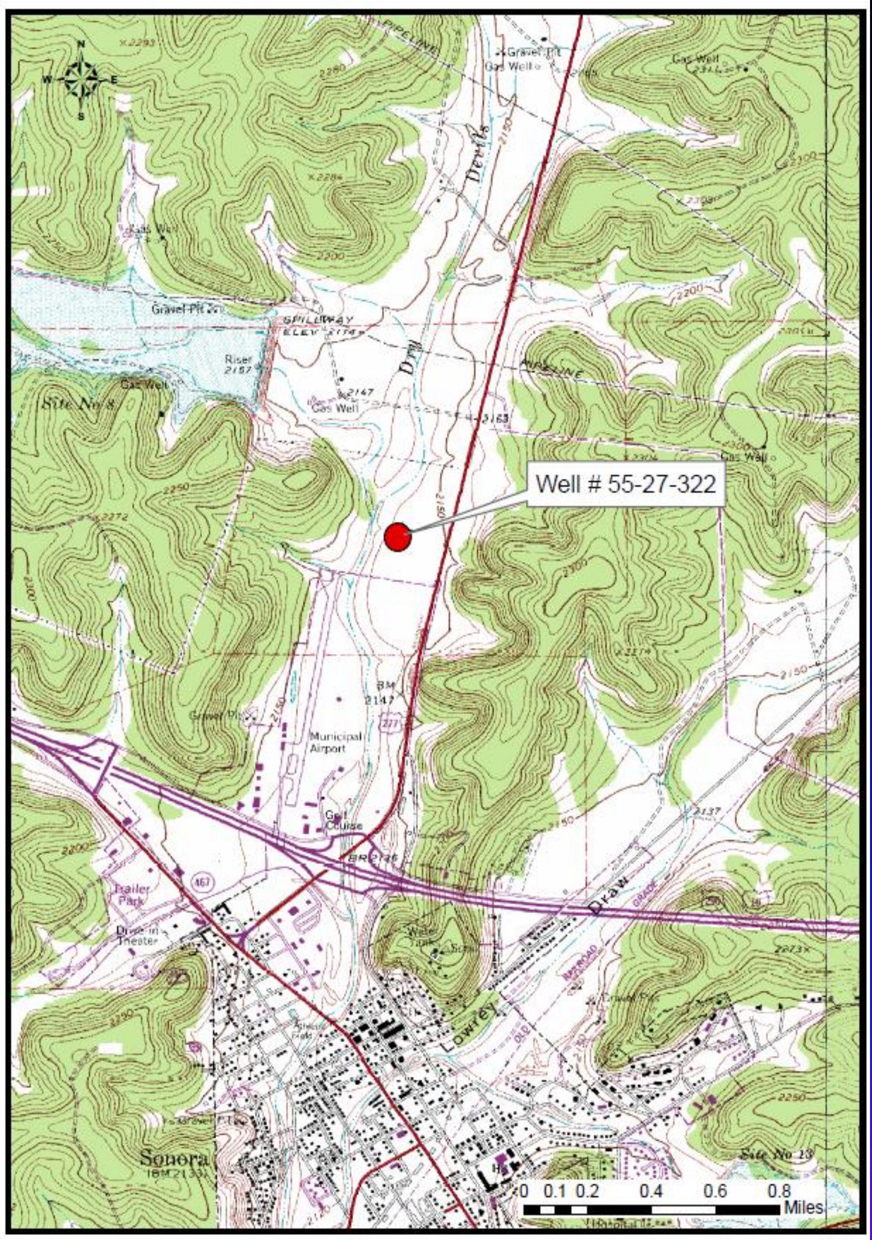
- Ordering the supplies
- Collection equipment used for test includes two automated water samplers and a number of charcoal packet fixtures
- Letters to Landowners
    - Requesting their participation by volunteering their wells for this study
    - Informing them of the importance of this test
    - Advocates encouraging their neighbors to participate



The Injection Site

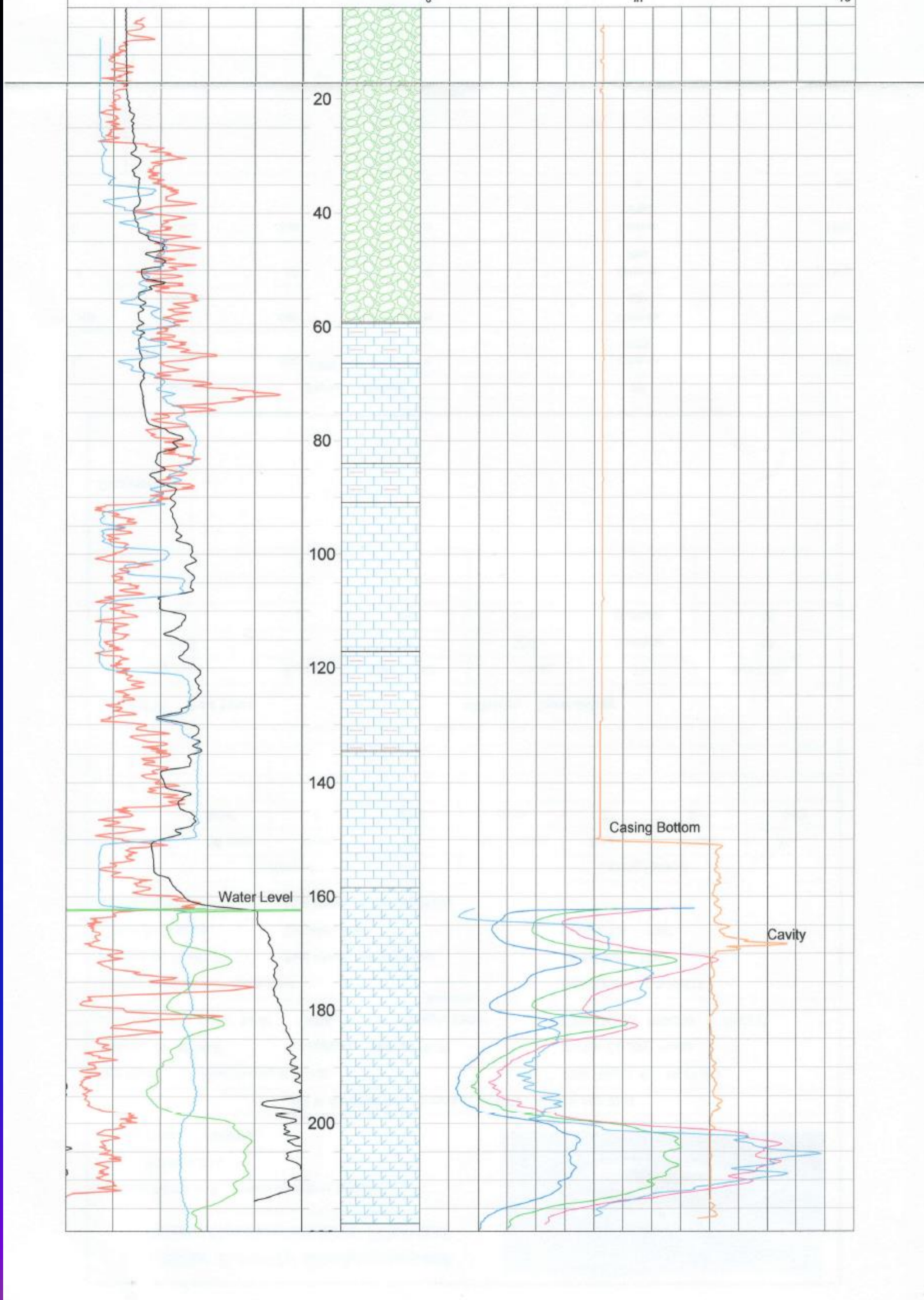
- The Drought Index Well
  - 55-27-322
- Located in the floodplain of the Dry Devils River
  - North end of the Sonora Golf Course
- Elevation from the top of the well is 2,148’ mean sea level (msl)
- Total depth is 217’ (1,931’ msl)





