

PEDERNALES FALLS STATE PARK SPRING DYE TRACE PROJECT

*Determining the Source of the Spring at
Pedernales Falls State Park*

The Meadows Center for Water and the Environment
October 2017



Photo by Jenna Walker



THE MEADOWS CENTER
FOR WATER AND THE ENVIRONMENT

TEXAS STATE UNIVERSITY

Douglas A. Wierman P.G., Researcher, Fellow
Jenna Walker, M.A. Geo., Researcher
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Performing Agency:

Texas State University, and
Meadows Center for Water and the Environment

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FOR WATER AND THE ENVIRONMENT
TEXAS STATE UNIVERSITY



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LIST OF ACRONYMS

BSEAGD: Barton Springs Edwards Aquifer Conservation District

CFS: Cubic Feet per Second

COAWPD: City of Austin Watershed Protection Department

EAA: Edwards Aquifer Authority

HTGCD: Hays Trinity Groundwater Conservation District

GIS: Geographic Information Systems

OUL: Ozark Underground Laboratory

PFSP: Pedernales Falls State Park

RM: Ranch to Market Road

TPWD: Texas Parks and Wildlife Department

USGS: United States Geological Survey

EXECUTIVE SUMMARY

The results of this dye trace study confirm that the source of the spring at the base of the falls at Pedernales Falls State Park (PFSP) is mainly a diversion of river water through a swallet or sink upstream of the park originating in the Marble Falls Formation. Continuous monitoring with a field fluorimeter, charcoal samplers and grab samples of water collected at the spring detected fluorescein dye poured near the area of the swallet. Dye breakthrough at the spring indicated a travel time of approximately 15.5 hours over a 2.4 mile distance.

BACKGROUND AND PURPOSE

Streamflow gain/loss studies conducted by the United States Geological Society (USGS) (Holland and Hughes, 1964) and The Meadows Center for Water and the Environment (The Meadows Center) (Wierman, et al, 2017) (Figure 1) indicate that the Pedernales River is an overall gaining stream. During the 2016 study, a losing reach was noted upstream of PFSP with significant gains occurring downstream of the park. There is a large spring at the base of the falls at the park. According to Brune (1981), the source of the water at the spring is likely a local “diversion” of water from the river several miles upstream of the park that returns to an otherwise gaining reach of the river via the spring. Brune and anecdotal information from long time local residents indicated that the losing feature (swallet) was immediately downstream of what remains of the old Robinson ranch house which was destroyed during the flood of 1952. The feature has been observed at the bottom of the lake formed by the river (Figure 2).

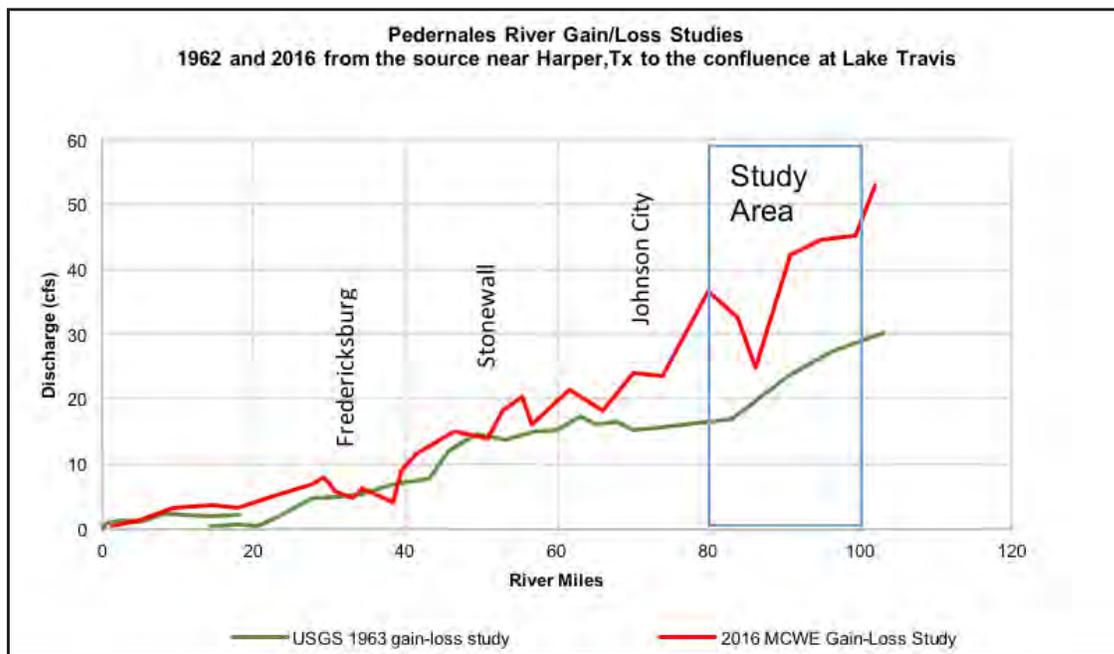


Figure 1. Pedernales River Gain-Loss Studies 1962 and 2016 (Wierman, et al., 2017).



Figure 2. Location of Swallet at the Bottom of the Lake. Photo by Brian Hunt.

STUDY AREA

The dye trace study area is located in the eastern portion of the Pedernales River watershed in Blanco County (Figure 3). The area is 28.20 total square miles and includes PFSP. The reach of the river within the study area is approximately 7 miles in length from Pedernales Hills Road to the swimming area at PFSP (Figure 3). The USGS gauge at Johnson City, TX (USGS 08153500) is approximately 10 miles upstream of the study area and was used as a benchmark for stream flow measurements. The only main road to access the study area is Ranch to Market Road (RM) 2766. Public access to some sites was available via Pedernales Hills Road and Park Road 6026. Private access was required for river sites that were only accessible through private property. Prior permission was obtained to access and conduct studies within the park and private properties. Table 1 and Figure 4 provide details on the PFSP dye trace study monitoring sites.

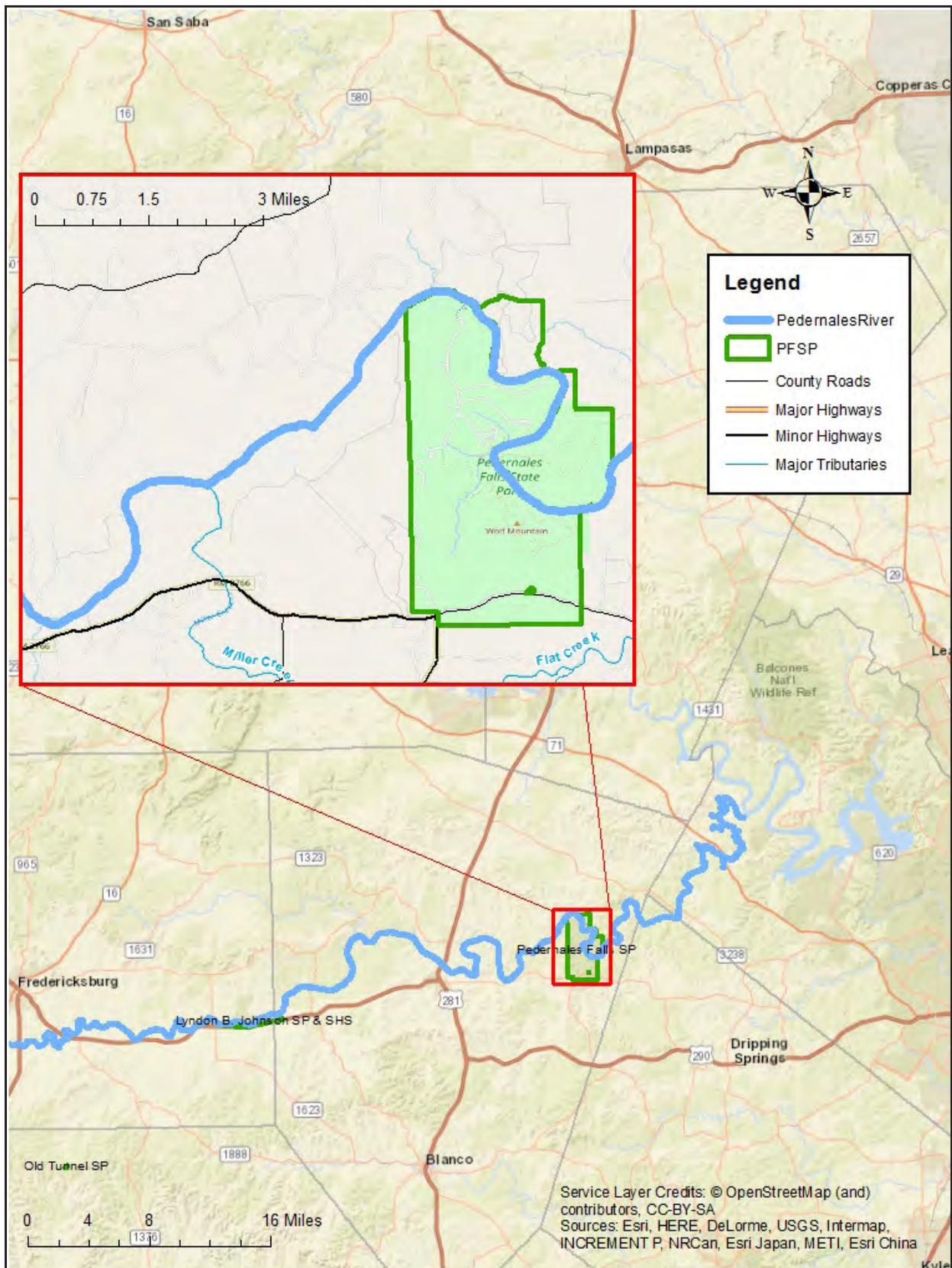


Figure 3. Dye Trace Study Area.

Table 1. Dye Trace Monitoring Sites Details.

Site Name	Latitude	Longitude	MSL (ft.)	River Mile
Robinson (BM1) Background Monitoring and Dye Injection Site	30.313629	-98.281067	897	85
MP1 Monitoring Site Falls @ PFSP	30.32972	-98.26806	888	86.5
MP3 Monitoring Site Spring @ PFSP	30.338041	-98.251373	836	87.8
MP4 Monitoring Site PFSP Swim Area	30.337621	-98.251376	820	88
MP5 Monitoring Site	30.311175	-98.239456	778	90.7

Note: River miles based on Google Earth measurements from headwaters near Harper, TX. MP2 excluded from study area.

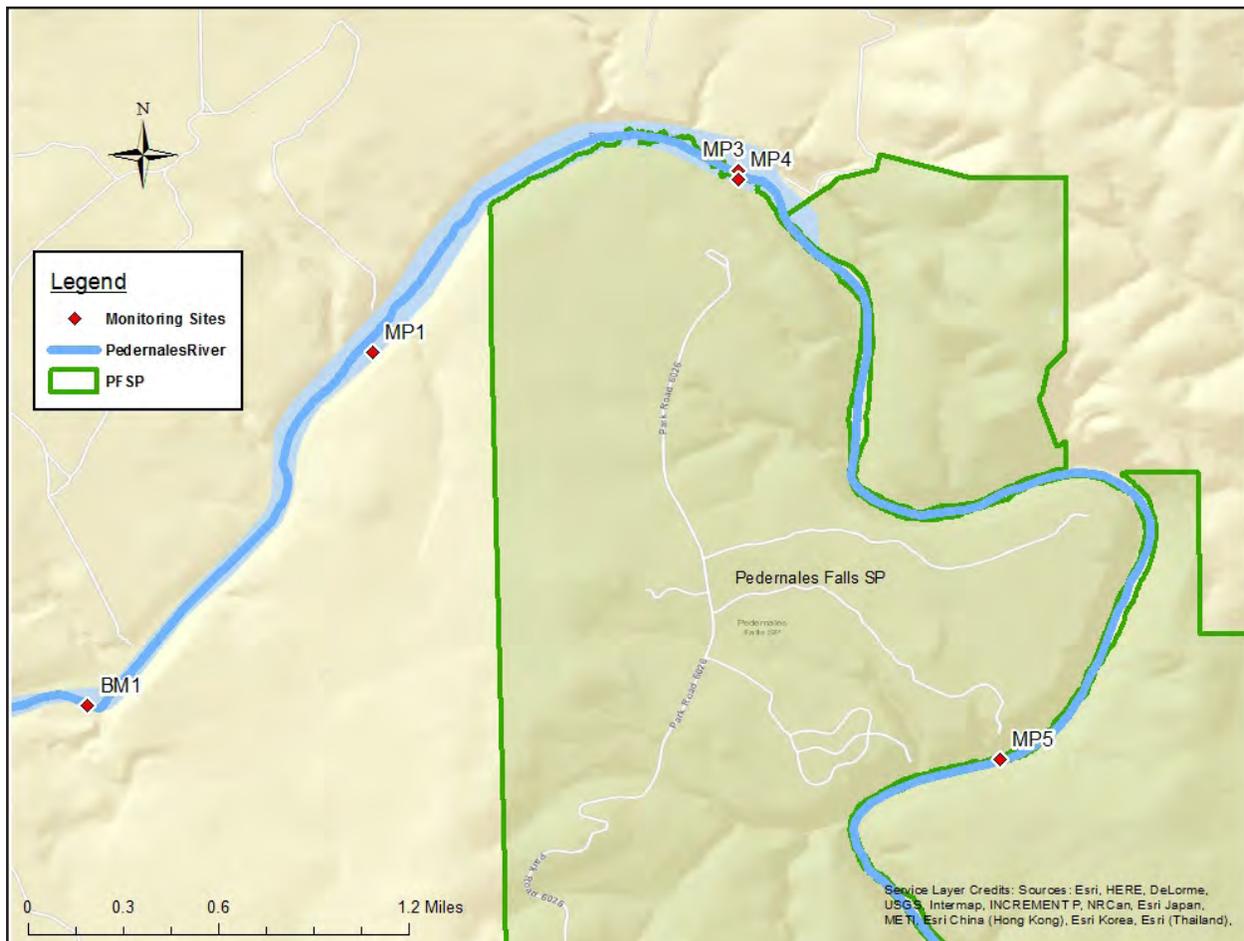


Figure 4. PFSP Spring Dye Tracing Monitoring Sites Map.

GEOLOGIC SETTING

The geologic units exposed in the study area range in age from Paleozoic to Quaternary (Figures 5 and 6). Pennsylvanian-age Marble Falls limestone crops out along both banks of the river upstream of PFSP and is the geologic unit underlying the falls at the park (Barnes, 1982; Barnes, 1982a; and Barnes, 1963). This unit generally dips to the southeast at approximately 10 degrees. The Marble Falls is dark-gray limestone containing large crinoid fossil columnar. Caves are present on both sides of the river near the western boundary of PFSP indicating some karst development (Figure 7). The main unit underlying the Marble Falls are the rocks of the Ordovician-age Ellenburger Group, a group of limestone and dolomite units. Numerous southwest/northeast trending parallel faults have been mapped, but do not appear to propagate up into the Marble Falls.

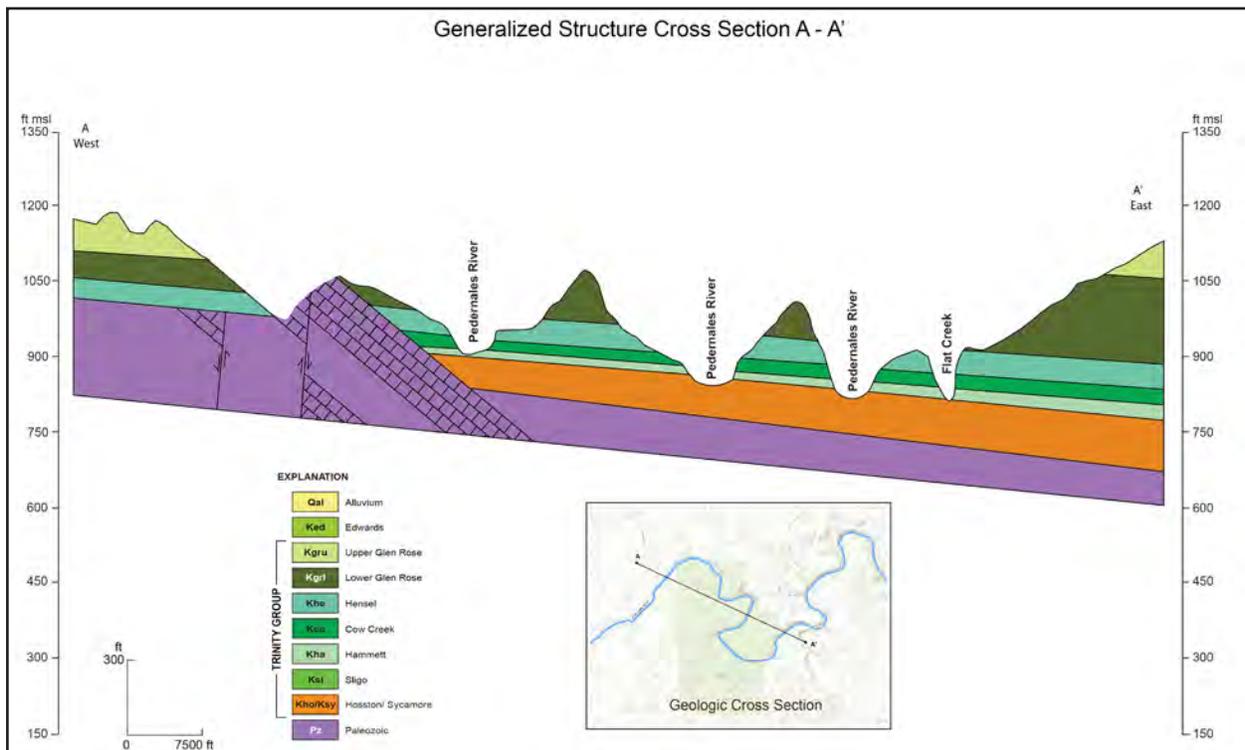


Figure 5. Generalized Structure Cross Section (Wierman et al., 2017).

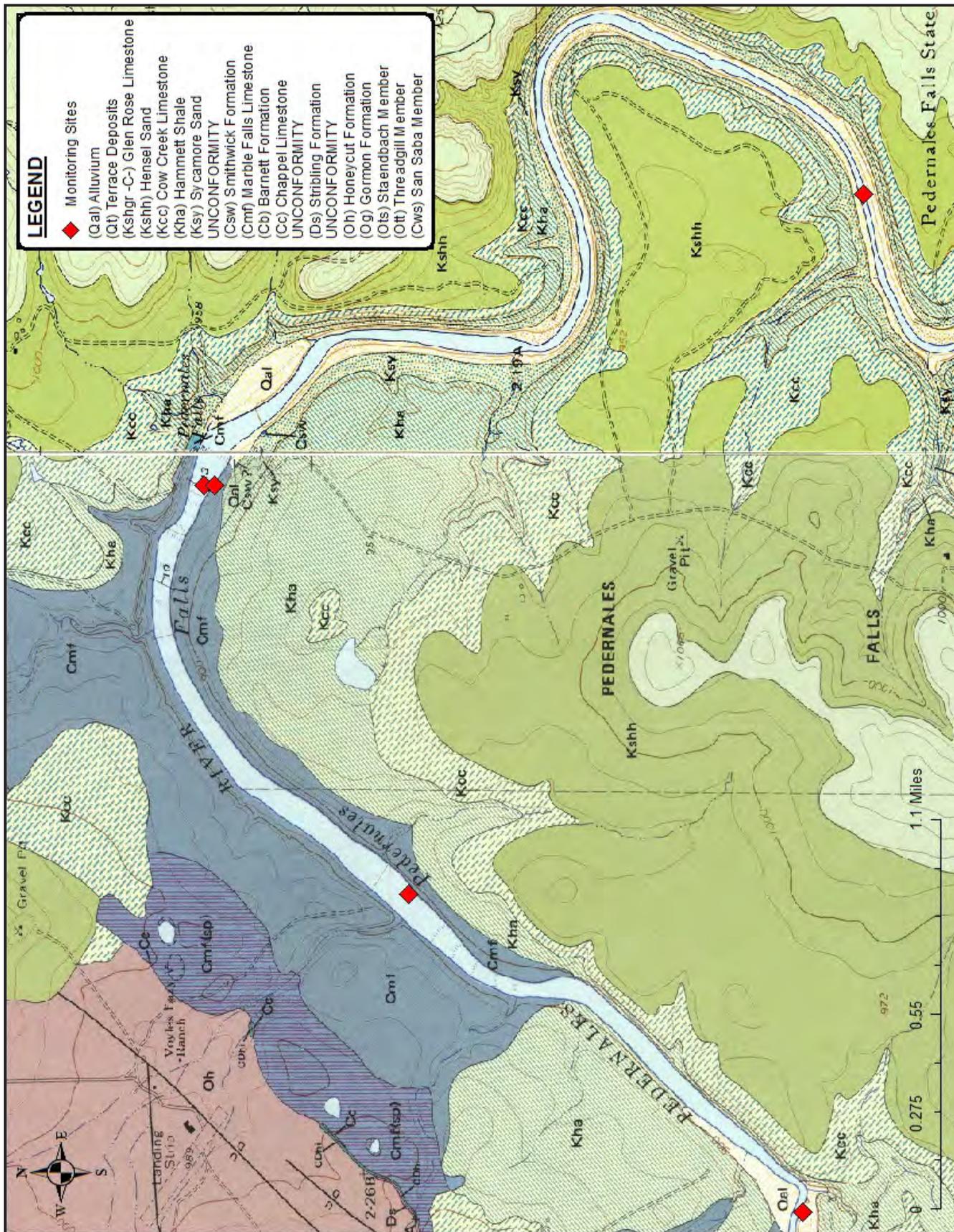


Figure 6. Pedernales Falls and Hammetts Crossing Geologic Map (Barnes, 1982, 1982a).