Connectivity to Aquifer Test

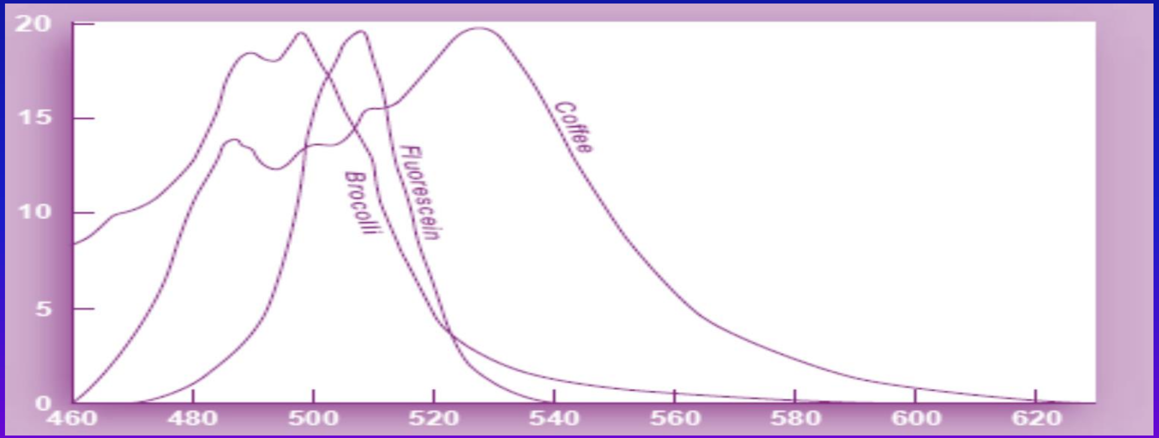
- Is our DIW really connected into the aquifer system?
- After injecting 500 gallons of water into well; every drop entered the system



Preliminary Charcoal & Water Sampling

- Checking for background fluorescing "noise" before the introduction of dye
  - Potential contaminates interfering with results of actual dye test?
  - Some compounds that will interfere with the fluorescence of Uranine. Examples include but are not limited to:
    - Storm water runoff from major roads and large parking areas
    - Automotive coolants (anti-freeze)
    - Residential and municipal sewage and discharge from sewage treatment plants
    - municipal landfill leachate
    - "Leak tracer" dyes used by plumbers and sanitarians
    - Colored paper and colored felt-tip pens
    - Natural compounds (humic and fulvic)

- These potential background interferences can be variable both geographically and temporally
- Fluorescence interference from natural compounds can sometimes result in fluorescence peaks in or near acceptable wavelength range for tracer dyes, especially Uranine
- The shape of fluorescence peaks associated with such natural materials typically appear broader, more irregular and less symmetrical than those resulting from tracer dyes

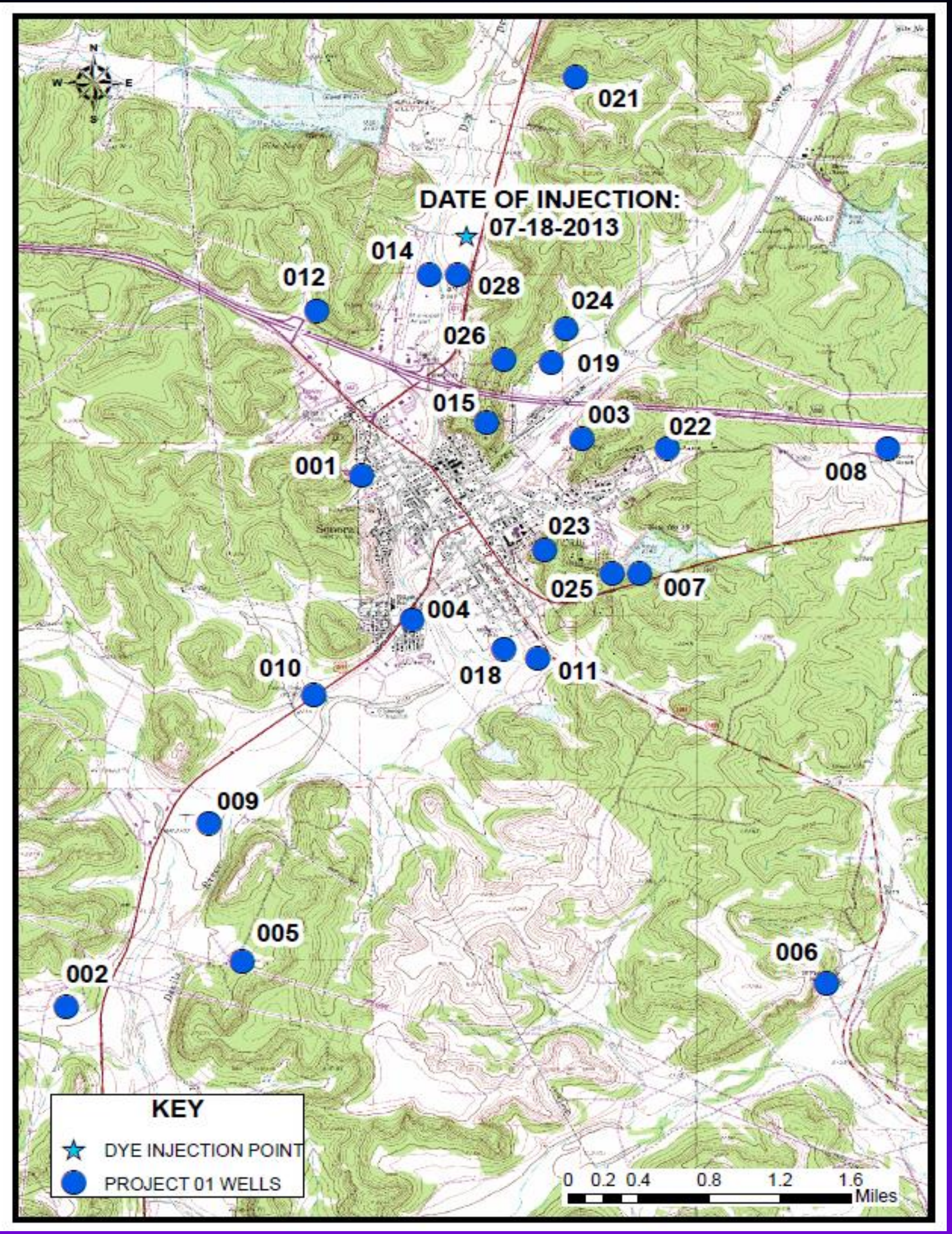


Results of Background Fluorescence Check

- Samples were collected at each candidate well
- Samples were taken to Edwards Aquifer Authority lab (EAA) lab for analysis all were reported negative
- We were **GOOD** to go!

Sample Locations

Sample Site #	Well Owner	State Well #
001	Anderson, Sonny	55-27-686
002	Bosch, Derry Kay	55-27-804
003	Brockman, Bob	55-27-631
004	Crites, Tracy	55-27-681
005	Bosch, Derry Kay	55-27-913
006	Fields, Tryon	55-28-714
007	Fisher, Glen	55-27-630
008	Howorth, Max	55-28-401
009	Jones, Claire	55-27-906
010	KHOS (Ward, Albert)	55-27-635
011	Powers, Jimmy (Houston)	55-27-666
012	Ross, Joe David	55-27-324
014	City Golf Course #7	55-27-318
015	City Well #3	55-27-603
018	Sonora ISD	55-27-659
019	Sutton County: Cemetery	55-27-615
021	Tedford, John (Walsh lease)	55-27-307
022	Tedford, John	55-27-673
023	Thorp, Tim	55-27-619
024	Walsh, David	55-27-685
025	Wamble, Frank	55-27-639
026	Wipff (McNeil, Charlotte)	55-27-684
027	Tedford, John (Walsh lease)	55-27-319
028	Golf Course Pond #6	
029	TXDOT Juno Hwy (8/19)	55-43-205
030	Ray Irrigation (8/20)	55-42-502



Preparations for Introduction of Dye Into Aquifer

- Protective ground cover, tarps
- Protective suits for personnel
  - Dye presents NO health or environmental problems at concentrations five orders of magnitude or more above the detection limits used in modern protocol
- Hoses, injector, container of dye