Figure 7. Cave in Marble Falls Formation. Photo by Doug Wierman.

Several of the beds of the Marble Falls Formation contain numerous fractures (Figure 7). The primary fracture set is nearly vertical and trends southwest to northeast at approximately N60E.



Figure 8. Fractures in the Marble Falls Formation. Photo by Doug Wierman

Along the southern side of the river upstream of PFSP and dominating the entire watershed downstream of the park are the Cretaceous-age units of the Trinity Aquifer. The Trinity section, from oldest to youngest, is composed of the Hammett Shale, Cow Creek Limestone, Hensel Sand and the Upper and Lower units of the Glen Rose Limestone (Barnes, 1982; Wierman et al, 2010) and lies unconformably on the older Paleozoic strata with the contact parallel to the river, trending southwest to northeast. These units have a slight dip to the southeast. The river has deeply incised the entire Trinity section which is exposed in outcrop from PFSP to Hammetts Crossing and in varying degrees in the major tributary valleys (Figure 6). The Lower Glen Rose, Hensel and Cow Creek comprise the Middle Trinity Aquifer. The Cow Creek pinches out in the study area and is not present in the western part of the study area (Figure 5). Similarly, the Sycamore formation, which is exposed in the deeper river and tributary valleys and makes up the Lower Trinity Aquifer, also pinches out against the Paleozoic strata.

Groundwater provides base flow to the river (Wierman, 2017). There are numerous documented springs along the north side of river originating from the Ellenburger Group, including springs near Honeycut Bend, the Winkler ranch (former Voyles Lazy V Ranch) and at PFSP (Figures 9 and 10) (Barnes, 1982 and Brune, 1981).



Figure 9. Exposed Outcrop of Marble Falls Fm at PFSP). Photo by Brian Hunt.



Figure 10. Spring at PFSP. Photo by Doug Wierman.

METHODOLOGY

The following parties partnered with The Meadows Center during various phases of the study:

- Barton Springs Edwards Aquifer Conservation District (BSEACD),
- City of Austin Watershed Protection Department (COA),
- Edwards Aquifer Authority (EAA),
- Hays Trinity Groundwater Conservation District (HTGCD), and
- Texas Parks and Wildlife Department (TPWD).

The Meadows Center met with private landowners and TPWD officials at PFSP to discuss the purpose of the dye trace study and arrange property access during the dye trace study period. See Appendix A for the PFSP permit (Permit # 2017-R3-11) and public notice documents. Fluorescein dye (Acid Yellow 73, CAS Number 518-47-8), charcoal samplers, and water bottles were provided by Ozark Underground Laboratory (OUL). Fluorescein is a non-toxic green, fluorescent dye commonly used in subsurface dye trace projects in karst areas. OUL provided laboratory services for analyzing water and charcoal samples. BSEACD provided and monitored a field fluorimeter placed in the spring during the study. OUL dye tracing procedures were generally followed as shown in Appendix B (Aley and Beeman, 2015).

The major project elements include the following:

- Stream discharge Measurements
- Background monitoring
- Temperature logger at MP4
- BSEACD fluorimeter at MP4
- Dye injection at site BM1
- Daily/weekly collection of charcoal samplers and grab samples of water at
- MP1, MP3, MP4, and MP5

Stream Discharge Measurements

During previous gain/loss studies, the intervals between discharge monitoring points were up to five miles apart. Two rounds of discharge measurements were made in the study area prior to dye injection to help “fine tune” the losing reach of interest. The multiple channels and dipping geologic beds of the river in the study area make it challenging to find representative stream gauging sites as shown on Figure 11. The discharge measurement details are shown in Table 2 and Figure 12.

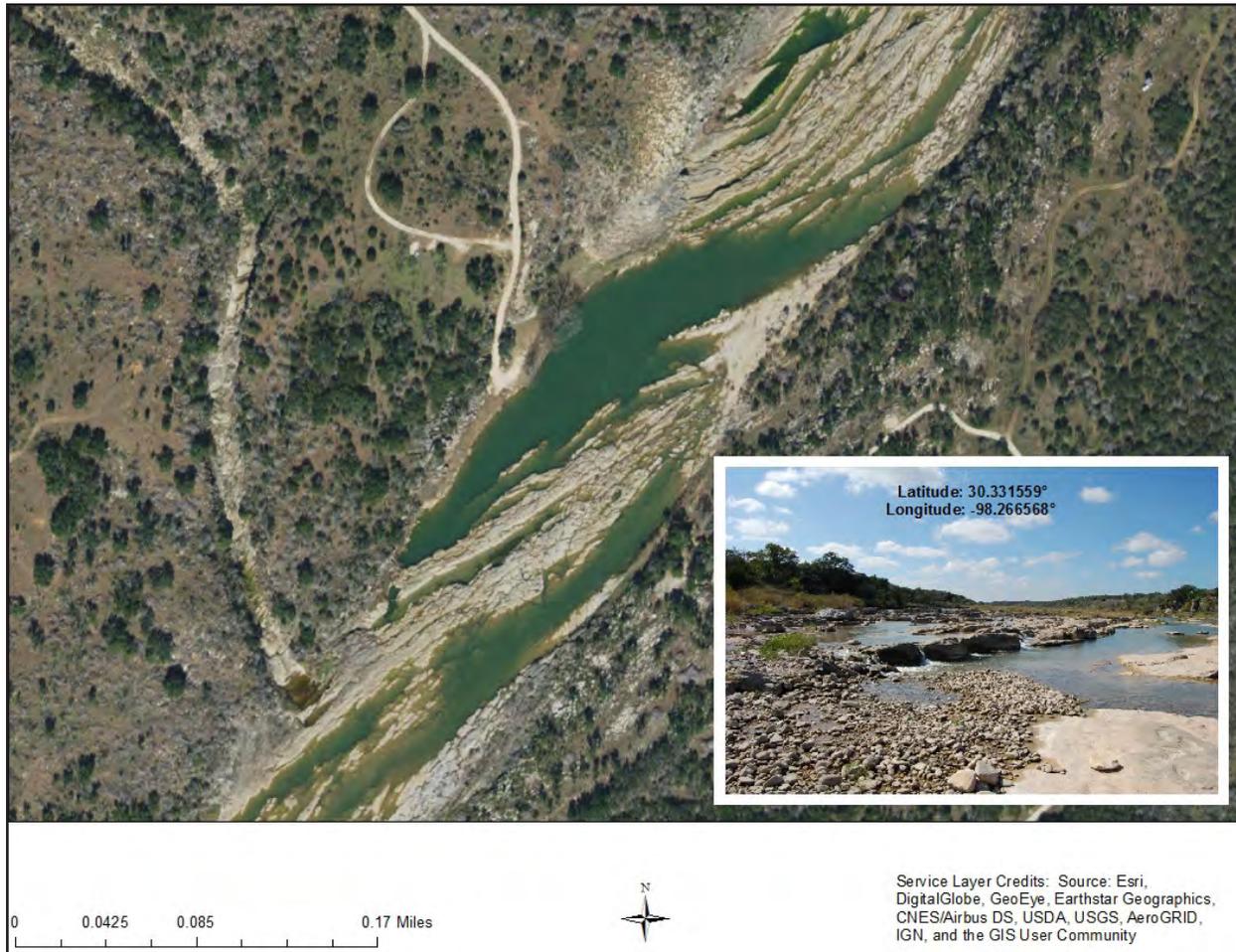


Figure 11. Complex Channels of the Study Area. Photo by Doug Wierman.

Table 2. Discharge Measurement Site Results

Site	Lat.	Long.	MSL (ft.)	Flow (CFS) 7/27/17	Flow (CFS) 8/21/17	River Mile
USGS 08153500 @ Johnson City, TX	30.291410	-98.400347	1109	35	18	70
Pedernales Hills Road Bridge	30.278035	-98.33469	987	8.2	9.5	80
Robinson (BM1) Dye Injection Site	30.313629	-98.281067	897	18.3	13.5	85
Falls @ PFSP MP3	30.338041	-98.251373	836	11.32	7.7	87.8
Spring @ PFSP MP4	30.337621	-98.251376	820	15.7	15.7	88
PFSP Swim Area MP5	30.311175	-98.239456	778	19.77	19.3	90.7

Note: River miles based on Google Earth measurements from headwaters near Harper, TX.

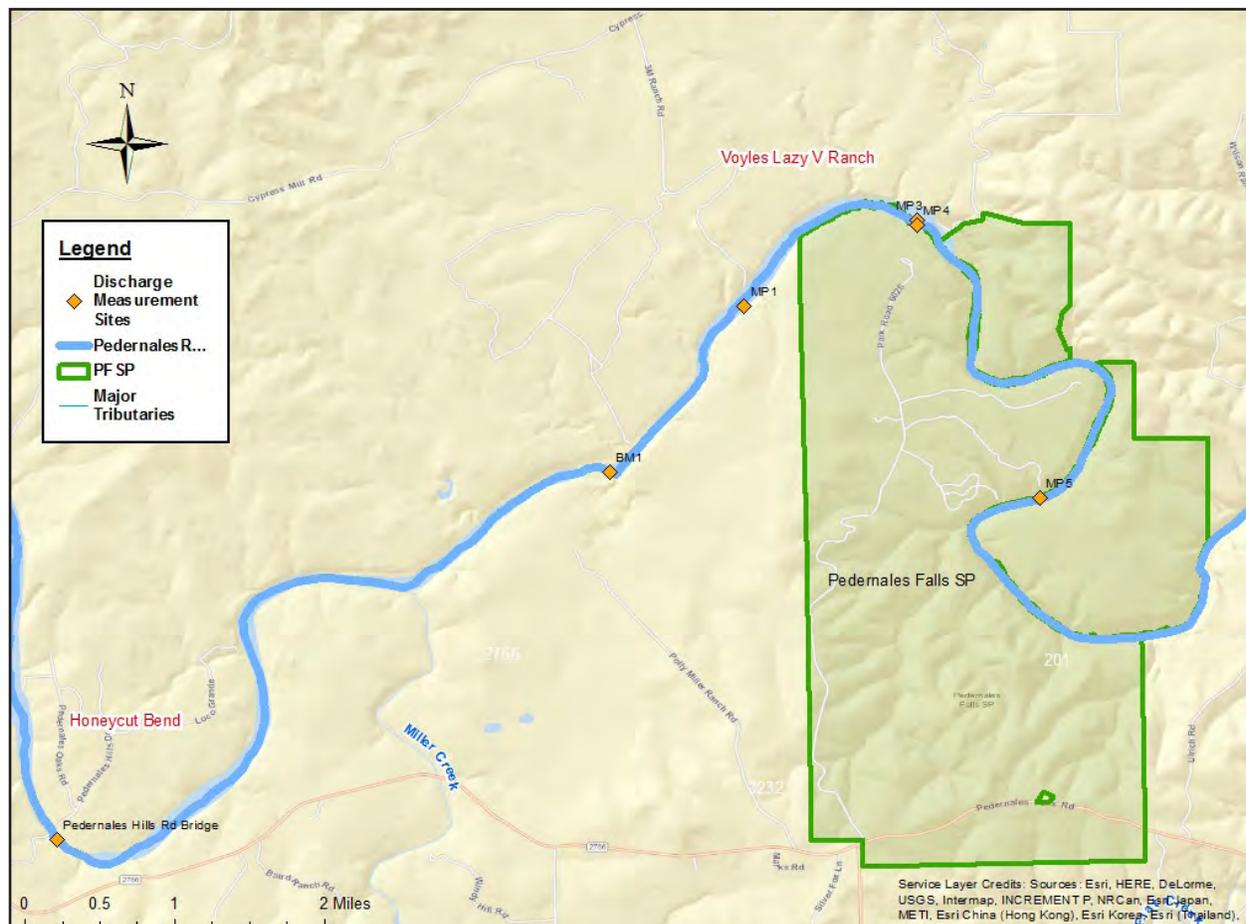


Figure 12. PFSP Spring Dye Tracing Discharge Measurement Sites.

Background Monitoring

Background monitoring is important in order to determine potential background levels of dye and the amount of dye that should be mixed for detection at monitoring sites. Fluorescent interference is typically found in small traces in rivers due to suspended solids, naturally occurring organic material, or man-made sources such as laundry detergent or anti-freeze (Alley, 2002). This fluorescent interference can be near the detection range of fluorescein dye and could potentially give false detections.

The background monitoring was conducted one week prior to dye injection. Charcoal samplers were deployed from 8/14/2017 to 8/21/2017. Activated charcoal samplers are cost effective and are able to absorb dyes and release them when eluted in a laboratory (Alley, 2002). The schedule for background monitoring is shown in Table 3. Charcoal samplers were attached to a concrete anchor and placed at sites BM1 and MP4 and left in place for a week.

In order to understand daily temperature variations between the surface and groundwater, Onset Hobo temperature loggers (Figure 13) were also placed at BM1 and MP4. The loggers were placed on 8/14/17 and removed and analyzed on 8/21/17. The logger at MP4 was placed several yards downstream of the spring discharge.

BSEACD placed a fluorimeter (Eureka Manta 2 with Cyclops Submersible Fluorescein Sensor by Turner Designs) calibrated to fluorescein at MP4 several hours prior to dye injection on 8/21/2017 and left in place throughout the dye trace study period (Figure 14).

Dye Injection

Fluorescein dye was injected at site BM1 at 15:00 on 8/21/2017 (Figures 15 and 16). The team followed the OUL dye tracing procedures shown in Appendix B (Aley and Beeman, 2015). Wearing personal protective equipment (PPE), two members of the field crew mixed three pounds of powdered fluorescein dye (75% As Sold) river water in two 5-gallon buckets and poured it into the river upstream of the suspected losing feature.



Figure 13. Onset Hobo Temperature Logger. Photo by Jaime Moreno.



Figure 14. BSEACD Fluorimeter at PFSP Spring. Photo by Brian Hunt.



Figure 15. Dye Injection Team. Photo by Chad Norris.

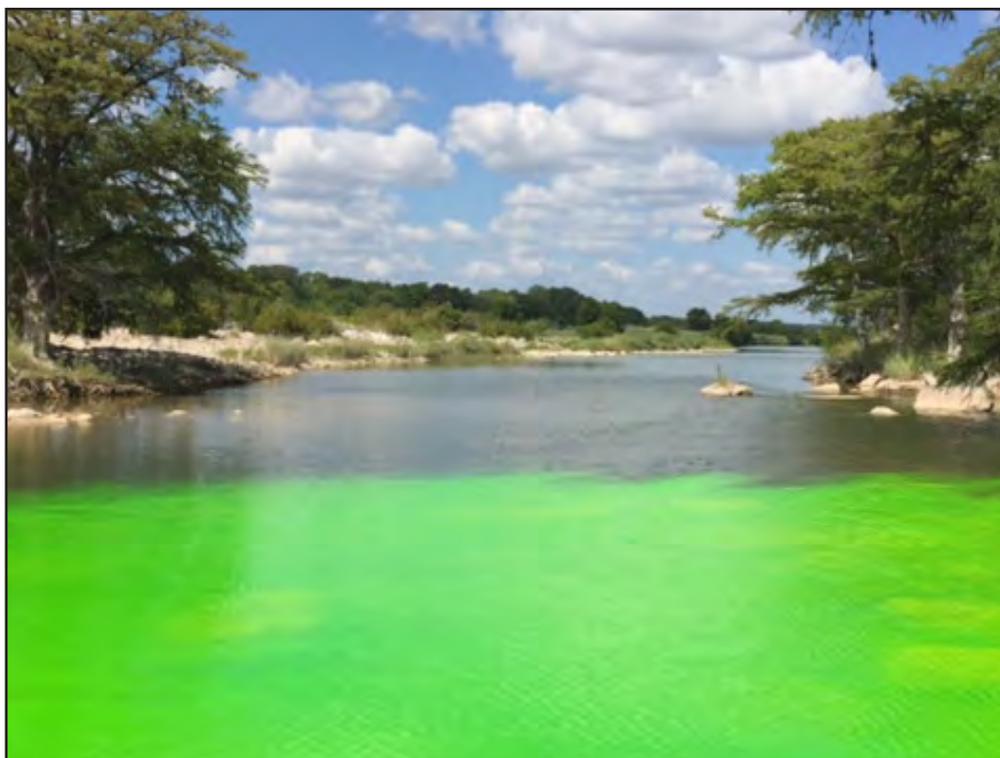


Figure 16. Dye Flowing Past Site BM1. Photo By Jaime Moreno.

Daily/Weekly Sampling

Daily/weekly collection and replacement of charcoal samplers were conducted following the schedule outlined in Table 3. Two charcoal samplers were placed at each site as shown in Figure 17. Duplicate water samples were also collected at each site. The original schedule for the program included sampling for several weeks after dye injection. Significant rainfall from Hurricane Harvey necessitated ending the program after one week. Charcoal samplers and grab samples of water were collected using latex gloves and carefully placed in Whirl-Pak sampling bags. All bags were labeled and documented as shown in Appendix B. See Figure 18 for daily sampling materials required.

Charcoal and water samples are easily diluted by light radiation and heat. Charcoal samplers and grab samples of water were stored in a sealed ice chest and kept cool using blue ice packs.

After completion of the project, The Meadows Center shipped the ice chest to the OUL laboratory in Protem, MO. Laboratory results are included in Appendix A.



Figure 17. Daily Charcoal and Water Sampling at MP1.
Photo by Doug Wierman.



Figure 18. Materials Required for Sampling.
Photo by Jaime Moreno.

Table 3. Dye Trace Study Schedule of Events

Background Monitoring 8/14/17-8/21/17; Dye Injection: 8/21/17; Daily Charcoal and Water sampling: 8/21/17-8/28/17

Monitoring Point	Background Monitor	Charcoal (Duplicates)	Water	Other
Robinson (BM1) Dye Injection Site	Yes	One week prior to dye injection	Sample one week prior to dye injection	Temperature monitoring during background sampling, flow measurement at injection
MP1 Monitoring Site	No	Daily for 7 days after injection	Sample at each charcoal change out.	N/A
Falls @ PFSP MP3 Monitoring Site	No	Daily for 7 days after injection	Sample at each charcoal change out.	Flow measurement at injection
Spring @ PFSP MP4 Monitoring Site	Yes	One week prior to dye injection, every 12 hours for 7 days after injection	Sample at each charcoal change out.	Temperature monitoring during background sampling and after dye injection, flow measurement at injection. BSEACD fluorimeter installed at spring location.
PFSP Swim Area MP5 Monitoring Site	No	Daily for 7 days after injection	Sample at each charcoal change out.	Flow measurement at injection

RESULTS

Stream Discharge Measurements

As shown on Figure 19, stream flow measurements were taken near historic median flow levels. Discharge measurements observed during the study indicate a gaining reach between Pedernales Hills Road and the Robinson site (BM1) with gains between 4 and 10 cubic feet per second (cfs) (Table 2). The springs mentioned in Brune and Barnes near Honeycut Bend probably account for the gain. There was a consistent ~7 cfs loss between BM1 and MP3, at the top of the falls at PFSP. BM1 is located just upstream from the assumed swallet in the bottom of the river. The discharge from the spring (MP4) was 15.7 cfs on both measurement dates. Downstream of the spring, discharge was approximately 19.5 cfs. There was a 7 cfs loss between BM1 and MP4.