Injection Day

- Dye was injected July 18, 2013
  - Approximately 200 gallons of water was used to prime the injection site between 10:25 and 11:05
  - Twelve pounds (5,828 grams) of Uranine dye in an aqueous solution was then injected
  - Approximately 300 gallons of fresh water injected to flush the well between 12:10 and 12:40
- All water and dye went into aquifer
- Automated samplers were already programmed to collect a sample every hour
  - Two automatic water samples were also deployed and programmed to collect 24 samples in varying intervals
  - At the end of each automatic sampler cycle, each bottle was decanted into a 13-mm screw-top glass vial and marked with an identification number and date collected in pencil
  - Recordation of the location, time and date, and bottle number was conducted during the retrieval process on a separate sheet
  - Vials were then placed in a rack and stored in a light-proof container. Duplicate samples were taken for bottles one (1), ten (10), twenty (20), and twenty-four (24) and labeled accordingly
  - Residual water was disposed and each bottle was rinsed three (3) times with distilled water to clean out any potential residual dye

Collection of Charcoal & Automated Water Sampler Samples

- Organized a number of volunteers to collect samples the next day starting at 0900
- Collected charcoal samples and grab samples
  - Charcoal receptor packets, commonly referred to as, "bugs," were used in conjunction with grab samples at each sample site, if circumstances allowed
  - Bugs were placed inside PVC pipe receptacles outfitted with various fittings depending on sample site conditions
  - The charcoal packets were constructed using nylon screen-mesh commonly used as pipeline milk filters that were cut to a size capable of holding one tablespoon of coconut charcoal and then stapled closed
  - Because the charcoal is capable of absorbing dye from the water as it flows thru the mesh packet, it can yield dye intensity information for that sample cycle
  - During sample extraction, each bug is placed in a sterile plastic bag with an aluminum engravable tag, both of which are labeled with the sample site location, time and date collected

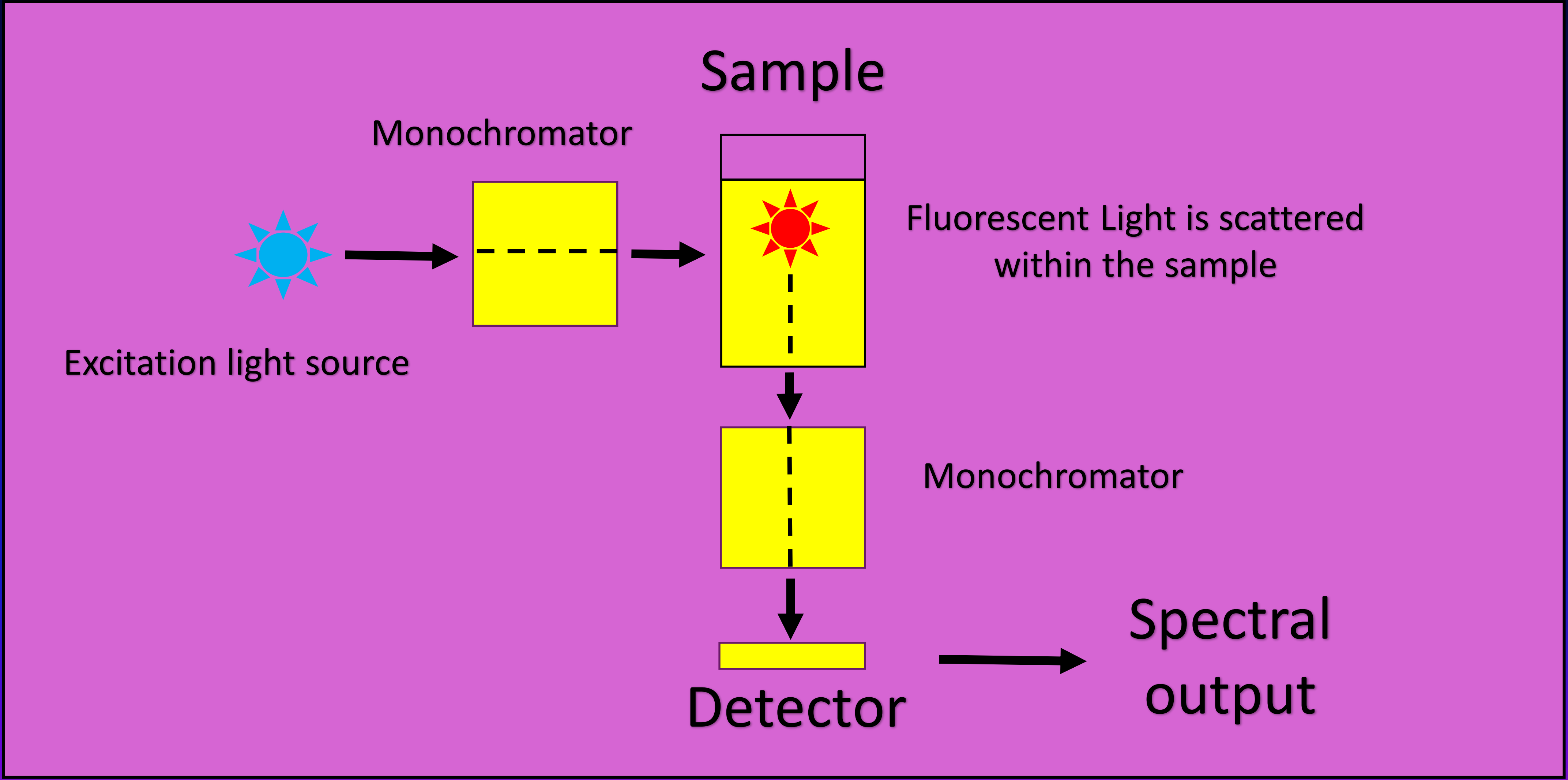
First trip to analyze initial batch of samples

- Analyzed charcoal and grab samples as well as water samples from automated samplers
- Analysis showed we had hits as early as late July through September
- Collections continued through the fall and winter and into the spring
- In early fall, people who volunteered their wells were becoming antsy. Basically, they did not want the water running on their plants. Some were worried about over watering; others were concerned about wasting water. Some would turn off the water so when we collected the charcoal sample it would be partially dried

Data Analysis of First Batch of Samples

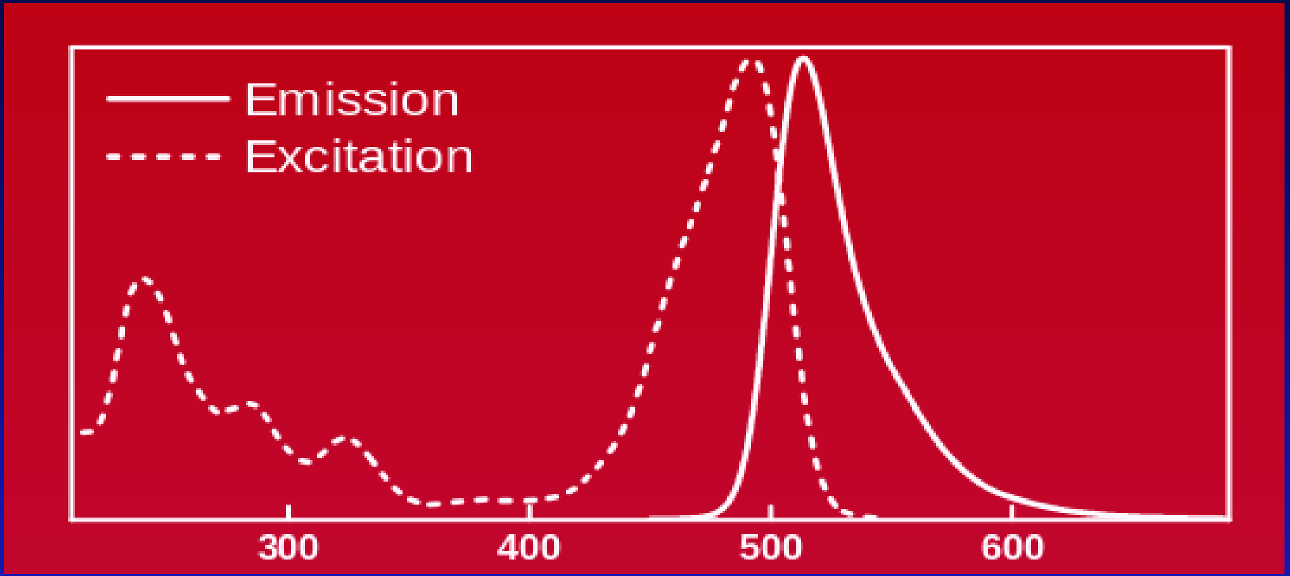
- Once the data was collected from the initial batch, we saw several places where we found dye hits
- This was very exciting news. However, on close examination it was suspect
- The dye should fluoresce at a peak of 493-494 nanometers (nm); instead it fluoresced between 500 and 520 nm. This finding nullified the hits we thought we had found

Schematic Diagram of a Fluorescence Spectrometer {light source – pulse Xenon lamp}



Excitation vs. Emission Wavelengths

- Excitation & emission wavelengths confusion
- Uranine (aka Fluorescein) has a peak excitation wavelength of 493/494 nm
- Peak emission wavelength of 520/521 nm
  - The EAA's Elmer machine is said to **only** record *excitation* values along the x-axis of the scans
  - The EAA's Elmer machine is set to utilize a 6 nm slit window
    - Therefore a range of ~487-499 nm is *assumed* to be acceptable

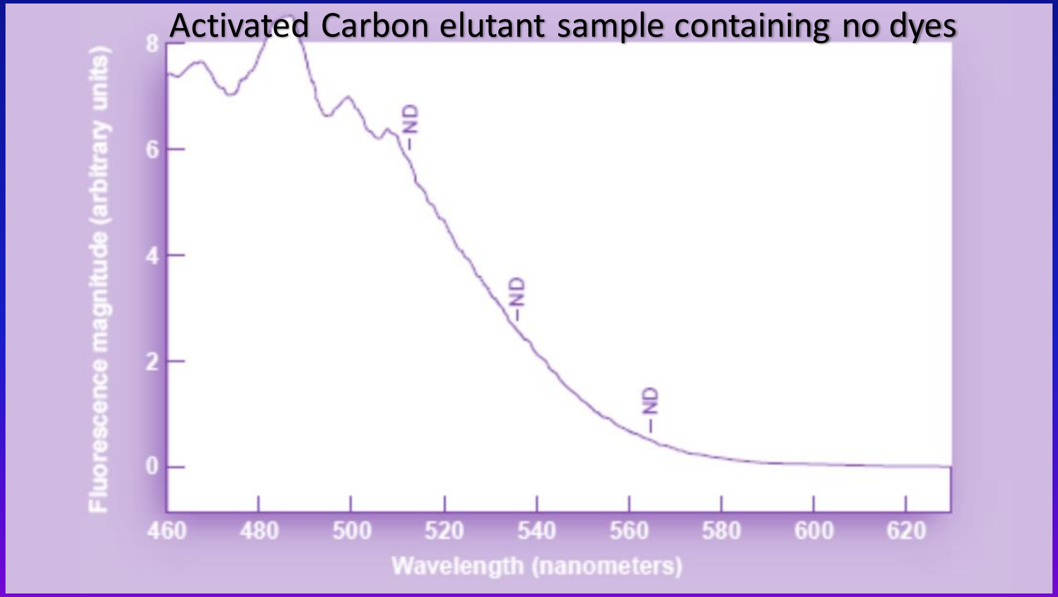


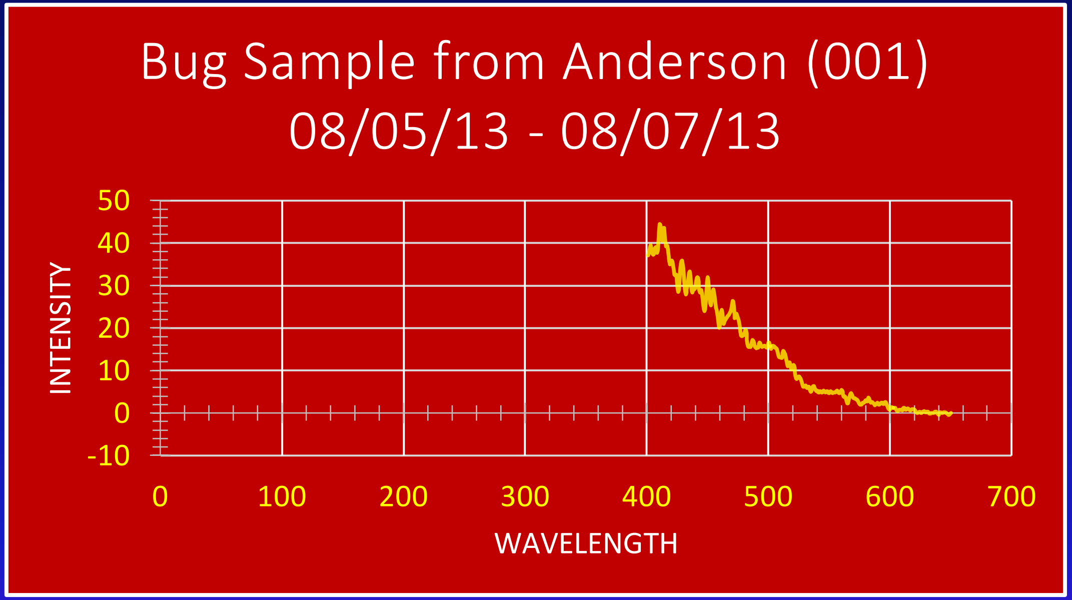
Collection & Analyses Continues

- Samples pile up
  - Scheduling conflicts with EAA laboratory cause massive accumulation of samples in need of scanning
- Data in need of analysis also piles up
  - Batch processing of samples results in a pile up of unanalyzed data

Understanding the Distributions of the Spectrofluorometric Scans

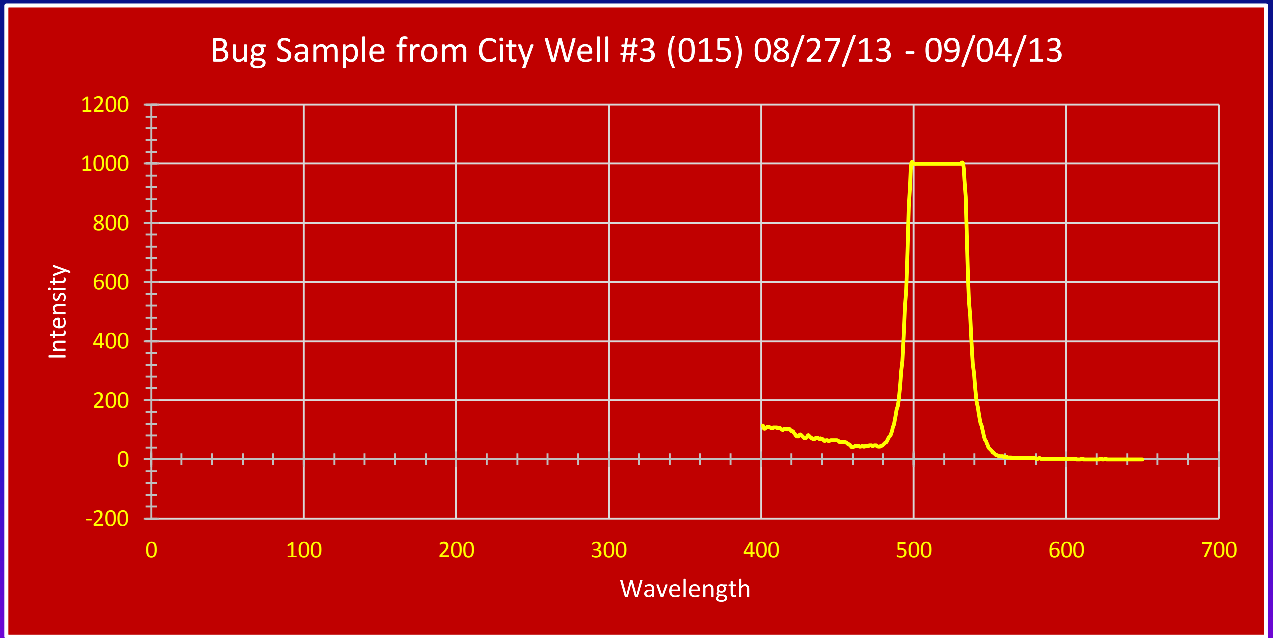
- First step is analyzing the scans produced by the spectrofluorometric equipment (Elmer) at the EAA
  - Learning how to interpret the graphs by recognizing a positive dye hit
    - Distribution
      - Example of negative hit
    - Wavelength
    - Intensity