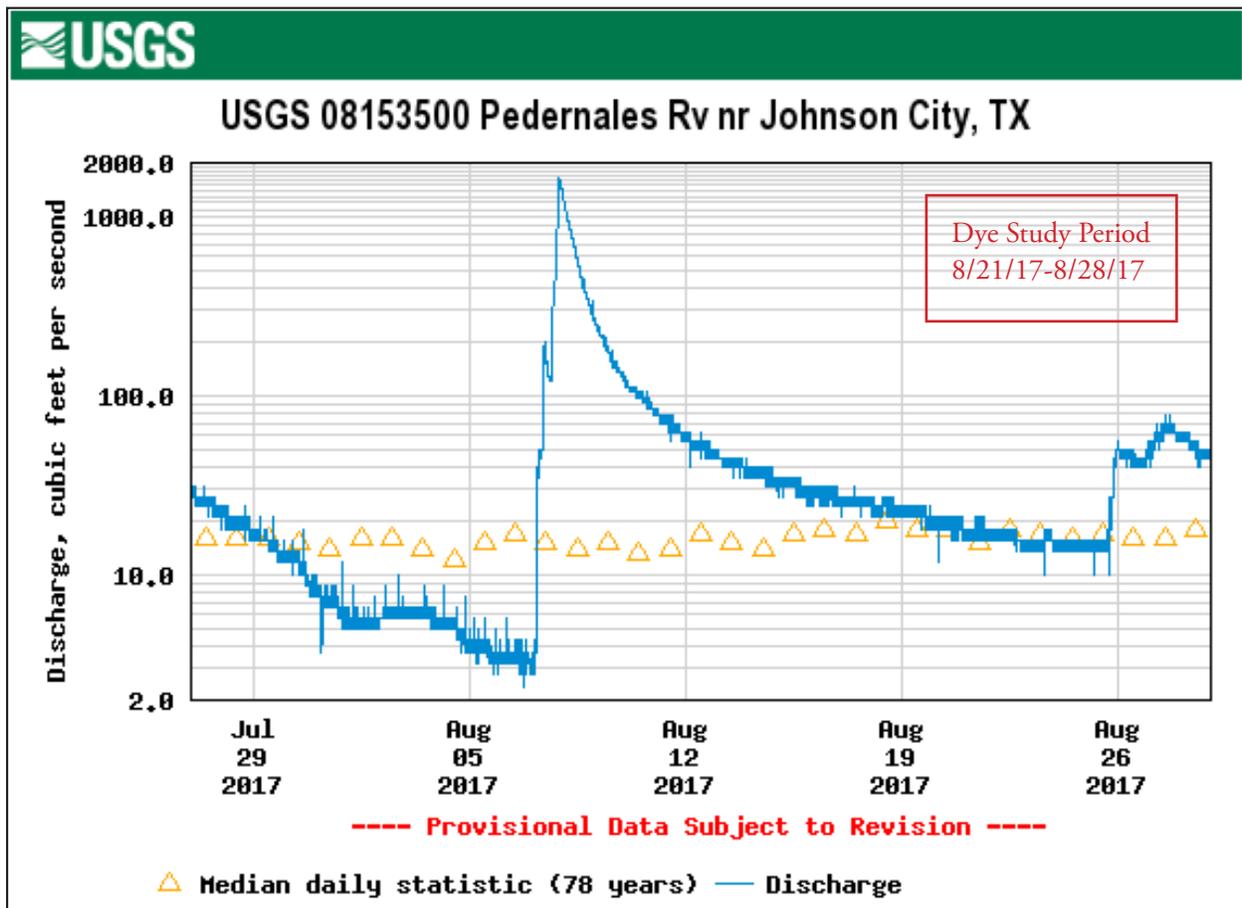


Figure 19. USGS 08153500 Discharge Data during the Study Period.

Charcoal and Water Analysis

Analysis of water samples and elutant from charcoal samplers are reported in the OUL Certificate of Analysis in Appendix B. The fluorescein dye detection criterion used by OUL is shown in Table 4 below.

Table 4. Fluorescein Dye Detection Criterion.

Fluorescent Dye	Normal Acceptable Emission Wavelength Range (nm)		Detection Limit (ppb)	
	Elutant	Water	Elutant	Water
Fluorescein	514.1 to 519.2	505.9 to 509.7	0.025	.002

The graphs in the Certificate of Analysis between 8/21/17 and 8/28/17 represent fluorescein detection at the PFSP Spring (MP4) that meet the criterion in Table 4.

Samples from the background monitoring program indicated no detectable fluorescein in charcoal or water. A background concentration in the 0.5 to 0.6 ppb range was noted with the fluorimeter.

Dye breakthrough at the spring was approximately 15.5 hours after injection as measured by the fluorimeter, elutant, and water samples as shown on Figure 20. There was good correlation between the three sampling methods as to the timing and extent of dye breakthrough

No fluorescein was definitely quantified at any of the other monitoring locations during the project. There was a fluorescein peak detected at MP1 on the final day of sampling (three days after injection) that did not meet all of the laboratory criteria for a positive dye result, but was calculated to be 0.162 and 0.175 ppb in duplicate samples. Dye was injected at the upstream end of a long lake, river flows were low and MP1 was downstream of the lake. It is possible there was a three day travel lag through the length of the lake.

Background Water Temperature Analysis

Background temperature monitoring indicate the diurnal cycle at BM1 and MP4 (Figure 21). Daily high air temperatures throughout the background monitoring period were in the mid 90°F range. The Robinson (BM1) probe indicated the warmest daily temperature late in the afternoon. The spring (MP4) temperature reached a daily high at mid-day, approximately 18 to 20 hours after the daily high temperature at BM1. This time interval is close to the dye break through period and may indicate a temperature influence at the spring from daily warming of river water at BM1.

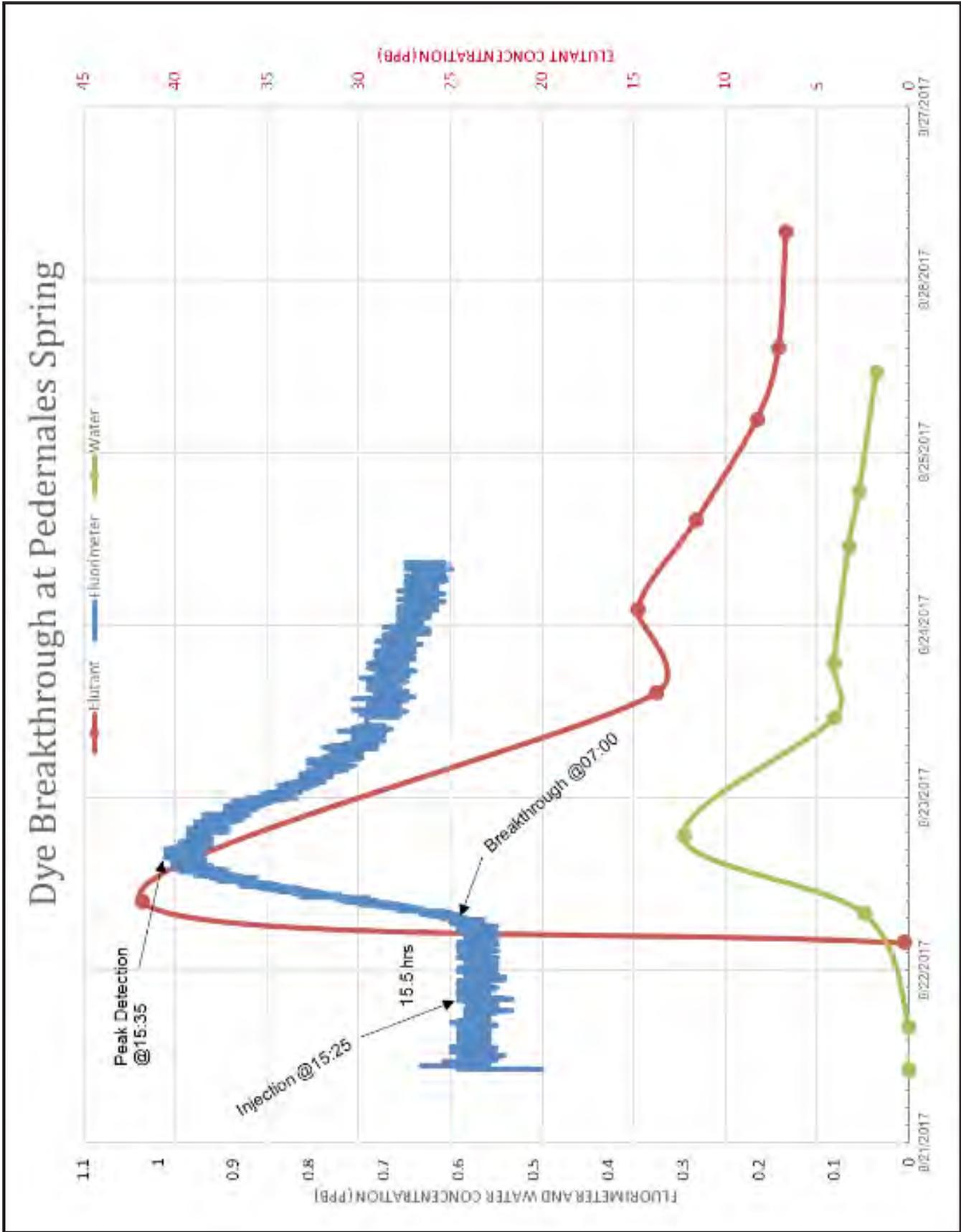


Figure 20. Dye Breakthrough at Pedernales Spring. (Note: Midpoint times & values used for Elutant).

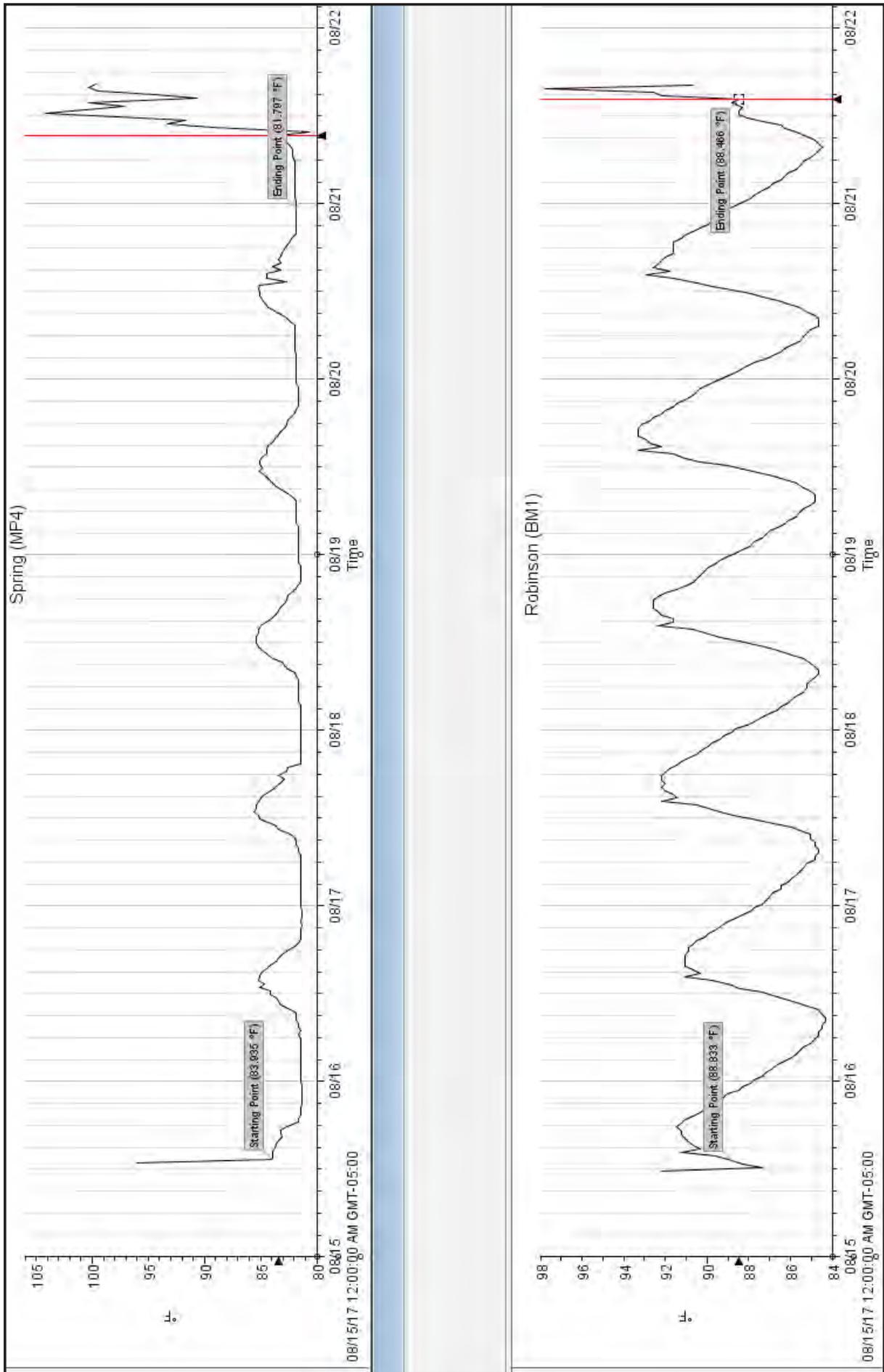


Figure 21. Background Water Temperature Analysis at BM1 & MP4 (Hoboware Screenshot).

CONCLUSIONS

Discharge measurements, field observations of long time local residents, and the results of this dye study indicate there is a losing feature just downstream of the old Robinson farmhouse and the feature is a major source of water to the spring at PFSP. The direct horizontal distance between the swallet and spring is approximately 2.4 miles (Figure 22), though the actual flowpath of the dye through the subsurface is not known. There is observed karst development (caves) in the Marble Falls formation in the study area and likely account for the pathway of water to the spring. There are several linear geologic features that also support the presence of the pathway. The contacts between the Ellenburger, Marble Fall and Trinity Formations all trend southwest to northeast and likely control direction of the river. There is also a series of faults mapped in the Ellenburger on the north side of the river that parallel the river and may extend beneath the Marble Falls, providing a potential pathway for karst development. Fractures in the Marble Falls formation also trend southwest to northeast.

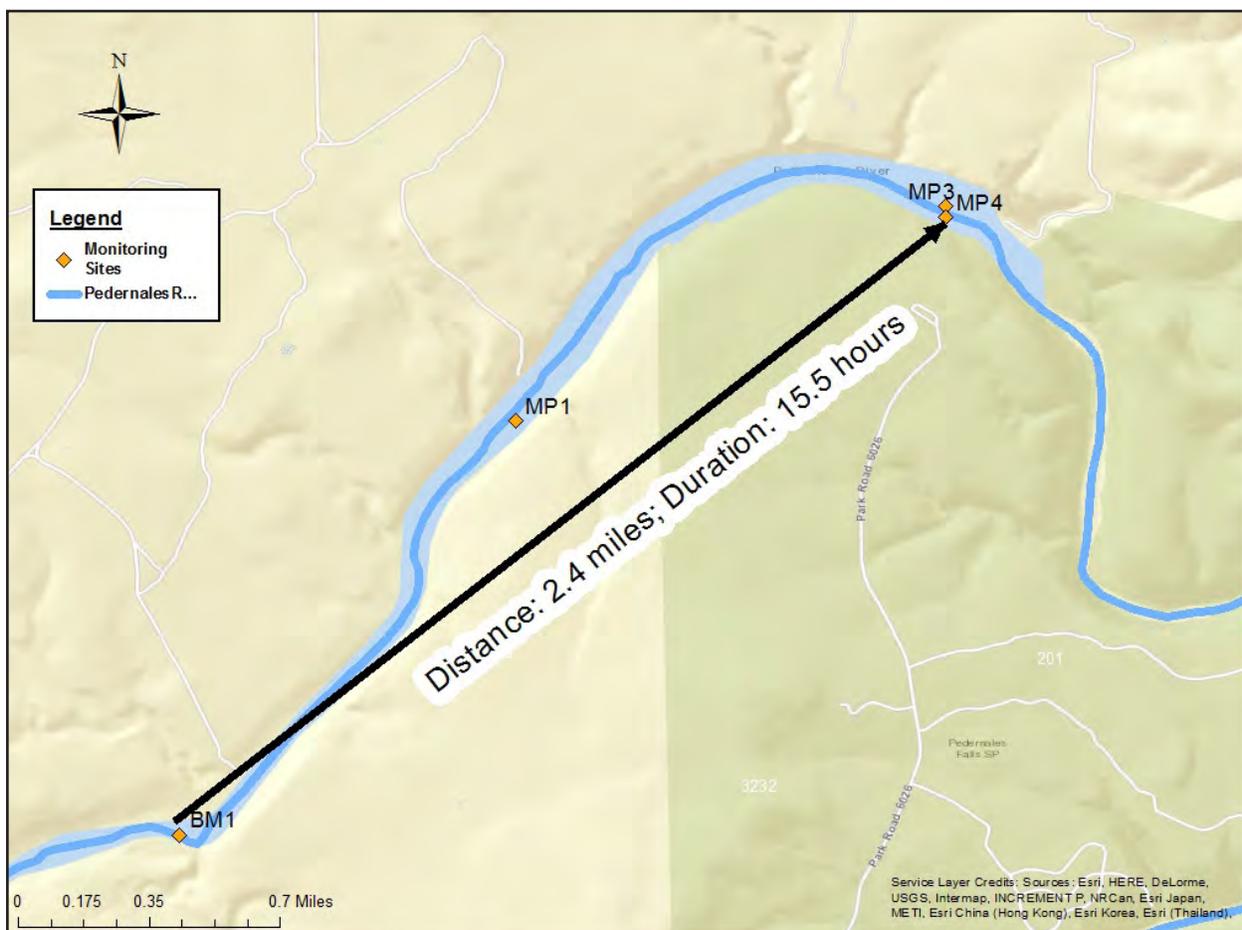


Figure 22. Dye Travel Time and Distance Between the Swallet and the Spring at PFSP.

The loss of 7 cfs between the swallet and the spring only accounts for approximately half of the spring discharge. At present, the source of the other half of the discharge is not known. The combined flow of the spring (MP4) and MP3 (just above the falls) is greater than the measured flow further downstream in the park indicating there may be another losing reach in this area.

SELECTED REFERENCES

Aley, T., (2002). Groundwater Tracing Handbook. Ozark Underground Laboratory, Inc.

Aley, T., and Beeman, S., (2015). Procedures and Criteria Analysis of Fluorescent Dyes in Water and Charcoal Samplers. Ozark Underground Laboratory, Inc.

Barnes, V.E., (1963). Geologic Map of the Johnson City Quadrangle, Blanco County, TX. Geologic Quadrangle Map No. 25, Bureau of Economic Geology, University of Texas, Austin, TX.

Barnes, V.E. (1982). Geologic Map of the Pedernales Falls Quadrangle, Blanco County, Texas. Geologic Quadrangle Map No. 49, Bureau of Economic Geology, University of Texas, Austin, TX.

Barnes, V.E. (1982a). Geologic Map of Hammets Crossing Quadrangle, Blanco, TX. Geologic Quadrangle Map No. 51, Bureau of Economic Geology, University of Texas, Austin, TX.

Brune, G., (1981). Springs of Texas – Volume 1. Texas A&M University Press, p566.

Holland, P.H., and Hughes, L.S., (1964). Bulletin 6407 Base Flow Studies Pedernales River, Texas, Texas Water Commission.

Wierman, D. A., Broun, A. S., Hunt, B. B., (2010). Hydrogeologic Atlas of the Hill Country Trinity Aquifer, Blanco, Hays, and Travis Counties, Central Texas. Hays-Trinity Groundwater Conservation District, United States.

Wierman, D.A. (2017). Determining the Source of Base Flow to the Pedernales River in Northern Blanco, Hays, and Travis Counties. Meadows Center for Water and the Environment, Texas State University, San Marcos, TX.

Wierman, D.A., Walker, J., Butler, W., Zapetello, S., and Warren, E., (2017). Occurrence of Flowing Water and Water Quality during Base Flow Conditions in the Pedernales River Basin, Meadows Center for Water and the Environment, Texas State University, San Marcos, TX.

APPENDIX A

STATE PARK SCIENTIFIC NOTICE PERMIT

TEXAS PARKS AND WILDLIFE

STATE PARK SCIENTIFIC STUDY PERMIT TEXAS PARKS AND WILDLIFE DEPARTMENT NATURAL RESOURCES PROGRAM

Telephone: 512/389-4679
FAX: 512/389-4495
Email: david.riskind@tpwd.state.tx.us

Permit No: 2017-R3-11
Date: 6/15/2017

Permit Period: From: 1 July 2017 To: 1 October 2017

Permit Scope: The Meadows Center has conducted previous studies quantifying Hill Country surface water. They have discovered an area of water loss in the Pedernales River upstream of Pedernales Falls State Park, and suspect that the water is returned to the river at a spring near the falls. They propose to release fluorescein tracer dye in the water upstream of Pedernales Falls to assess the flow, with the objective of identifying the path of the river's 'missing' water. The permittee(s) may release **fluorescein tracer dye** on a non-holiday Monday, Tuesday, or Wednesday in July, August, or September of 2017, after receiving appropriate approvals from river and water quality authorities. Thursday, Friday, and weekend release are prohibited because park guests may be discomfited by dyed water. Fluorescein concentration in the river must stay below 1 mg per liter, the concentration at which there are observed health effects in humans. Permittee(s) are also authorized to install temporary equipment near the spring in Pedernales Falls to monitor for presence of fluorescein dye. **Permittee(s) may not substitute another dye for fluorescein without clearance by TPWD natural resource staff. Permittee(s) are required to contact park and natural resource staff in advance of dye release and equipment placement.**

Permittee(s): Jenna Walker
MAGeo Program Coordinator
The Meadows Center for Water and the Environment
512-762-4667
jjwalker@txstate.edu

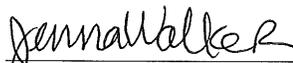
General Provisions: The permittee agrees to the following provisions (1) discretely conduct such studies so as not to unduly disturb or destroy any physical, natural or aesthetic features within said parks (other than the specimens collected) or disturb park visitors; (2) to notify the Park Superintendent upon arrival at the site; (3) to abide by any special directives issued by or through the Park Superintendent concerning the area(s) in which studies may be conducted. (4) The permittee understands that no study shall take place in the park before or after the permit period designated above; (5) that all studies be conducted by the requestee or by collaborators or assistants as designated above; (6) that none of the specimens may be sold or used for barter or trade; (7) that the permit issued may be revoked by the Texas Parks and Wildlife Department at any time; and (8) a copy of this permit must be available for inspection during field work at park site.