Spectrofluorometric Scans Example

- "Right" distribution but likely the wrong wavelength
  - How do we know it's the right distribution?
  - How do we know if a hit is being masked by a peak belonging to some other fluorescing material?
    - Had to find comparative material to facilitate answering those questions



Understanding Spectrofluorometric Graphs

- Finding a standard for comparison
  - Image taken from Taylor and Greene (USGS), Chapter 3 in, Field Techniques for Estimating Water Fluxes between Surface Water and Ground Water (2008, edited by Rosenberry and LaBaugh)
  - Used as a reference for how a typical single dye hit is depicted when graphed by spectrofluorometric instrumentation and an example of a multiple dye hit
    - Please note this image depicts the EMISSION wavelengths rather than the EXCITATION wavelengths along the X-axis (so ignore the x values)

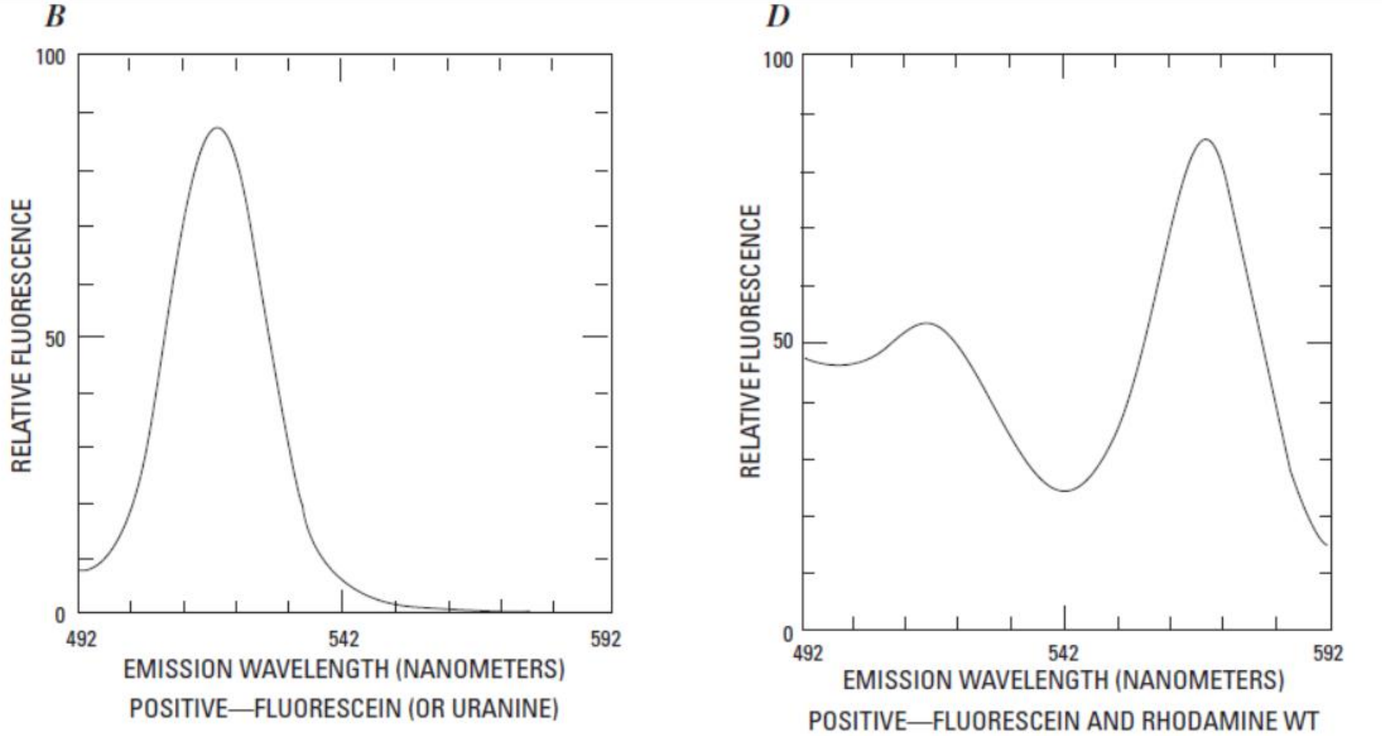
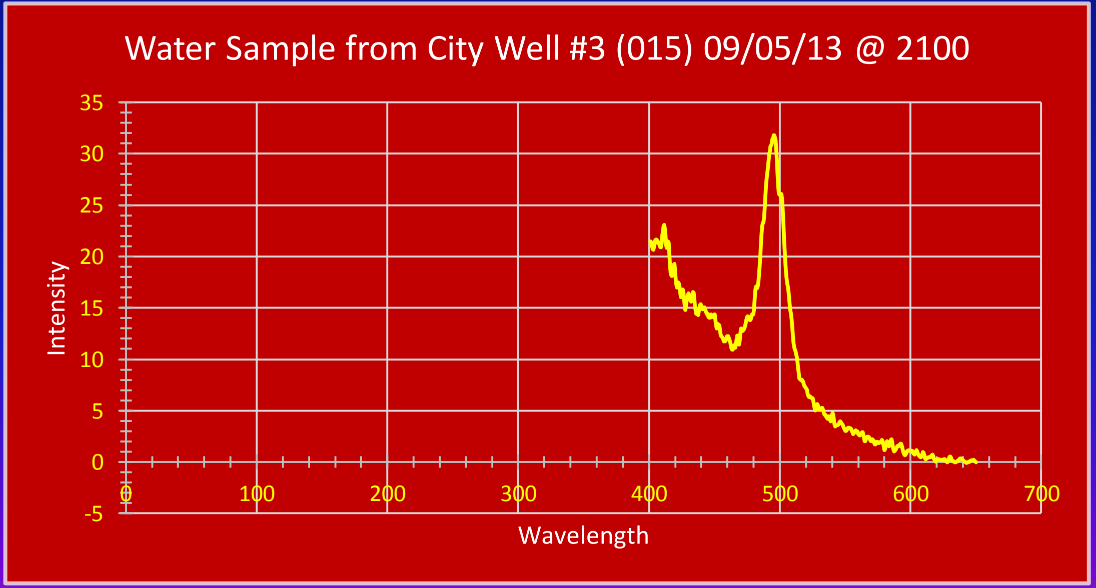


Figure 17. Dye spectral "fingerprints" obtained from use of the synchronous scanning method: *A*, no fluorescent tracer dye is present; *B*, sodium fluorescein (or uranine) tracer dye is present; *C*, Rhodamine WT tracer dye is present; *D*, sodium fluoresein and Rhodamine WT tracer dyes are present (after Vandike, 1992).

Minimum Detection Limit

- According Rosenberry and LaBaugh (2008, pg. 96), a typical value for tracer detection using spectrofluorometric instrumentation is 0.002 micrograms per liter (µg/L)
- When utilizing the calibration curve/regression formula to convert intensity units into concentration values (µg/L), an intensity of 30-35 would equate to approximately a value between 0.5-0.6 (µg/L)
  - With an R^2 (correlation coefficient) of nearly 1 (0.95-0.99), in my opinion, this graph indicates the presence of Uranine dye or a similar fluorescing substance



Conclusion of Dye Test

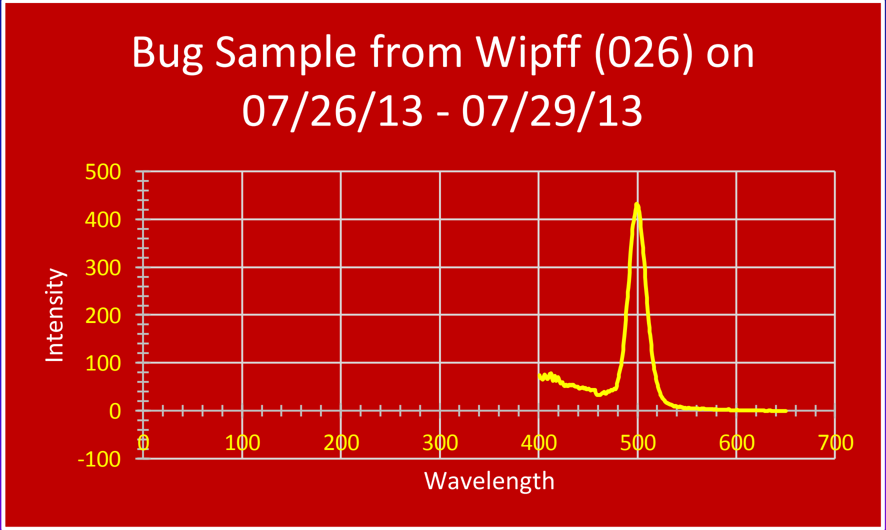
- Finally reached a point where we were not obtaining any confirmation of the presence of the dye
- Interpreting the results
  - Rethinking initial results of the study
  - Data collected showed dye peaks were shifted, out of range for the dye we were using
  - After re-examination of the raw data, only 3 locations now believed to have exhibited presence of dye

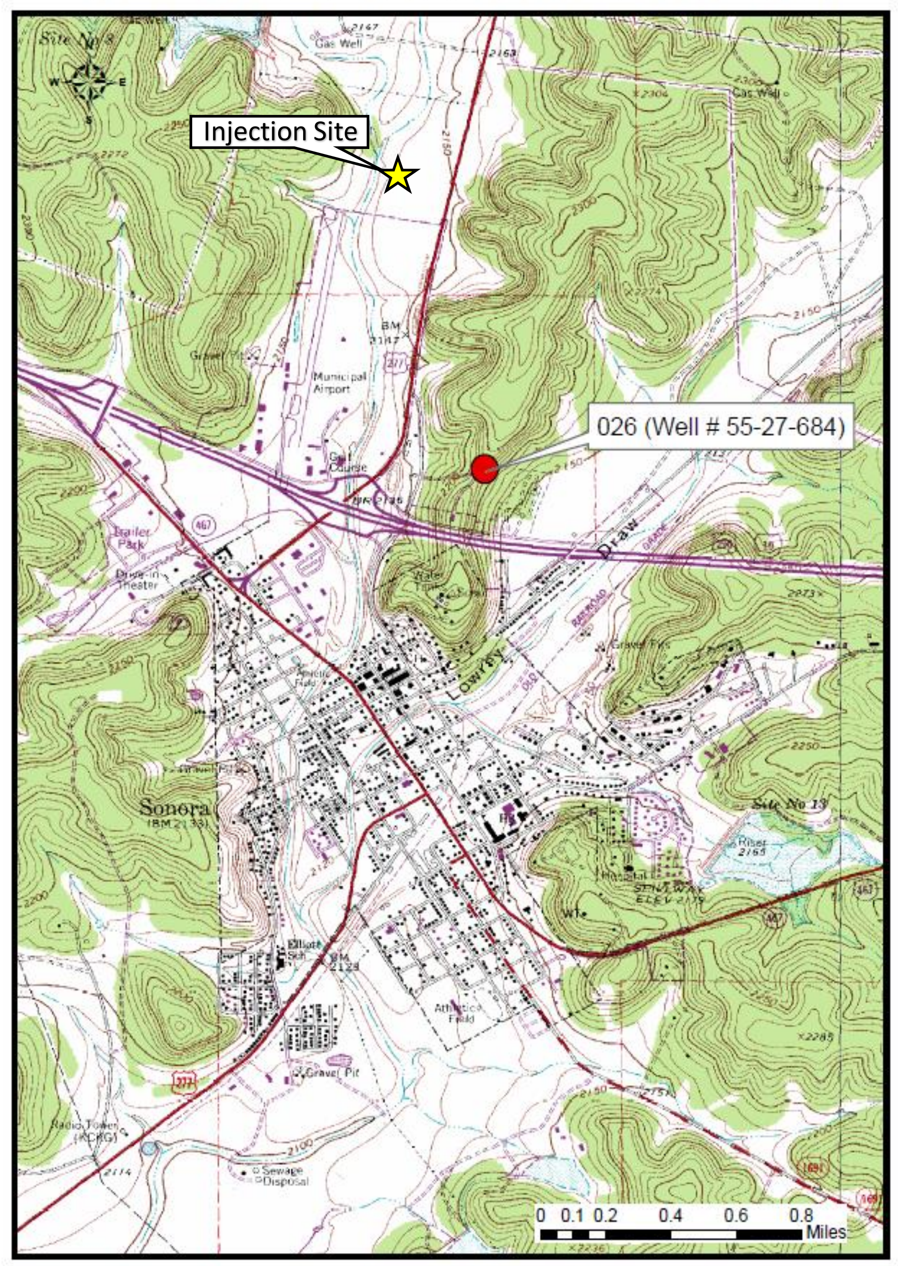
Results of the Testing

- Locations of dye occurrence
  - Wipff Well (026)
  - Golf Course Well (014)
  - City Well # 3 (015)
- Not enough information to run *quantitative* analysis using QTRACER II program which can elucidate goals of study
  - How fast does it flow –transmissivity?
  - What volume of water flows through this area?
  - What is the storage capability of the aquifer at this point?
- Can use qualitative data during planning process of future dye study

Positive Dye Hits for the Wipff Well (026)

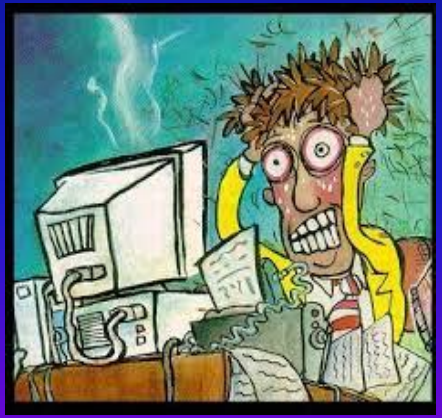
- Positive dye hits observed at this location **6** times
  - 07-26-13 to 07-29-13 with an intensity of 430 at a wavelength of 499
  - 07-31-13 to 08-02-13 with a trace intensity of 63 at a wavelength of 494
  - 08-05-13 to 08-07-13 with an intensity of 300 at a wavelength of 494
  - 08-07-13 to 08-14-13 with an intensity over 1007 at a wavelength between 480-520 (off the chart)
  - 08-21-13 to 08-27-13 with an intensity over 1007 at a wavelength between 480-520 (off the chart)
  - 08-27-13 to 09-04-13 with an intensity of over 1007 at a wavelength between 480-520 (off the chart)