Special Provisions: (1) The permittee agrees to furnish the Texas Parks and Wildlife Department a copy of a summary of the studies conducted under the provisions of this permit by March of the year following this permit and any published account resulting from investigations authorized by this permit, (2) **the permittee must provide the Texas Parks and Wildlife Department a copy of all publications and a report detailing the survey and sampling efforts,** (3) the permittee agrees to furnish the Texas Parks and Wildlife Department a list of all collections made during this study and as well must furnish the Department with the name and location of the institution or collection in which the specimens are deposited, and (4) the permittee shall acknowledge the Texas Parks and Wildlife Department in any published article regarding research carried out under the terms of this permit. The acknowledgement shall include the appropriate permit number(s).

Waiver: See park superintendent for scientific study/educational day-use entrance fee waiver.

By affixing their signature hereon, the permittee agrees to all terms and conditions of this permit.

Approved by Texas Parks and Wildlife
Dept. Anne Stine for



Signature
Date: 8/9/17



Signature David H. Riskind
Natural Resources Program
Date: 8/9/2017

PUBLIC NOTICE

PUBLIC NOTICE

The Meadows Center for Water and the Environment at Texas State University will be conducting a study on the Pedernales River from **mid-August to mid-September**. The purpose of the study is to learn more about the source of local springs and groundwater-surfacewater interactions of the river. The study involves placing scientific instrumentation in the river at various points inside park boundaries. Tampering with this instrumentation is strictly prohibited.

For questions, please contact a park ranger.

For more information regarding the Pederales River Study, visit **Pedernales.MeadowsWater.org**.



APPENDIX B

OUL PROCEDURES AND CRITERIA

See Attached

OUL CRITERIA OF ANALYSIS

See Attached

Certificate of Analysis

Date of certificate: September 7, 2017

Client: Texas State University

201 San Marcos Springs Drive

San Marcos, TX 78666

Project name / location: PFPS Spring Dye Trace Project

Pedernales River, TX

Purchase Order #: 4500119941

Contact person: Jaime Moreno (jpm114@txstate.edu)

Samples collected by: Jaime Moreno

Date samples shipped: August 29, 2017

Date samples rec'd at OUL: August 30, 2017

Date analyzed by OUL: September 1 and 5, 2017

Included with certificate of analysis: Table of results, copies of OUL sample collection data sheets, copy of Texas State chain of custody, discrepancy sheet and analysis graphs

Results for charcoal and water samples analyzed for the presence of fluorescein dye.

Peak wavelengths are reported in nanometers (nm); dye concentrations are reported in parts per billion (ppb).

All results are for charcoal unless indicated otherwise.

OUL Number	Station Number	Station Name	Date/Time Placed	Date/Time Collected	Fluorescein	
					Peak (nm)	Conc (ppb)
C4832	BM1	BM120170821-1	8/15/17 1200	8/21/17 1445	ND	
C4832D	BM1	BM120170821-2	8/15/17 1200	8/21/17 1445	ND	
C4836	MP1	MP120170822-1	8/21/17 1215	8/22/17 1130	ND	
C4836D	MP1	MP120170822-2	8/21/17 1215	8/22/17 1130	ND	
C4842	MP1	MP120170823-1	8/22/17 1130	8/23/17 1150	ND	
C4842D	MP1	MP120170823-2	8/22/17 1130	8/23/17 1150	ND	
C4848	MP1	MP120170824-1	8/23/17 1150	8/24/17 1145	ND	
C4848D	MP1	MP120170824-2	8/23/17 1150	8/24/17 1145	ND	
C4849	MP1	MP120170825-1	8/24/17 1145	8/25/17 1230	514.8 *	0.175
C4849D	MP1	MP120170825-2	8/24/17 1145	8/25/17 1230	515.6 *	0.162
C4835	MP3	MP320170822-1	8/21/17 1020	8/22/17 1009	ND	
C4835D	MP3	MP320170822-2	8/21/17 1020	8/22/17 1009	ND	
C4841	MP3	MP320170823-1	8/22/17 1009	8/23/17 1045	ND	
C4841D	MP3	MP320170823-2	8/22/17 1009	8/23/17 1045	ND	
C4844	MP3	MP320170824-1	8/23/17 1045	8/24/17 1015	ND	
C4844D	MP3	MP320170824-2	8/23/17 1045	8/24/17 1015	ND	
C4850	MP3	MP320170825-1	8/24/17 1015	8/25/17 1030	ND	
C4850D	MP3	MP320170825-2	8/24/17 1015	8/25/17 1030	ND	
C4833	MP4	MP420170821-1	8/15/17 1300	8/21/17 0951	ND	
C4833D	MP4	MP420170821-2	8/15/17 1300	8/21/17 0951	ND	
C4834	MP4	MP420170822-1	8/21/17 0956	8/22/17 0745	ND	
C4834D	MP4	MP420170822-2	8/21/17 0956	8/22/17 0745	514.2 *	0.258
C4838	MP4	MP420170823-1	8/22/17 0800	8/23/17 1100	515.0	39.2

OUL Number	Station Number	Station Name	Date/Time Placed	Date/Time Collected	Fluorescein	
					Peak (nm)	Conc (ppb)
C4838	MP4	MP420170823-2	8/22/17 0800	8/23/17 1100	515.4	44.4
C4839	MP4	MP420170823-1	8/23/17 1100	8/23/17 1830	515.2	14.7
C4839D	MP4	MP420170823-2	8/23/17 1100	8/23/17 1830	515.2	12.8
C4845	MP4	MP420170824-1	8/23/17 1830	8/24/17 1045	515.6	13.2
C4845D	MP4	MP420170824-2	8/23/17 1830	8/24/17 1045	515.6	16.4
C4846	MP4	MP420170824-1	8/24/17 1045	8/24/17 1830	515.4	8.74
C4846D	MP4	MP420170824-2	8/24/17 1045	8/24/17 1830	515.2	14.4
C4851	MP4	MP420170825-1	8/24/17 1830	8/25/17 1100	515.4	7.90
C4851D	MP4	MP420170825-2	8/24/17 1830	8/25/17 1100	515.2	8.71
C4852	MP4	MP420170825-1	8/24/17 1100	8/25/17 1830	515.4	25.9
C4852D	MP4	MP420170825-2	8/25/17 1100	8/25/17 1830	515.4	7.13
C4853	MP4	MP420170828-1	8/25/17 1830	8/28/17 1100	516.0	6.75
C4853D	MP4	MP420170828-2	8/25/17 1830	8/28/17 1100	515.8	6.64
C4837	MP5	MP520170822-1	8/21/17 1345	8/22/17 1230	ND	
C4837D	MP5	MP520170822-2	8/21/17 1345	8/22/17 1230	ND	
C4843	MP5	MP520170823-1	8/22/17 1230	8/23/17 0950	ND	
C4843D	MP5	MP520170823-2	8/22/17 1230	8/23/17 0950	ND	
C4847	MP5	MP520170824-1	8/23/17 0950	8/24/17 1100	ND	
C4847D	MP5	MP520170824-2	8/23/17 0950	8/24/17 1100	ND	
C4840	Laboratory control charcoal blank					
C4871	MP1	MP120170821OZ	Water	8/21/17 1215	ND	
C4870	MP1	MP120170822OZ	Water	8/22/17 1130	ND	
C4875	MP1	MP120170823OZ	Water	8/23/17 1150	ND	
C4881	MP1	MP120170824OZ	Water	8/24/17 1145	ND	
C4879	MP1	MP120170825OZ	Water	8/25/17 1230	ND	
C4869	MP3	MP320170822OZ	Water	8/22/17 1015	ND	
C4877	MP3	MP320170823OZ	Water	8/23/17 1045	ND	
C4878	MP3	MP320170824OZ	Water	8/24/17 1015	ND	
C4882	MP3	MP320170825OZ	Water	8/25/17 1030	ND	
C4865	MP4	MP420170821OZ	Water	8/21/17 0956	ND	
C4866	MP4	MP420170821OZ	Water	8/21/17 1556	ND	
C4867	MP4	MP420170822OZ	Water	8/22/17 0745	506.2	0.060
C4868	MP4	MP420170822OZ	Water	8/22/17 1830	507.8	0.333
C4873	MP4	MP420170823OZ	Water	8/23/17 1100	506.8	0.128
C4874	MP4	MP420170823OZ	Water	8/23/17 1830	507.0	0.124
C4883	MP4	MP420170824OZ	Water	8/24/17 1045	507.2	0.081
C4884	MP4	MP420170824OZ	Water	8/24/17 1830	506.6	0.067
C4887	MP4	MP420170825OZ	Water	8/25/17 1100	506.6	0.044
C4872	MP5	MP520170821OZ	Water	8/21/17 1338	ND	
C4888	MP5	MP520170822OZ	Water	8/22/17 1230	ND	
C4876	MP5	MP520170823OZ	Water	8/23/17 0950	ND	

Removed

OUL Number	Station Number	Station Name	Date/Time Placed	Date/Time Collected	Fluorescein	
					Peak (nm)	Conc (ppb)
C4885	MP5	MP520170824OZ	Water	8/24/17 1100	ND	
C4886	MP5	MP520170825OZ	Water	8/25/17 1130	ND	
C4880	Laboratory control water blank					

Note: Dye concentrations are based upon standards used at the OUL. The standard concentrations are based upon the as sold weight of the dye that the OUL uses. If the client is not using OUL dyes, the client should provide the OUL with a sample of the dye to compare to the OUL dyes.

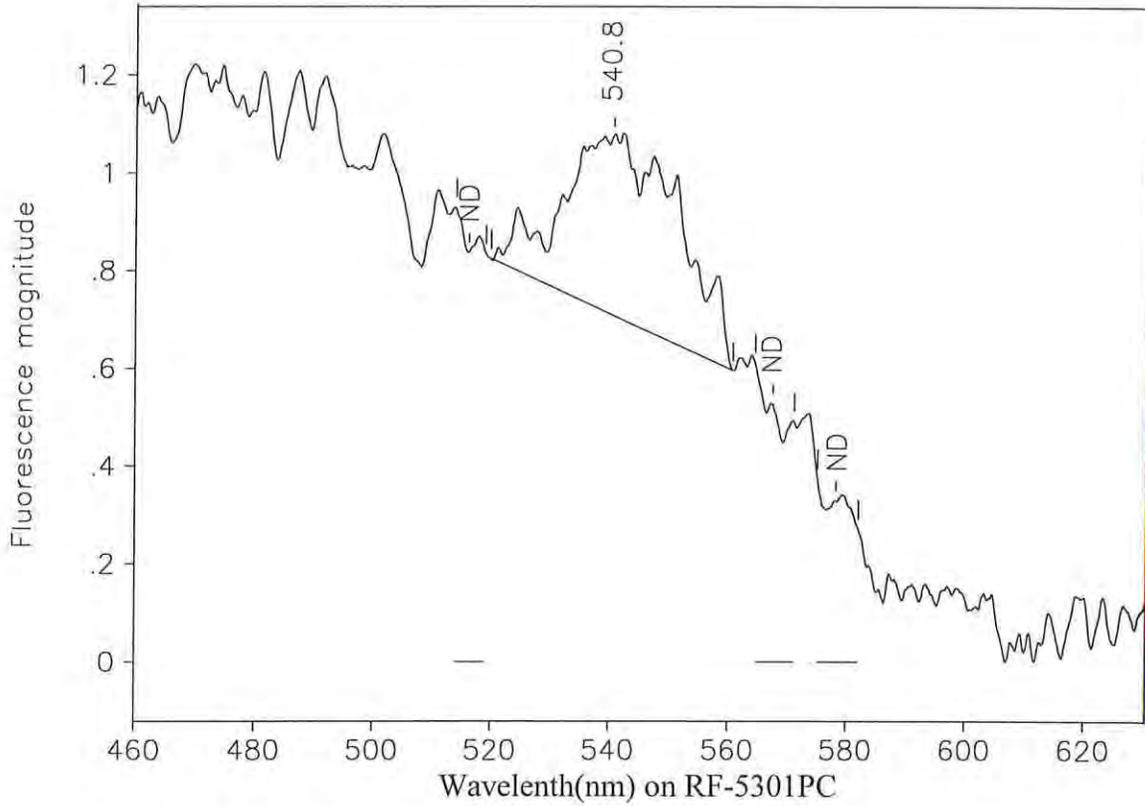
Footnote: ND = No dye detected NDT = No date or time given

* = A fluorescence peak is present that does not meet all the criteria for a positive dye result. However, it has been calculated as though it was the tracer dye.

Thomas J. Aley, PHG and RG



Ozark Underground Laboratory



Station BM1: BM120170821
 OUL Number: C4832
 Matrix: Elutant
 Date Placed: 8/15/17 1200

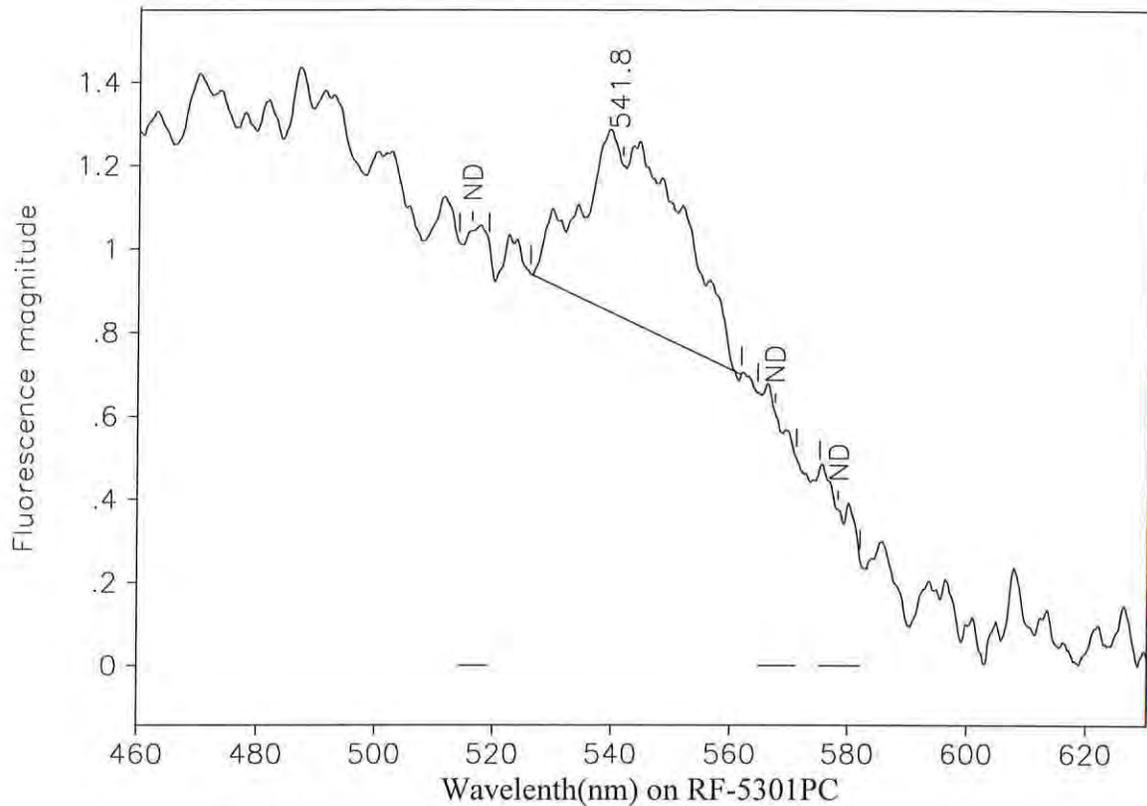
Analyzed: 9/1/17
 Duration: 6.11 days
 Date collected: 8/21/17 1445

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
540.8	520.0	560.8	0.37	8.37	0.065	0.396 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station BM1: BM120170821
 OUL Number: C4832D
 Matrix: Elutant
 Date Placed: 8/15/17 1200

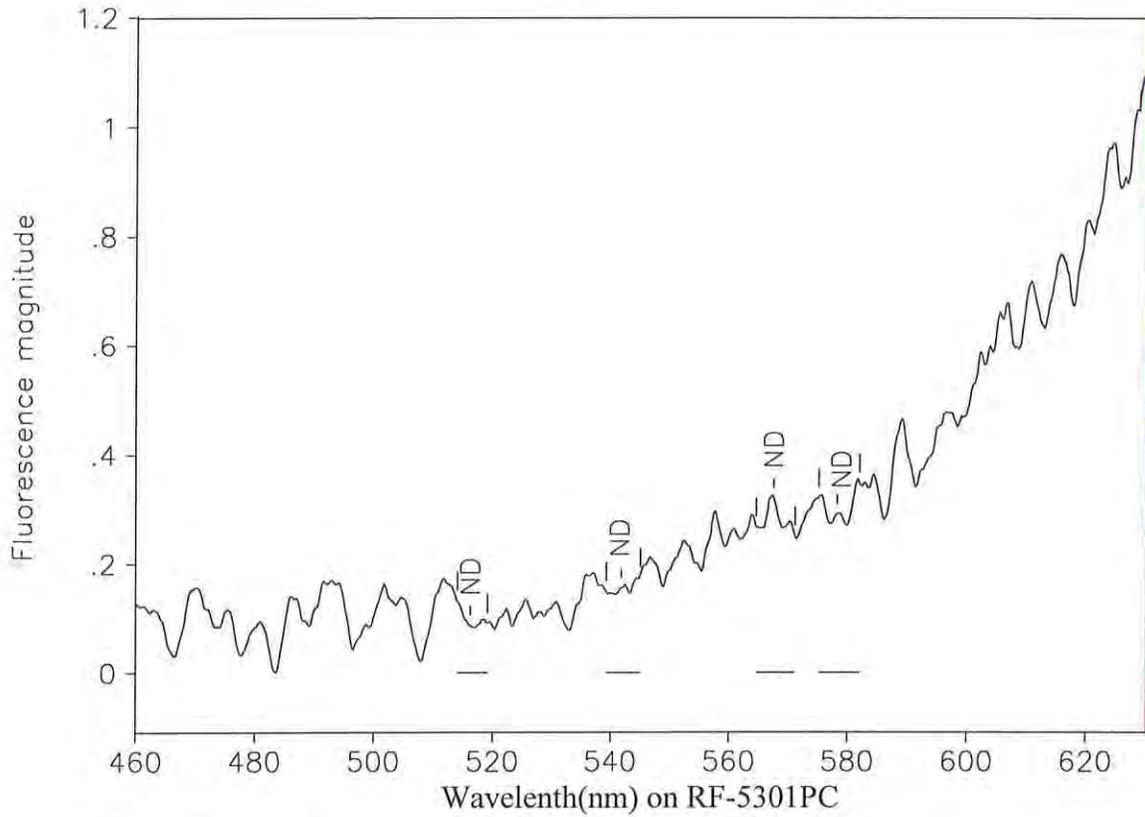
Analyzed: 9/1/17
 Duration: 6.11 days
 Date collected: 8/21/17 1445

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	526.2	561.8	0.36	8.64	0.067	0.408 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170822
 OUL Number: C4836
 Matrix: Elutant
 Date Placed: 8/21/17 1215

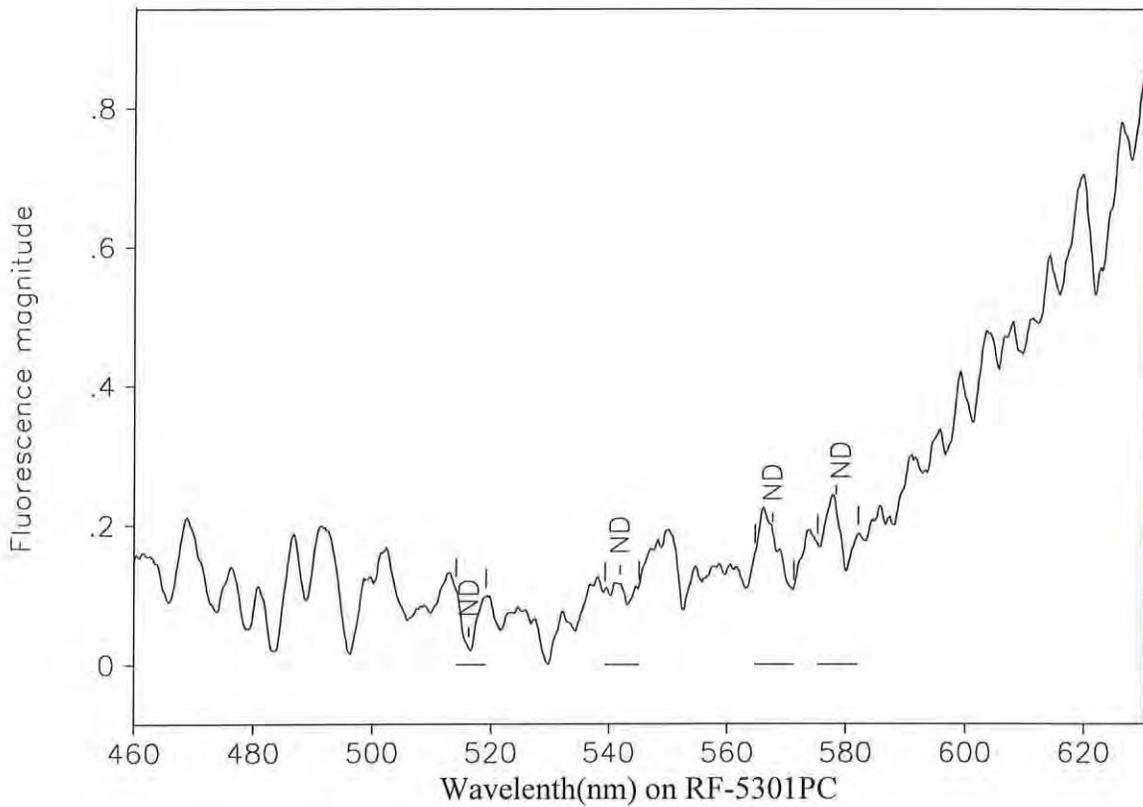
Analyzed: 9/1/17
 Duration: 0.969 days
 Date collected: 8/22/17 1130

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170822
 OUL Number: C4836D
 Matrix: Elutant
 Date Placed: 8/21/17 1215

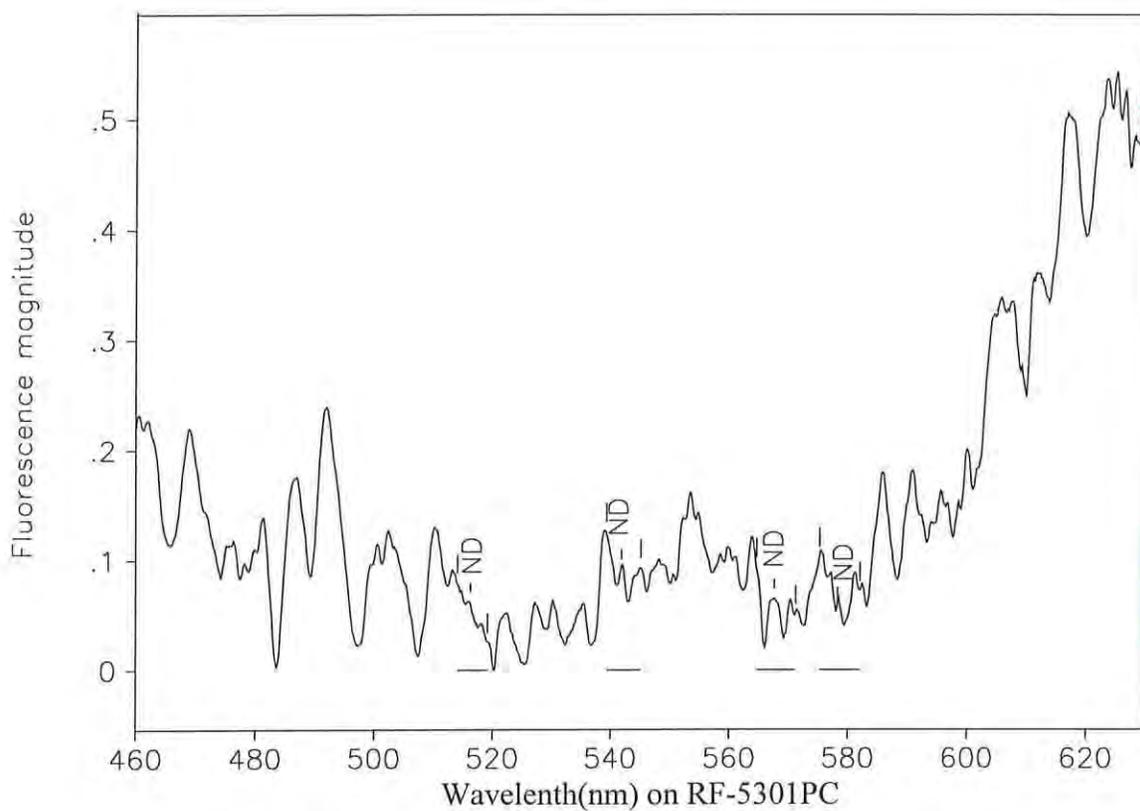
Analyzed: 9/1/17
 Duration: 0.969 days
 Date collected: 8/22/17 1130

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170823
 OUL Number: C4842
 Matrix: Elutant
 Date Placed: 8/22/17 1130

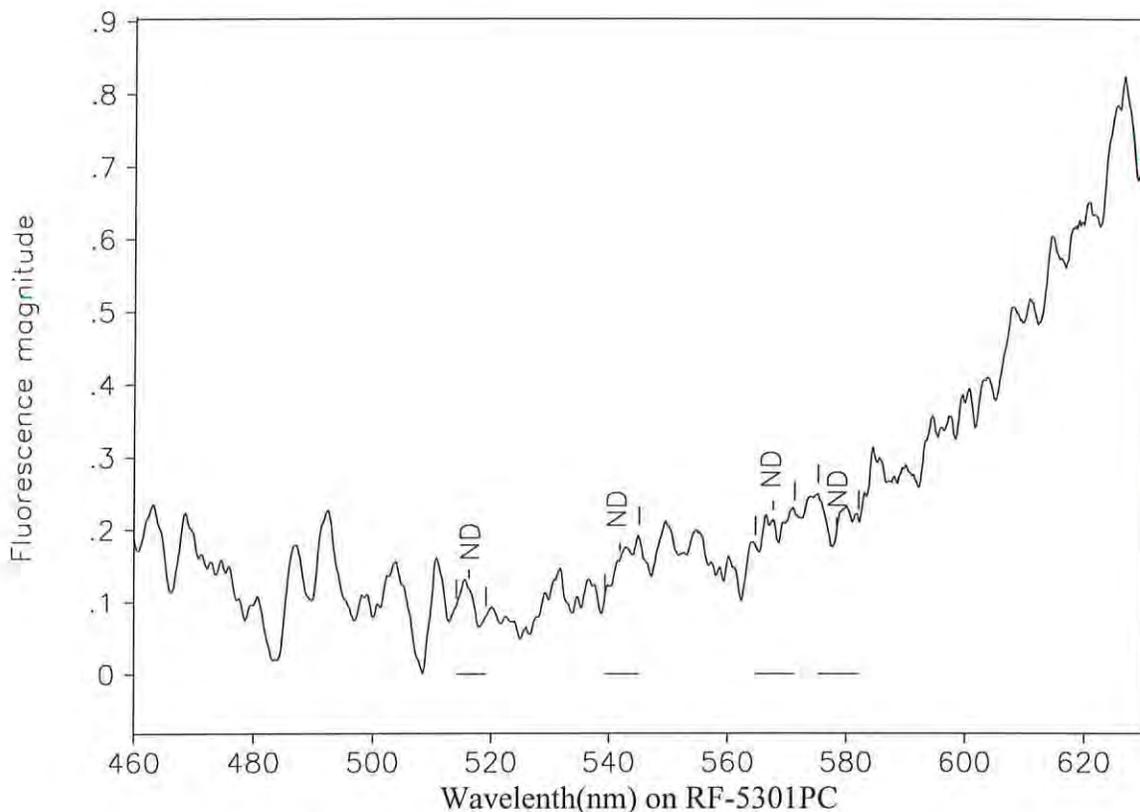
Analyzed: 9/1/17
 Duration: 1.01 days
 Date collected: 8/23/17 1150

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170823

OUL Number: C4842D

Matrix: Elutant

Date Placed: 8/22/17 1130

Analyzed: 9/1/17

Duration: 1.01 days

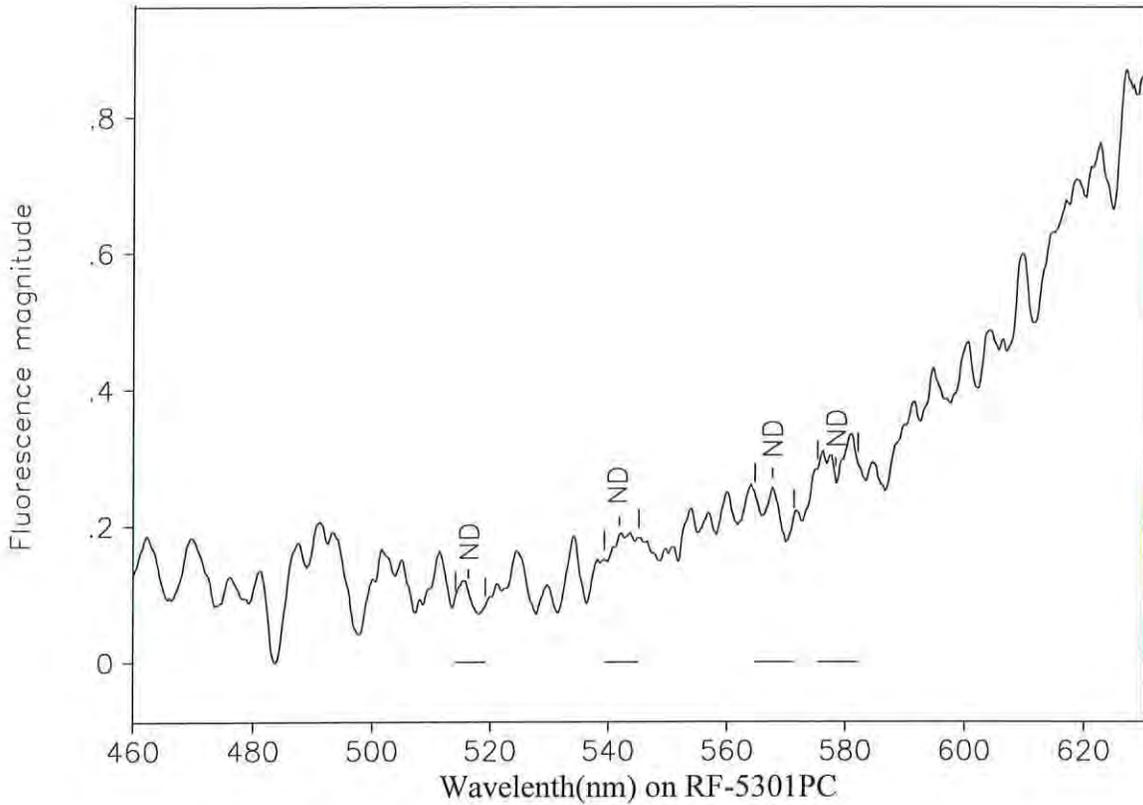
Date collected: 8/23/17 1150

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170824
 OUL Number: C4848
 Matrix: Elutant
 Date Placed: 8/23/17 1150

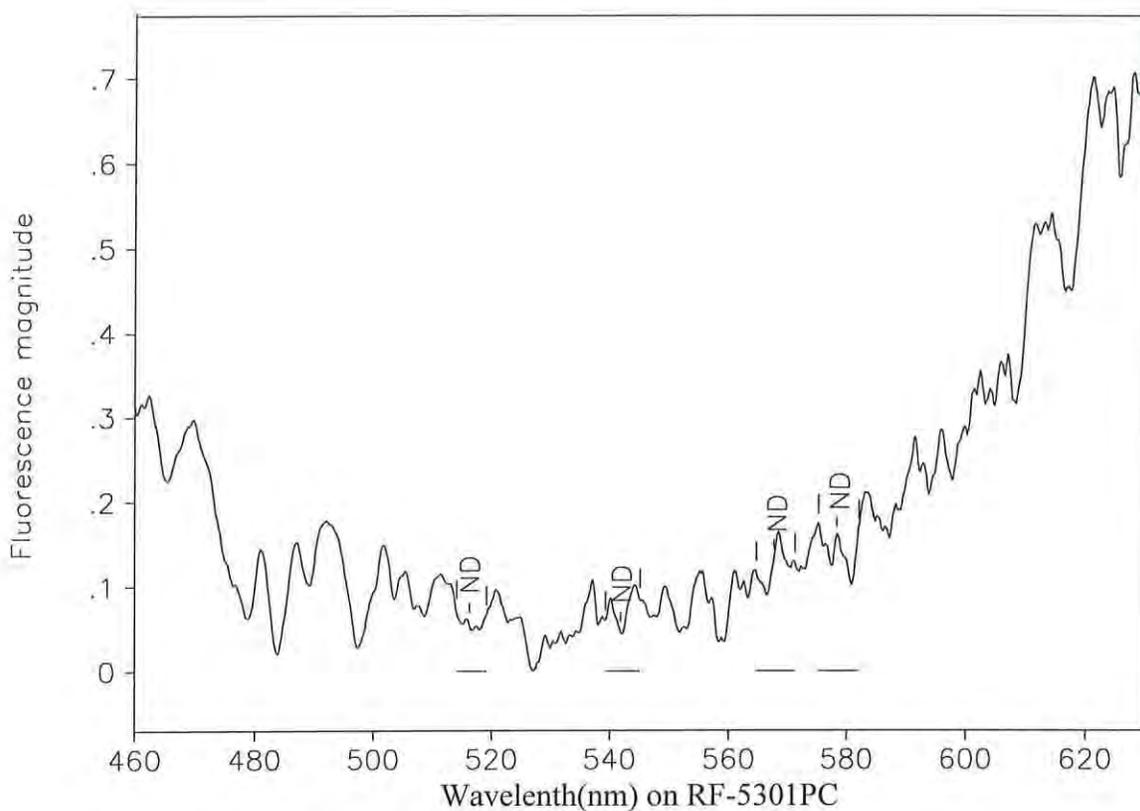
Analyzed: 9/1/17
 Duration: 0.997 days
 Date collected: 8/24/17 1145

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170824
 OUL Number: C4848D
 Matrix: Elutant
 Date Placed: 8/23/17 1150

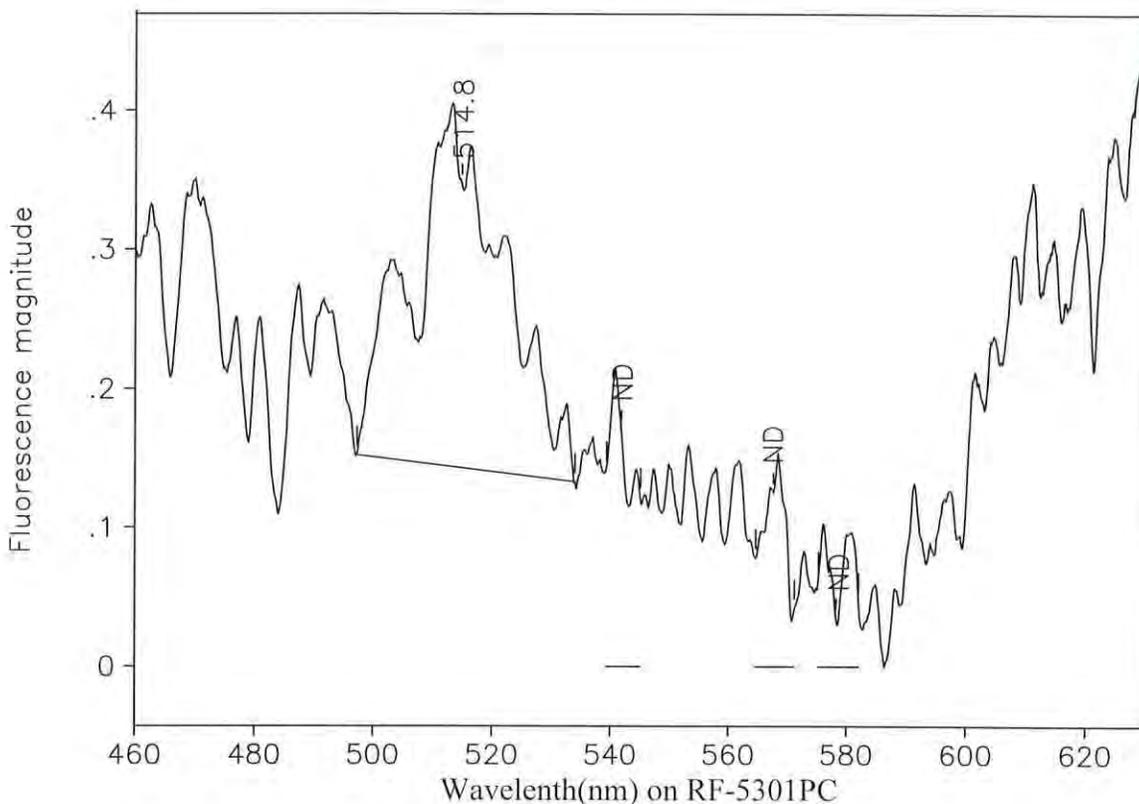
Analyzed: 9/1/17
 Duration: 0.997 days
 Date collected: 8/24/17 1145

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170825
 OUL Number: C4849
 Matrix: Elutant
 Date Placed: 8/24/17 1145

Analyzed: 9/1/17
 Duration: 1.03 days
 Date collected: 8/25/17 1230

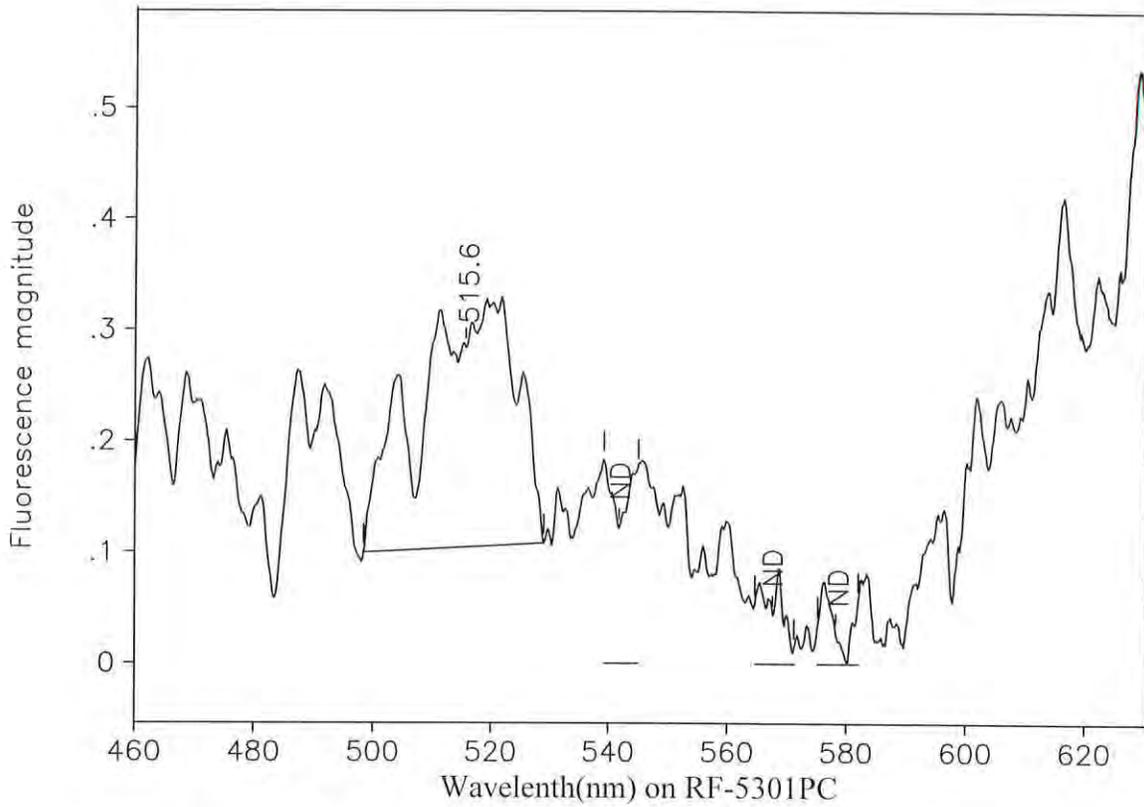
Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	
514.8	497.2	534.0	0.20	4.65	0.169	0.175	Fl *
541.8	539.3	545.1	0.00	0.00		ND	
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Calom