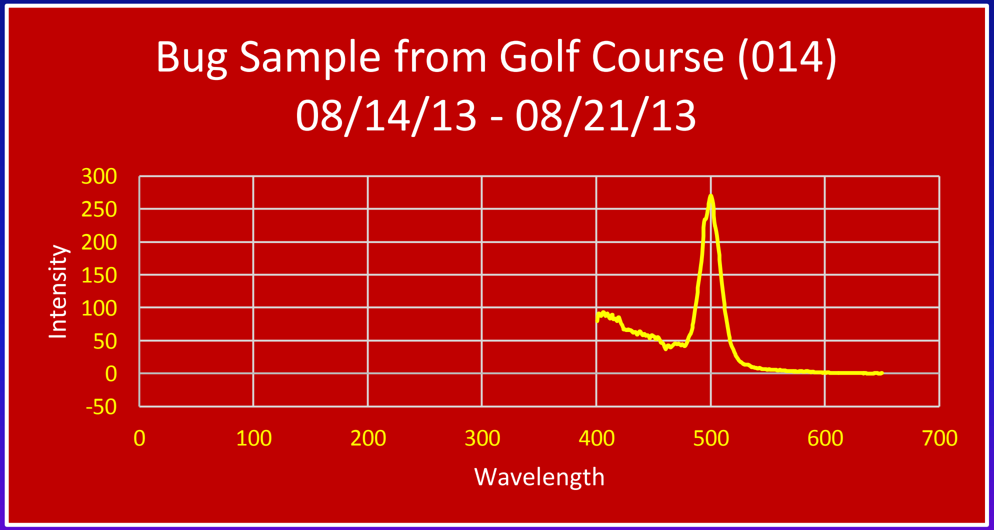
Problems with the Wipff Well

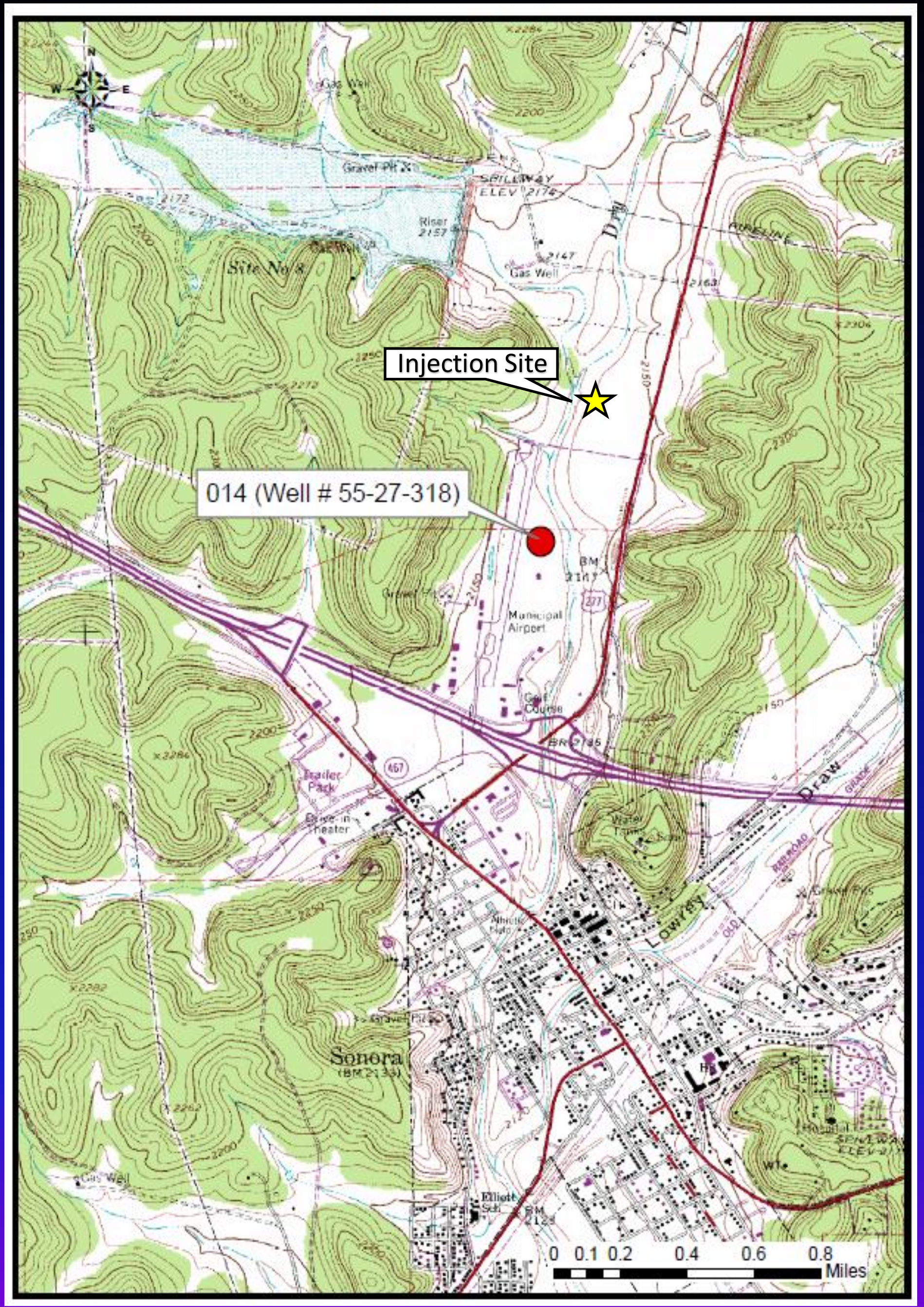
- This residential well was used inconsistently with the electricity to the pump turned off intermittently during the study due to unforeseen residential renovations.
- In future studies, it would be extremely useful to include this sample site again as it does demonstrate connectivity to both the aquifer and injection site
  - Care **MUST** be given to ensure continual water flow to the charcoal receptacle in order to fully extrapolate the pertinent information this location can yield
- Too many variables with this data to utilize with QTRACER II program
  - Cannot generate accurate breakthrough curve given all the inconsistencies



Positive Dye Hits for the Golf Course Well (o14)

- Positive dye hits occurred at this location **6** times
  - 08-02-13 to 08-07-13 with a trace intensity of 97 at a wavelength of 497
  - 08-07-13 to 08-14-13 with an intensity of 195 at a wavelength of 499
  - 08-14-13 to 08-21-13 with an intensity of 262 at a wavelength of 499
  - 08-21-13 to 08-27-13 with a trace intensity of 84 at a wavelength of 499
  - 08-27-13 to 09-04-13 with an intensity of 119 at a wavelength of 498
  - 09-04-13 to 09-10-13 with an intensity of 258 at a wavelength of 599