Ozark Underground Laboratory



Station MP1: MP120170825
 OUL Number: C4849D
 Matrix: Elutant
 Date Placed: 8/24/17 1145

Analyzed: 9/1/17
 Duration: 1.03 days
 Date collected: 8/25/17 1230

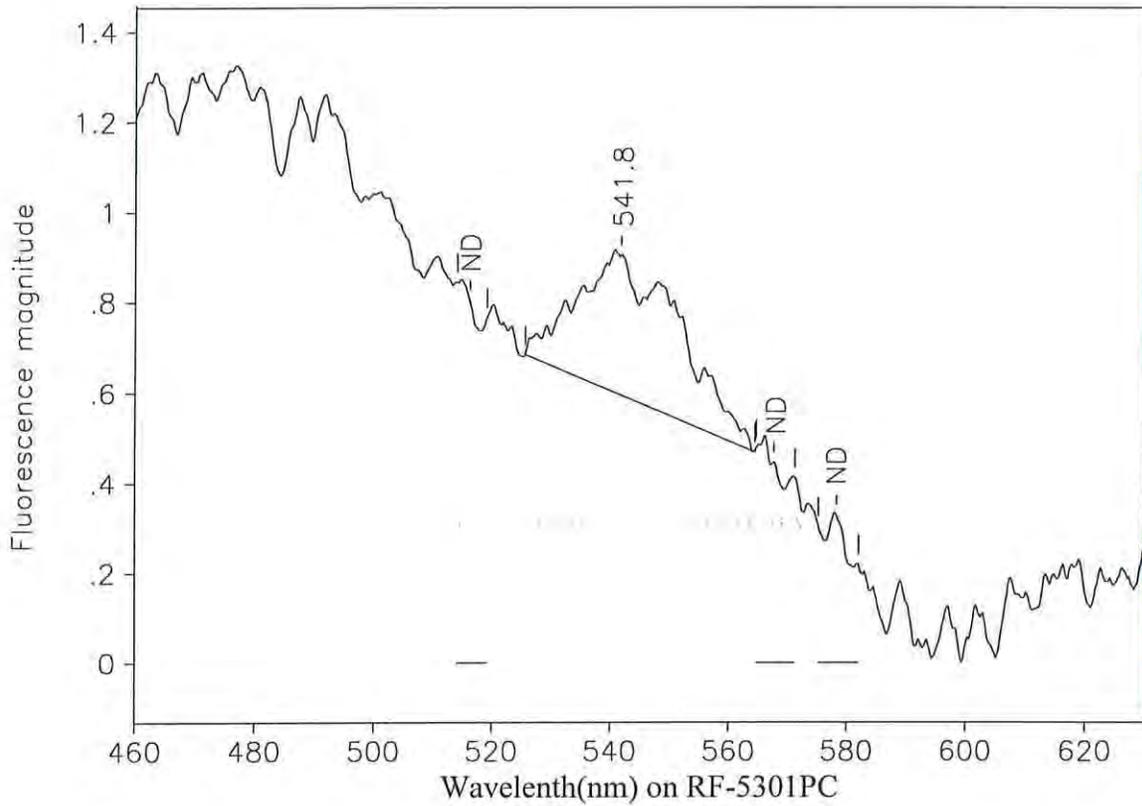
Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	
515.6	498.4	529.0	0.18	4.31	0.157	0.162	FI *
541.8	539.3	545.1	0.00	0.00		ND	
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Cafou

Ozark Underground Laboratory



Station MP3: MP320170822
 OUL Number: C4835
 Matrix: Elutant
 Date Placed: 8/21/17 1020

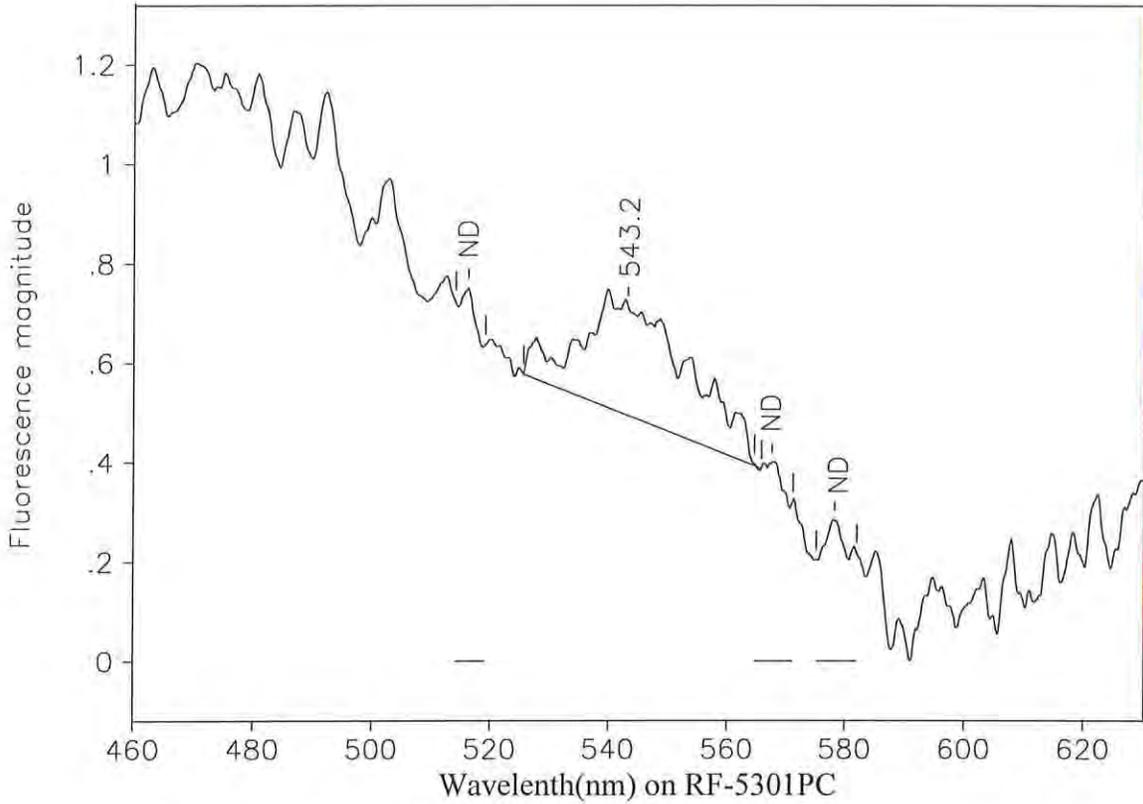
Analyzed: 9/1/17
 Duration: 0.992 days
 Date collected: 8/22/17 1009

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	525.6	564.4	0.31	6.25	0.298	0.295 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170822
 OUL Number: C4835D
 Matrix: Elutant
 Date Placed: 8/21/17 1020

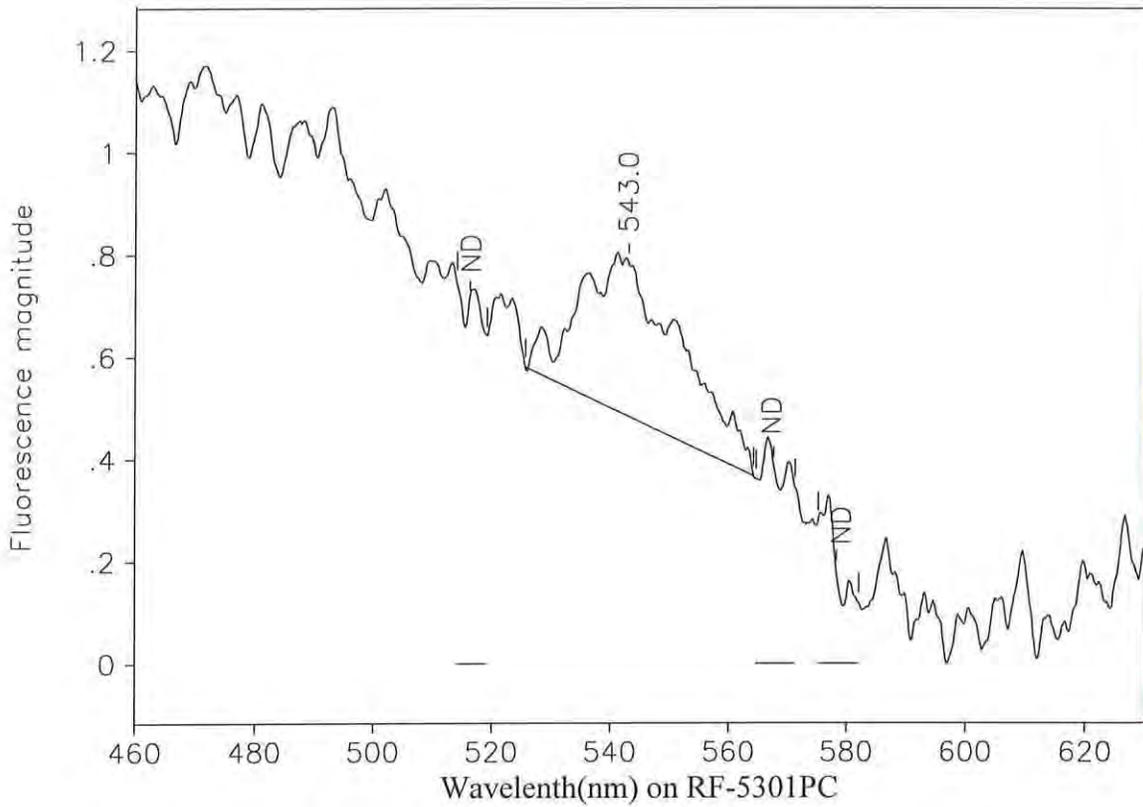
Analyzed: 9/1/17
 Duration: 0.992 days
 Date collected: 8/22/17 1009

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.2	525.6	565.8	0.22	4.92	0.234	0.232 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170823
 OUL Number: C4841
 Matrix: Elutant
 Date Placed: 8/22/17 1009

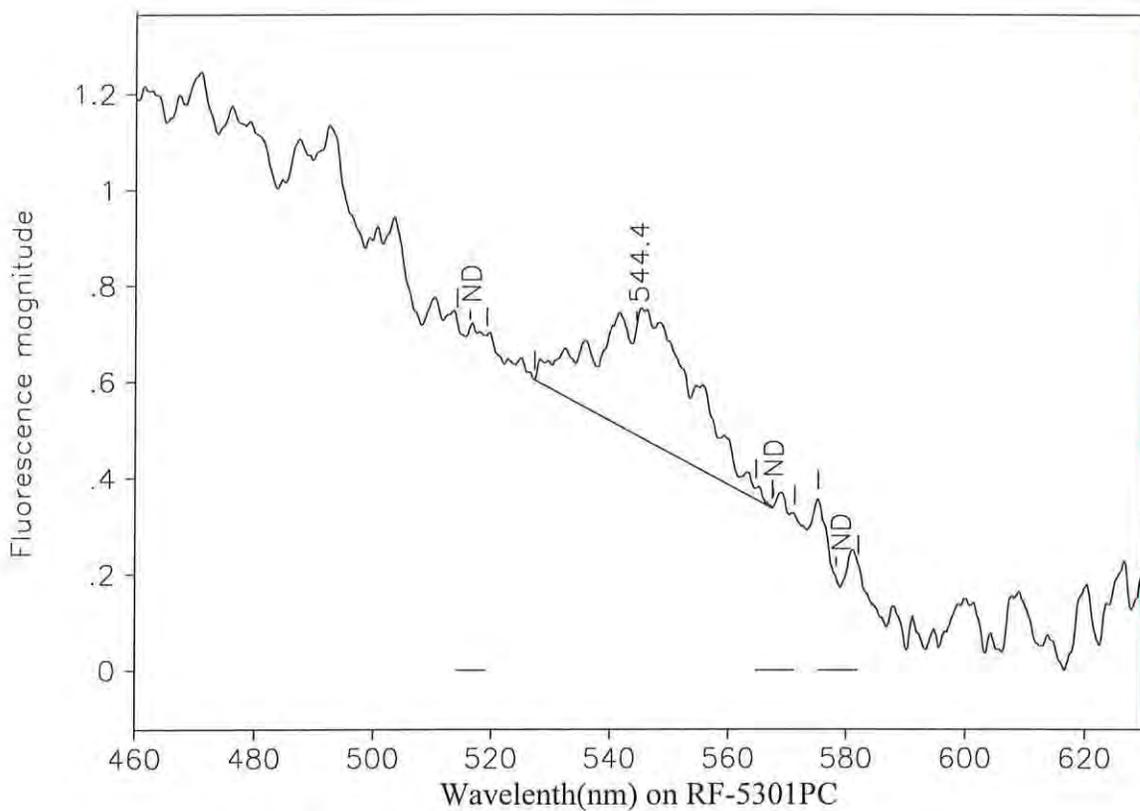
Analyzed: 9/1/17
 Duration: 1.02 days
 Date collected: 8/23/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.0	525.6	564.2	0.30	6.08	0.282	0.287 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170823
 OUL Number: C4841D
 Matrix: Elutant
 Date Placed: 8/22/17 1009

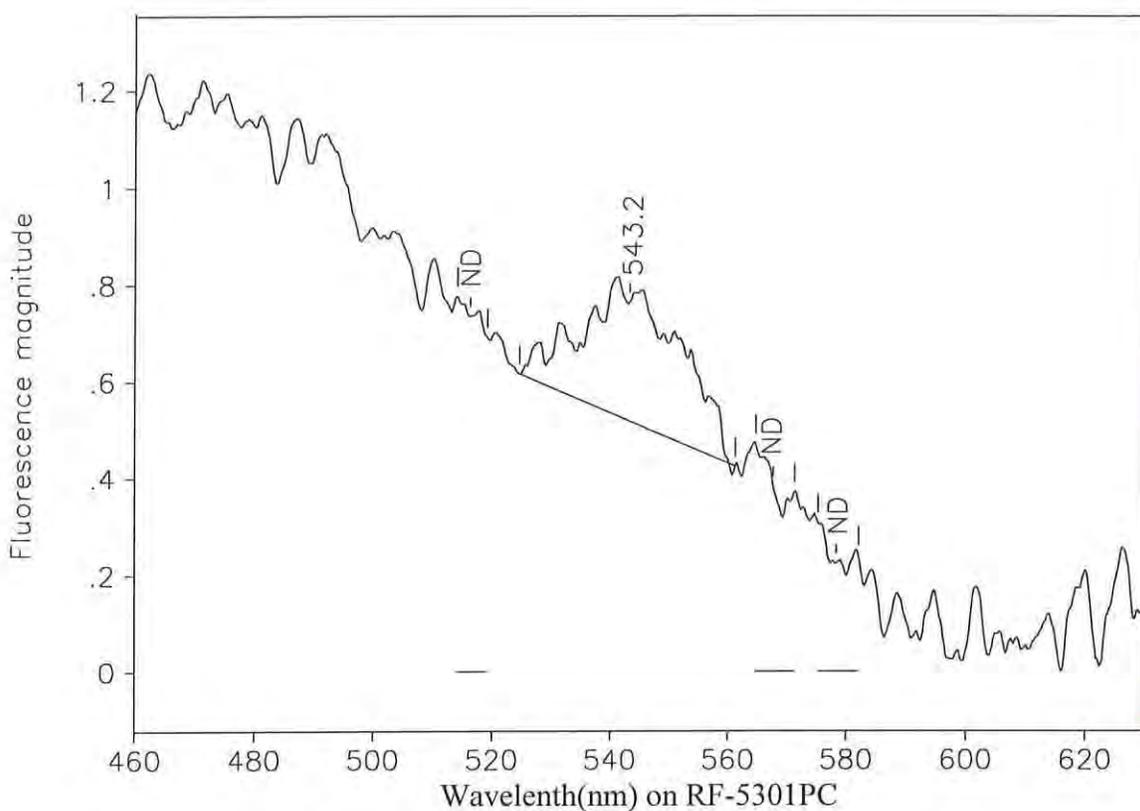
Analyzed: 9/1/17
 Duration: 1.02 days
 Date collected: 8/23/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
544.4	527.2	567.4	0.22	5.17	0.240	0.244 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170824
 OUL Number: C4844
 Matrix: Elutant
 Date Placed: 8/23/17 1045

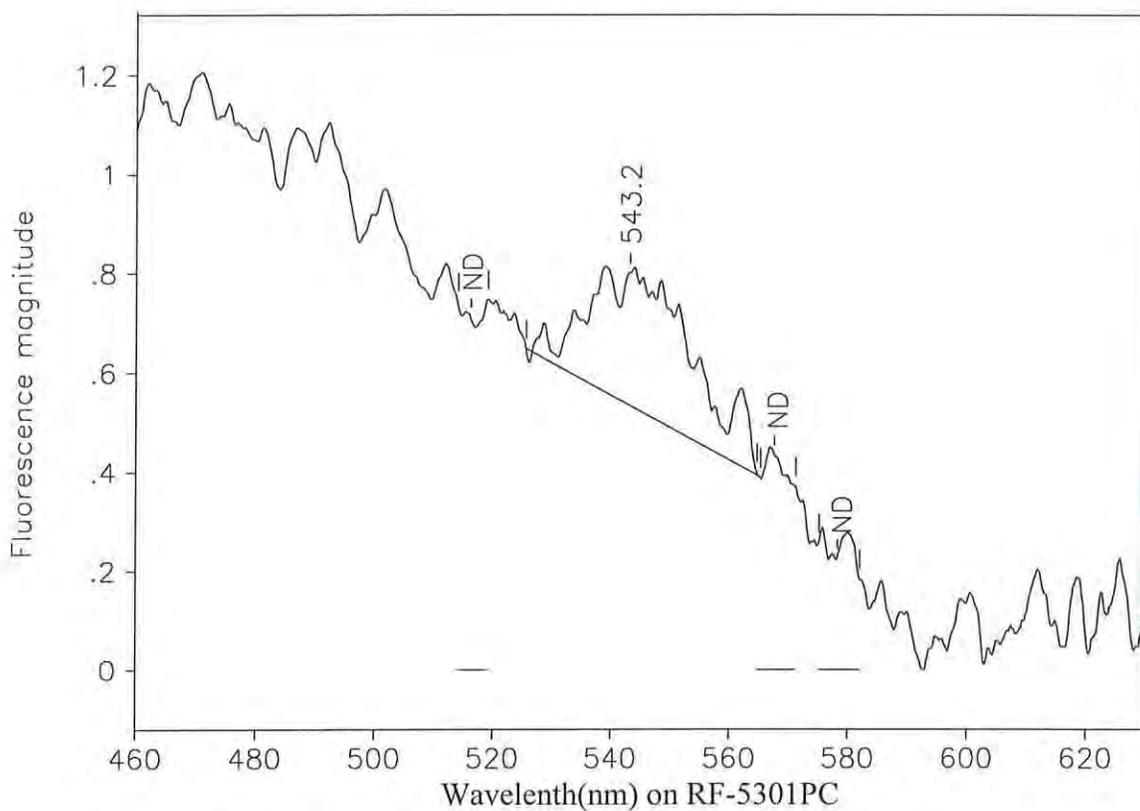
Analyzed: 9/1/17
 Duration: 0.979 days
 Date collected: 8/24/17 1015

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	
516.3	514.1	519.2	0.00	0.00		ND	
543.2	524.6	561.2	0.24	5.54	0.267	0.262	EO
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170824
 OUL Number: C4844D
 Matrix: Elutant
 Date Placed: 8/23/17 1045

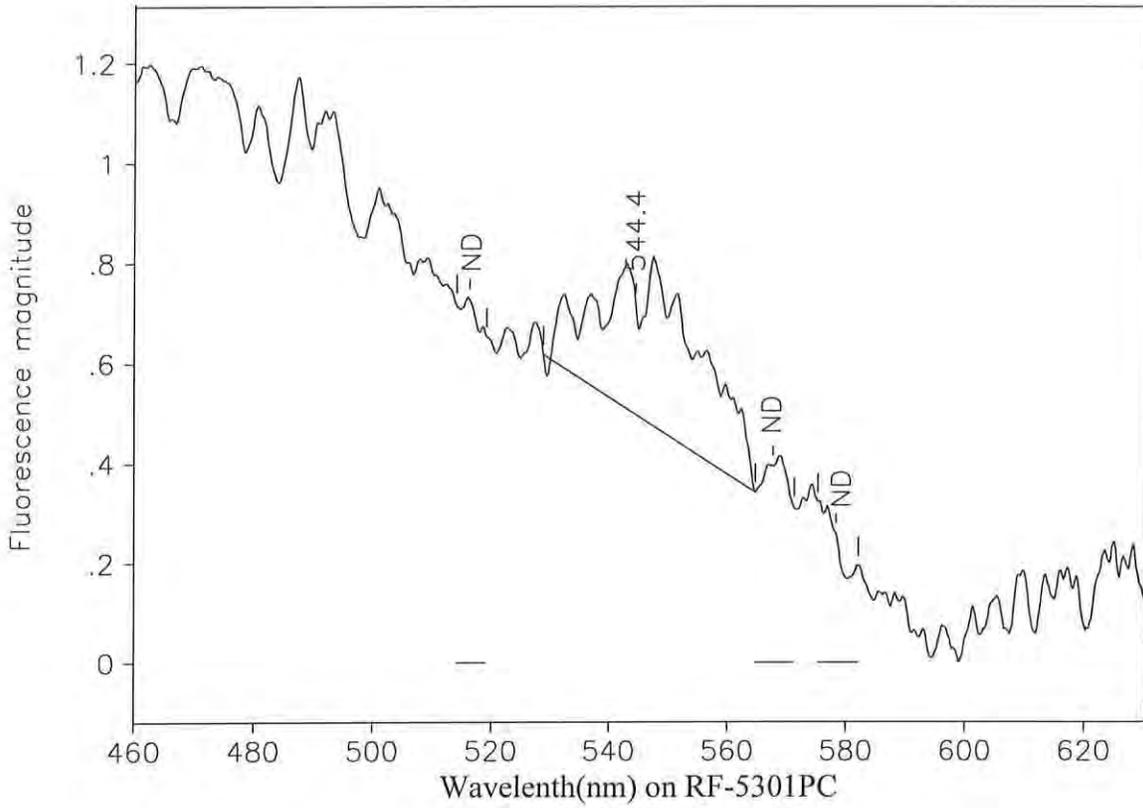
Analyzed: 9/1/17
 Duration: 0.979 days
 Date collected: 8/24/17 1015

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.2	525.6	565.2	0.27	5.73	0.277	0.271 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170825
 OUL Number: C4850
 Matrix: Elutant
 Date Placed: 8/24/17 1015

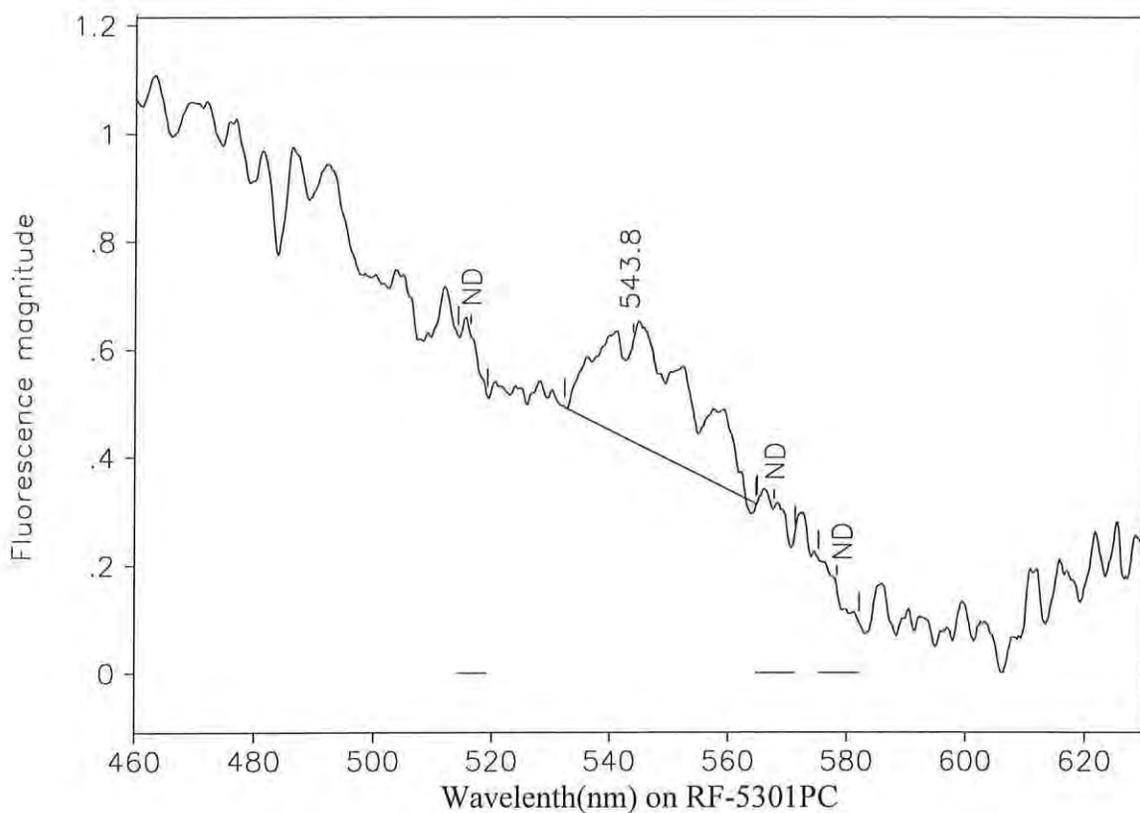
Analyzed: 9/1/17
 Duration: 1.01 days
 Date collected: 8/25/17 1030

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
544.4	528.8	564.6	0.23	6.30	0.295	0.298 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170825
 OUL Number: C4850D
 Matrix: Elutant
 Date Placed: 8/24/17 1015

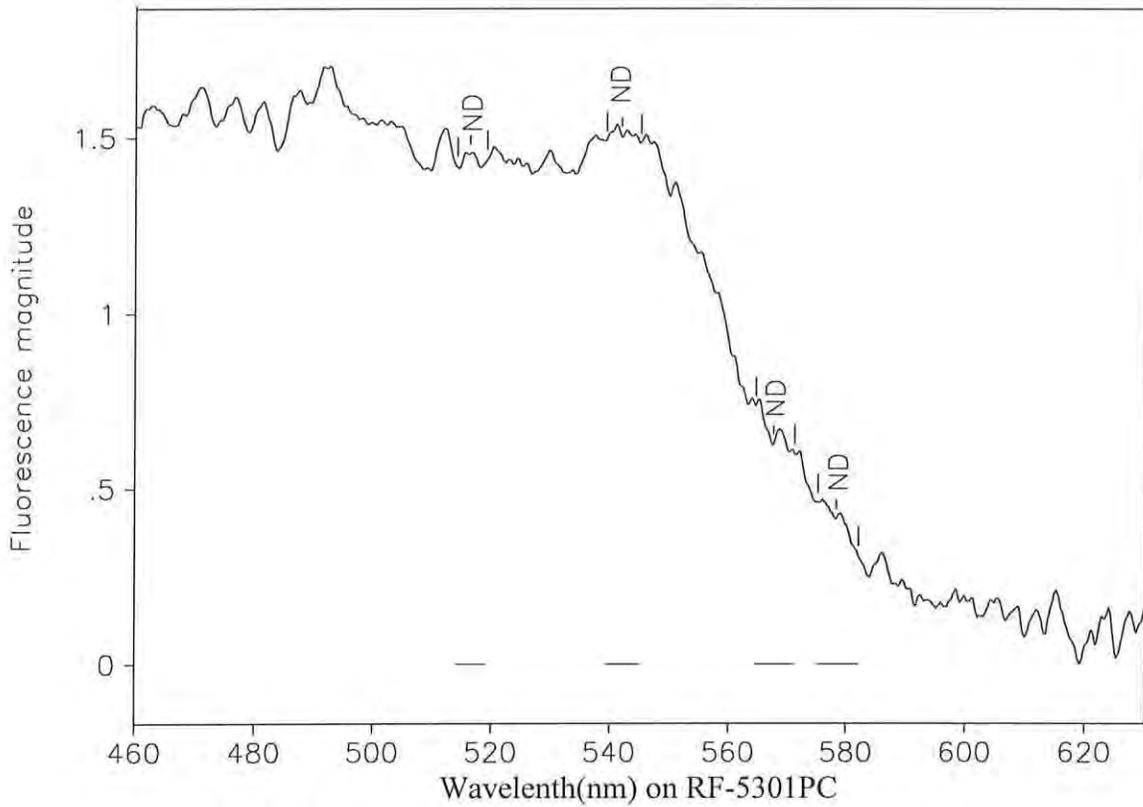
Analyzed: 9/1/17
 Duration: 1.01 days
 Date collected: 8/25/17 1030

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.8	532.2	564.8	0.18	3.97	0.185	0.187 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170821
 OUL Number: C4833
 Matrix: Elutant
 Date Placed: 8/15/17 1300

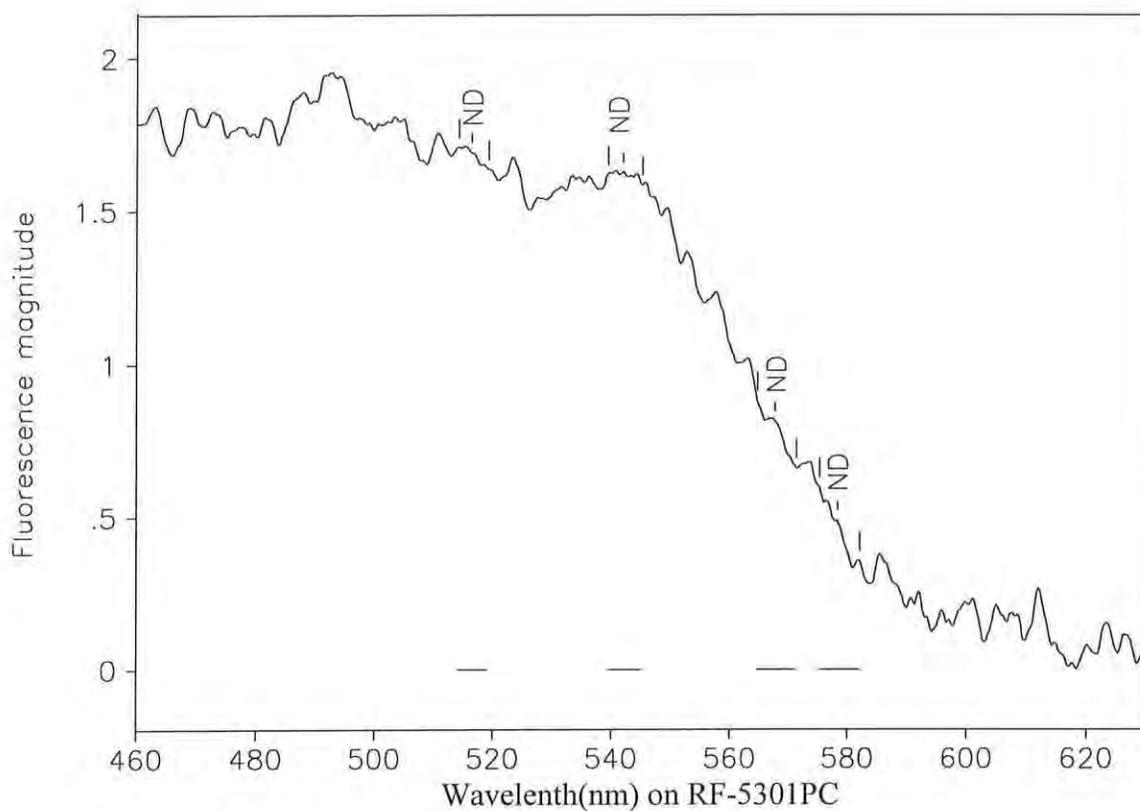
Analyzed: 9/1/17
 Duration: 5.87 days
 Date collected: 8/21/17 0951

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170821
 OUL Number: C4833D
 Matrix: Elutant
 Date Placed: 8/15/17 1300

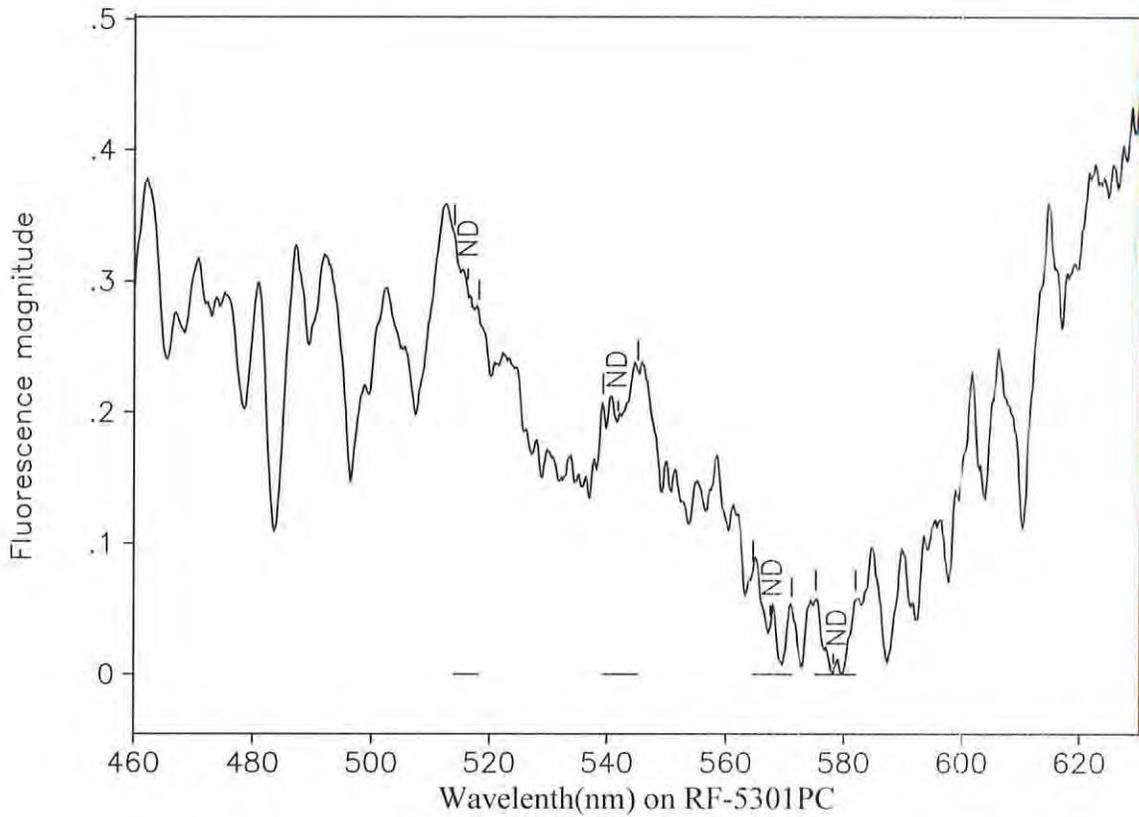
Analyzed: 9/1/17
 Duration: 5.87 days
 Date collected: 8/21/17 0951

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170822
 OUL Number: C4834
 Matrix: Elutant
 Date Placed: 8/21/17 0956

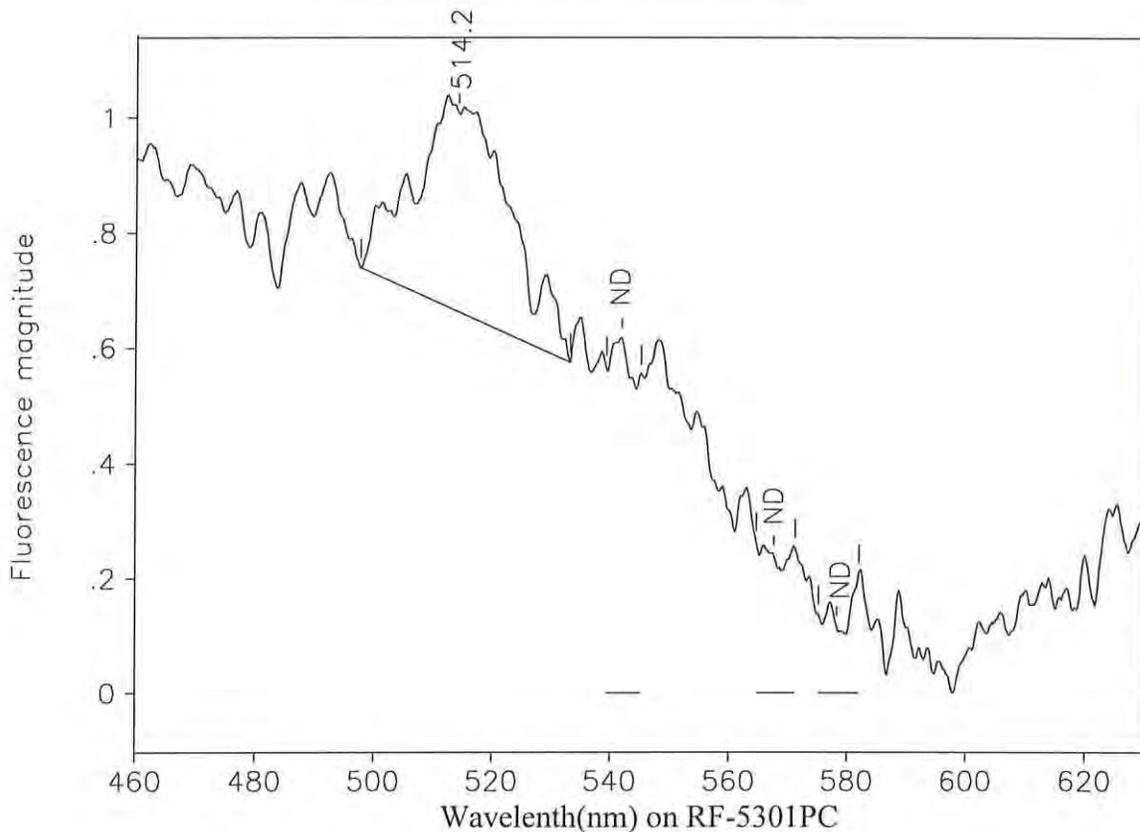
Analyzed: 9/1/17
 Duration: 0.909 days
 Date collected: 8/22/17 0745

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.0	518.1	0.00	0.00		ND
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170822
 OUL Number: C4834D
 Matrix: Elutant
 Date Placed: 8/21/17 0956

Analyzed: 9/1/17
 Duration: 0.909 days
 Date collected: 8/22/17 0745

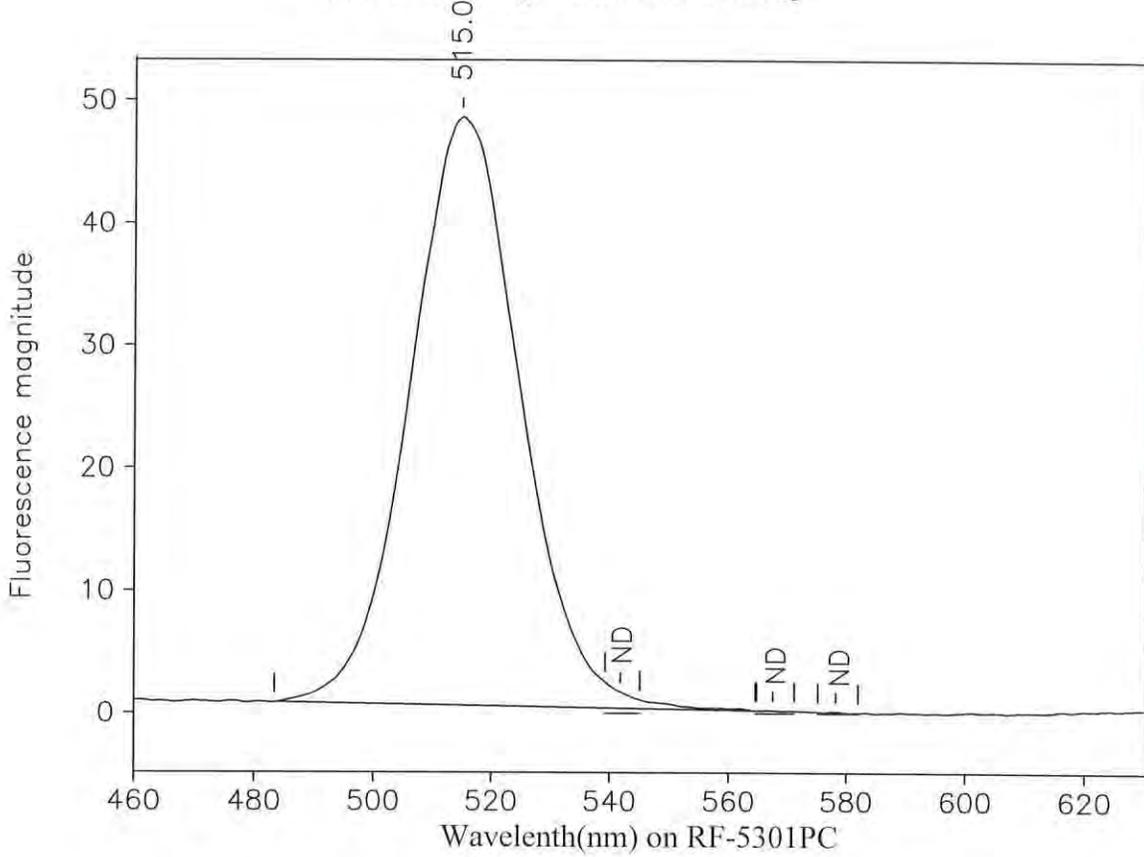
Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	FI
514.2	497.6	533.2	0.34	6.87	0.283	0.258	FI
541.8	539.3	545.1	0.00	0.00		ND	
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Calson