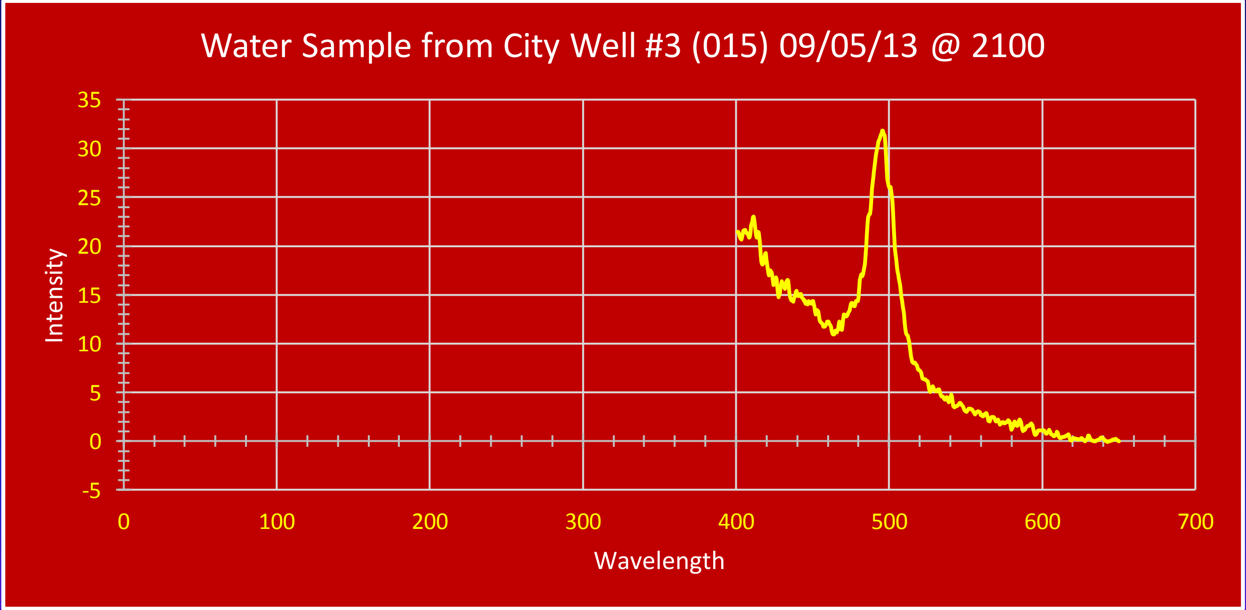


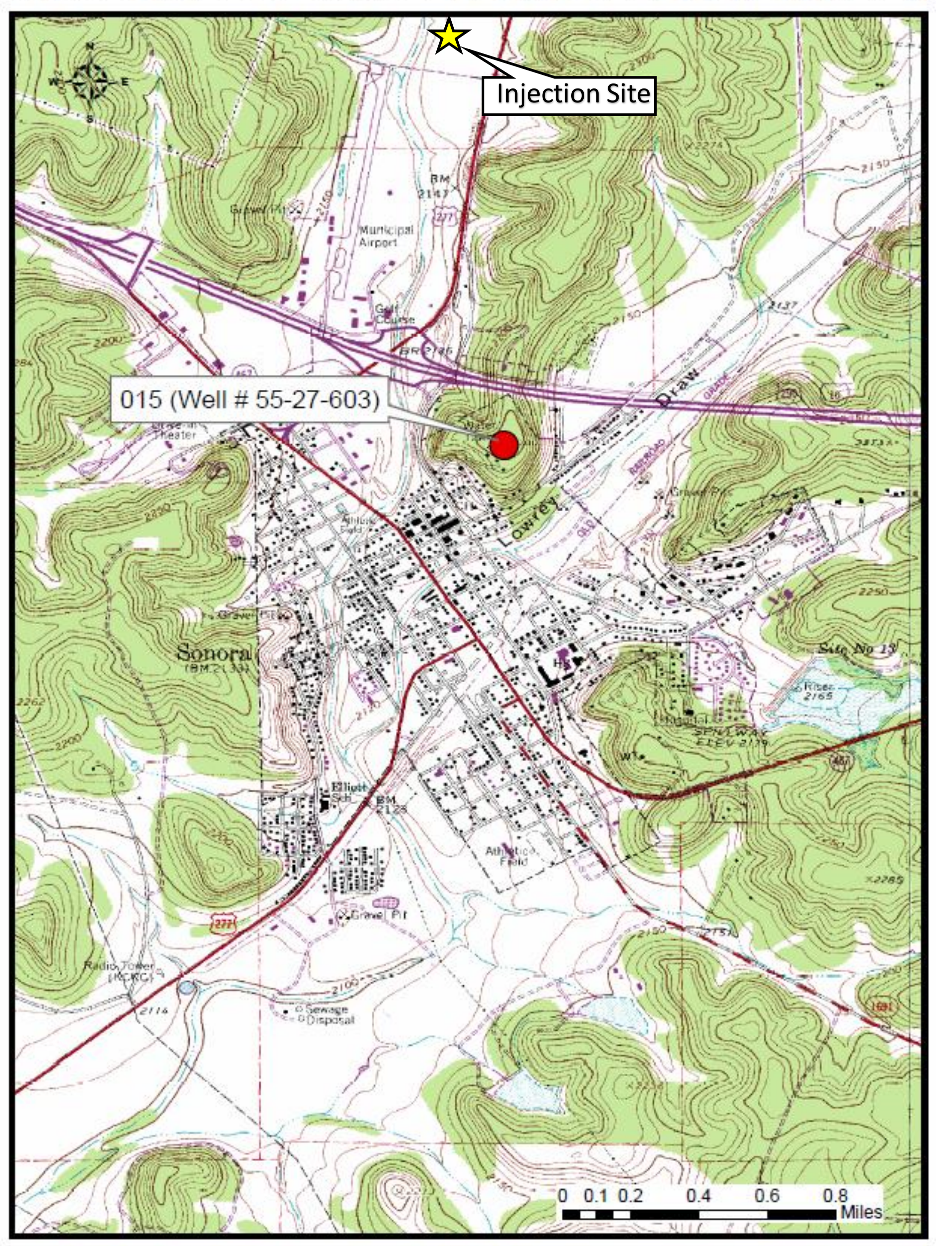
Problems with the Golf Course Well (014)

- The water within this storage tank is used for ground maintenance and therefore has a high, yet variable, turn-around rate
- Care should be given when interpreting the qualitative patterning of positive dye hits from this sample site
  - Due to its submergence
  - Potential inconsistent amounts of water pumpage (corresponding to lawn care needs)
    - Variable duration of water storage within the tank
  - Potential cross-contamination of residual dye concentrations remaining in the stored water from one sample cycle to the next
- Too many variables with this data to utilize with QTRACER II program
  - Cannot generate accurate breakthrough curve given all the inconsistencies

Positive Dye Hits for the City Well # 3 (015)

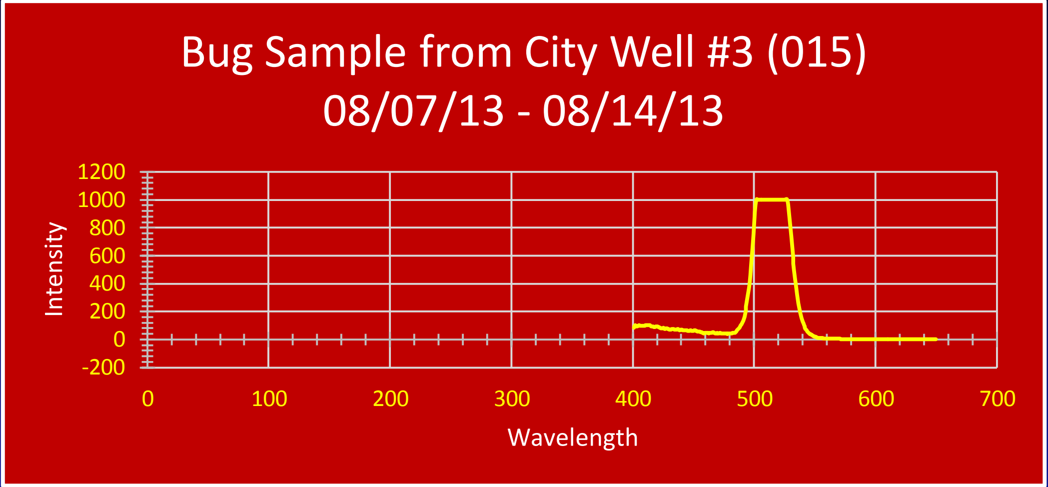
- Positive dye hits occurred at this locate at least once!

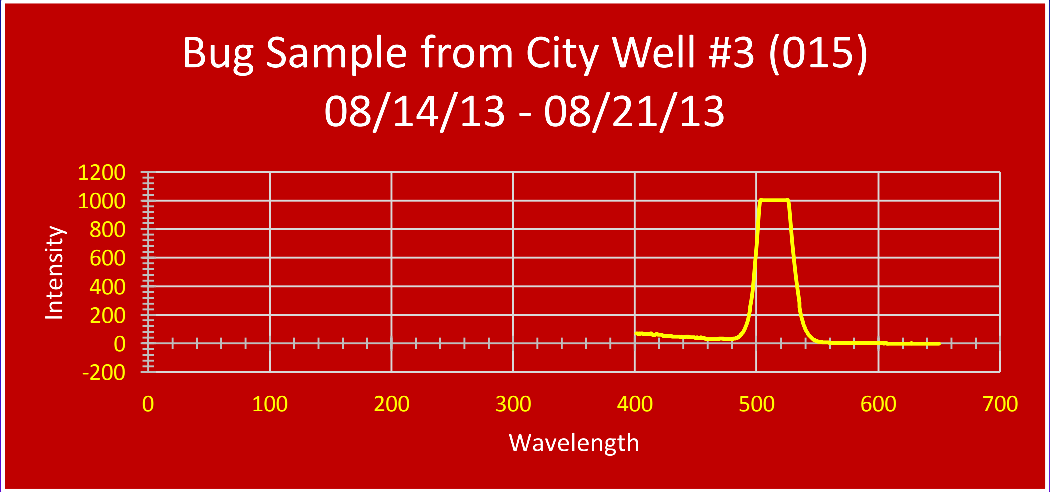




Problems with the City Well # 3 (015)

- Other potential hits are indeterminate because the readings are off the chart
  - Very frustrating because we have excellent pumpage reports for this well provided by the city





Lessons Learned

- Concentrate efforts at locations previously determined to have dye present
  - Obtain pumpage data for these critical locations
  - Deploy automated water samplers at these locations and begin data collection immediately after injection in smaller time intervals
  - Ensure water flow to the charcoal packets at these crucial locations!
- Minimum Detection Limit set according to professional standards used
- Consistent interpretation of spectrofluorometric scans is a must
- But hey, this was our first rodeo!