Ozark Underground Laboratory



Station MP4: MP420170823
 OUL Number: C4838
 Matrix: Elutant
 Date Placed: 8/22/17 0800

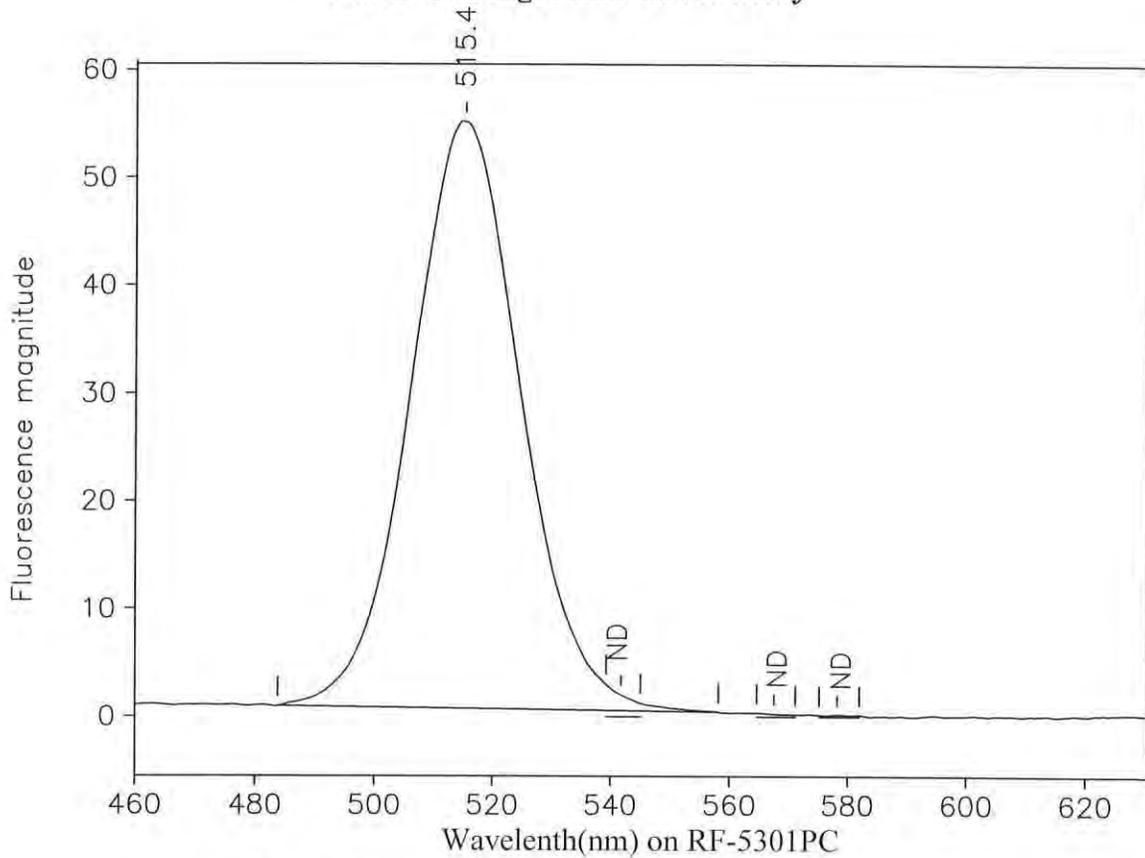
Analyzed: 9/1/17
 Duration: 1.13 days
 Date collected: 8/23/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.0	483.4	564.8	48.01	1,043.91	34.7	39.2 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170823
 OUL Number: C4838D
 Matrix: Elutant
 Date Placed: 8/22/17 0800

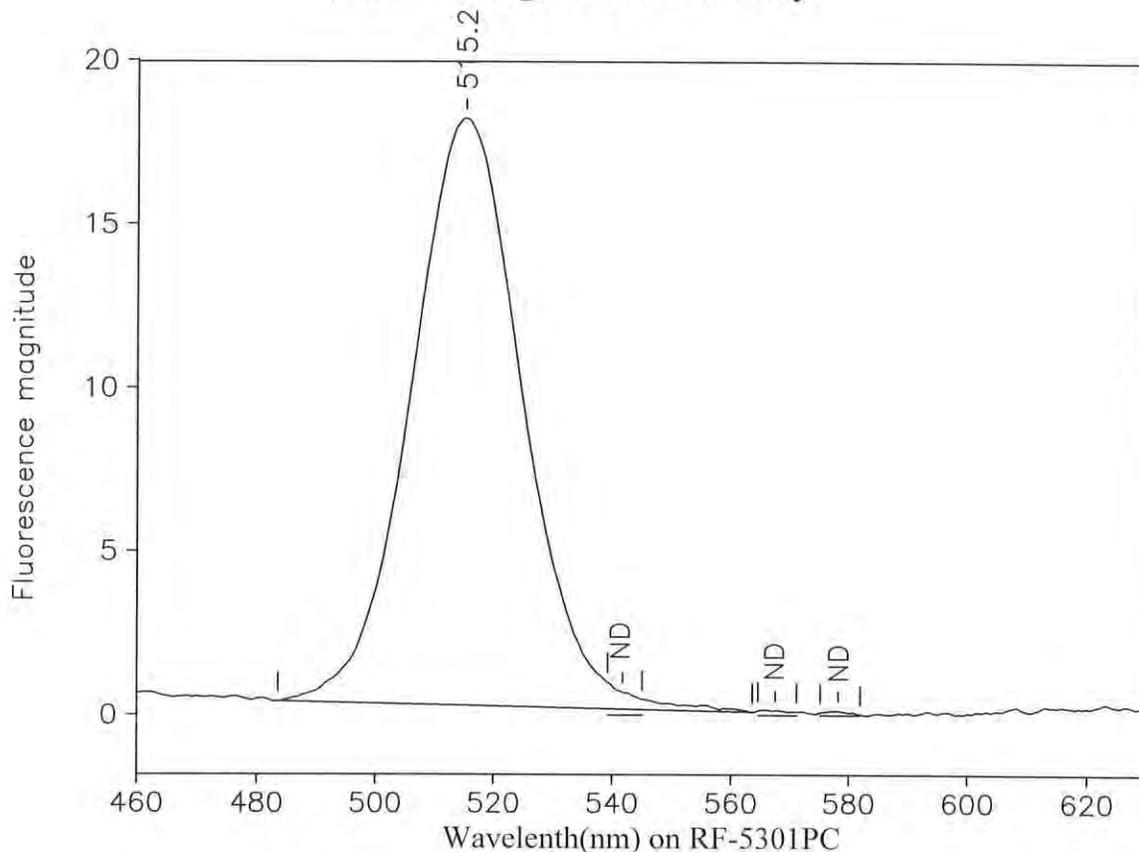
Analyzed: 9/1/17
 Duration: 1.13 days
 Date collected: 8/23/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.4	483.8	558.2	54.45	1,182.12	39.3	44.4 F1
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170823

OUL Number: C4839

Matrix: Elutant

Date Placed: 8/23/17 1100

Analyzed: 9/1/17

Duration: 0.313 days

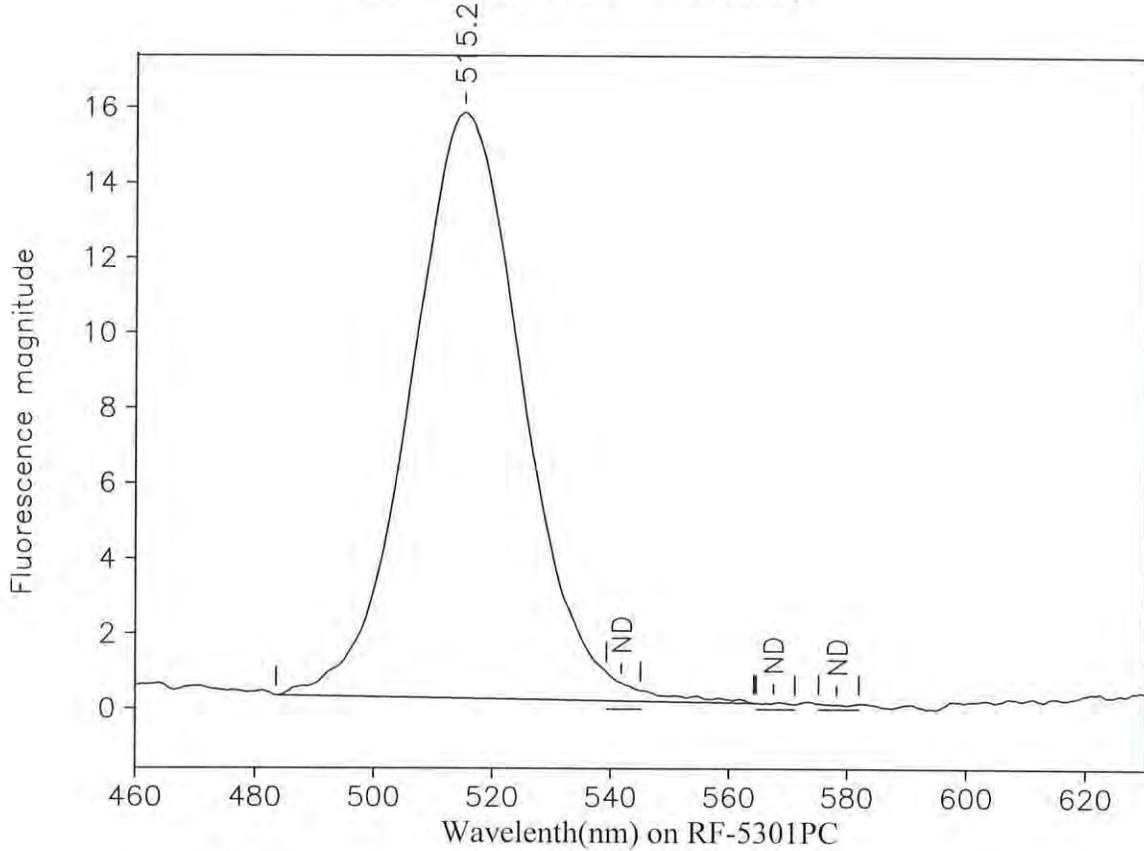
Date collected: 8/23/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.2	483.6	563.6	17.92	391.62	47.0	14.7 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170823
 OUL Number: C4839D
 Matrix: Elutant
 Date Placed: 8/23/17 1100

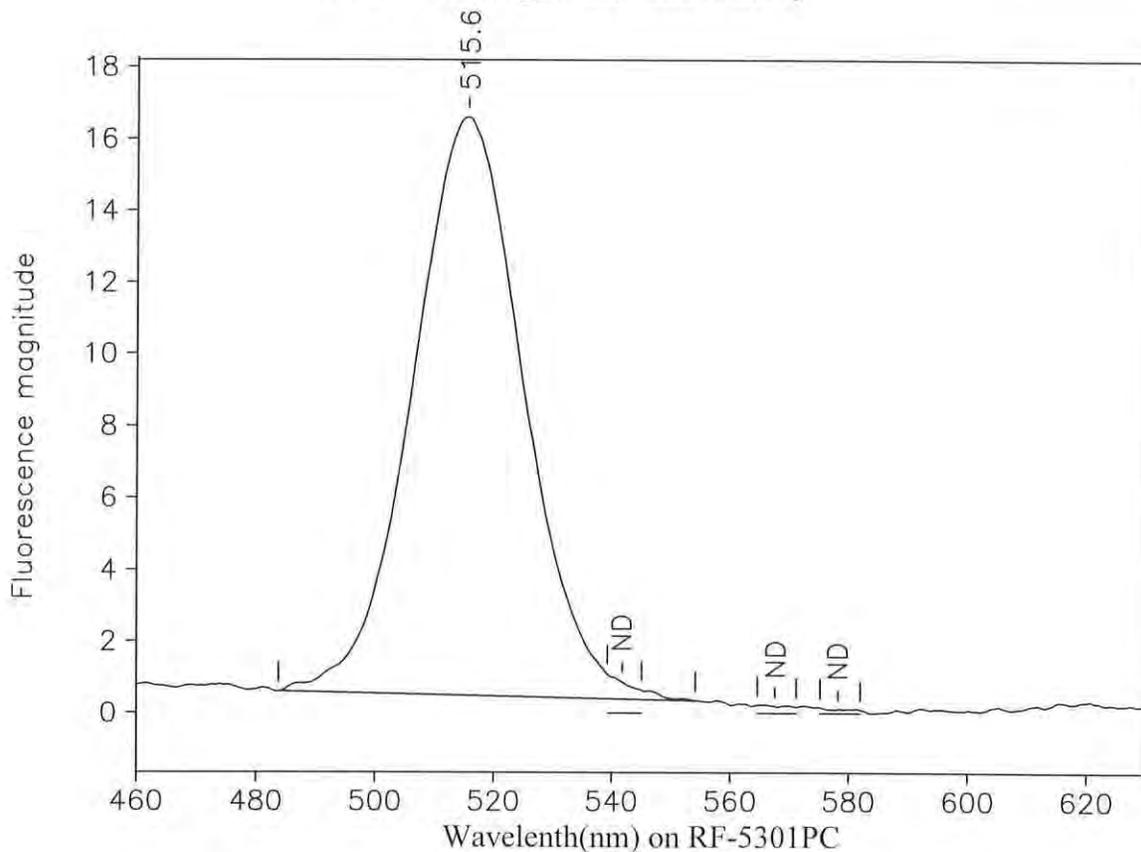
Analyzed: 9/1/17
 Duration: 0.313 days
 Date collected: 8/23/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.2	483.6	564.2	15.58	341.07	40.9	12.8 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824
 OUL Number: C4845
 Matrix: Elutant
 Date Placed: 8/23/17 1830

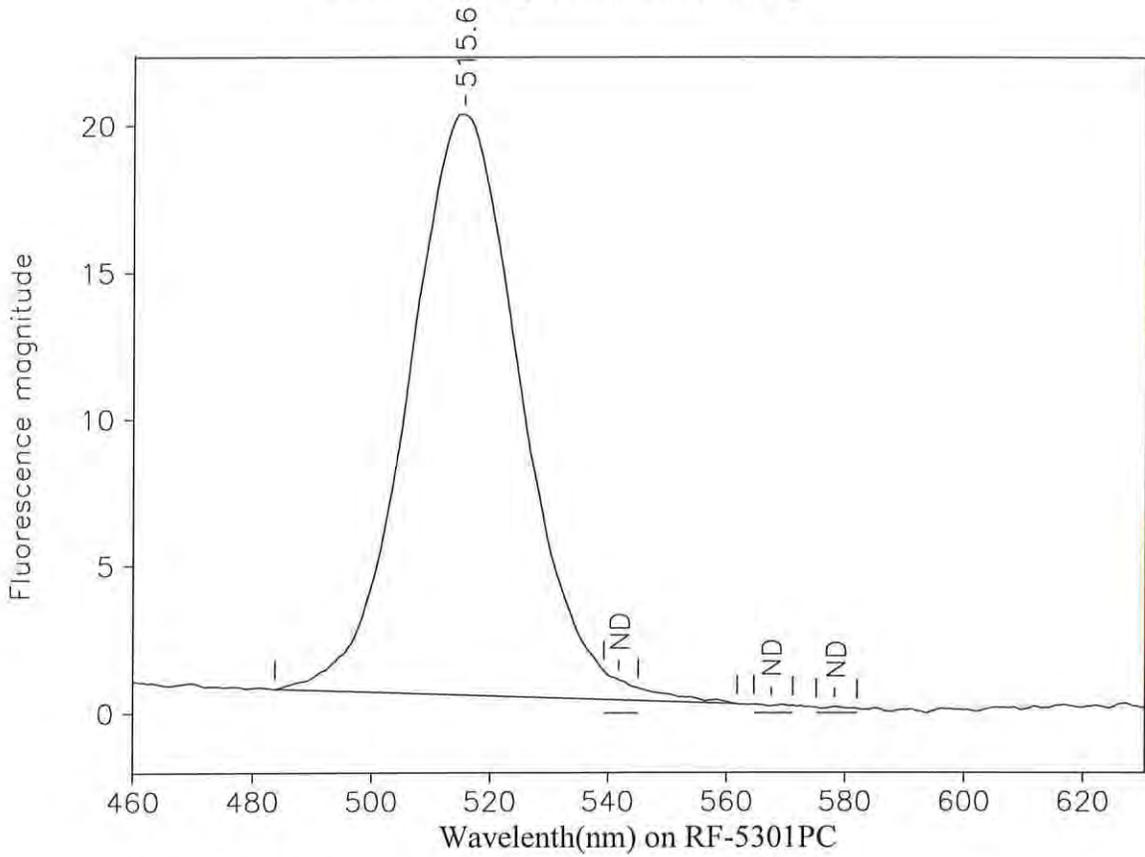
Analyzed: 9/1/17
 Duration: 0.677 days
 Date collected: 8/24/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.6	483.8	554.2	16.11	350.65	19.4	13.2 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824
 OUL Number: C4845D
 Matrix: Elutant
 Date Placed: 8/23/17 1830

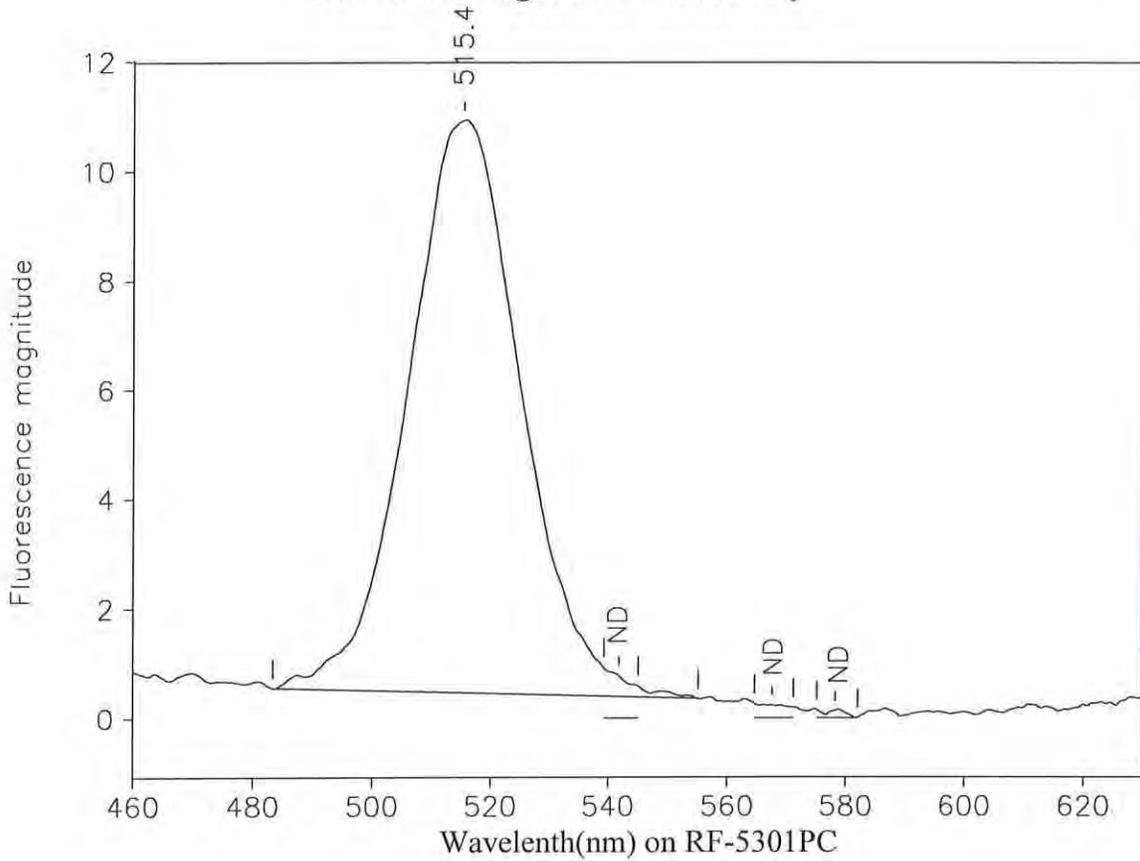
Analyzed: 9/1/17
 Duration: 0.677 days
 Date collected: 8/24/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.6	483.8	561.8	19.76	435.87	24.2	16.4 F1
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824
 OUL Number: C4846
 Matrix: Elutant
 Date Placed: 8/24/17 1045

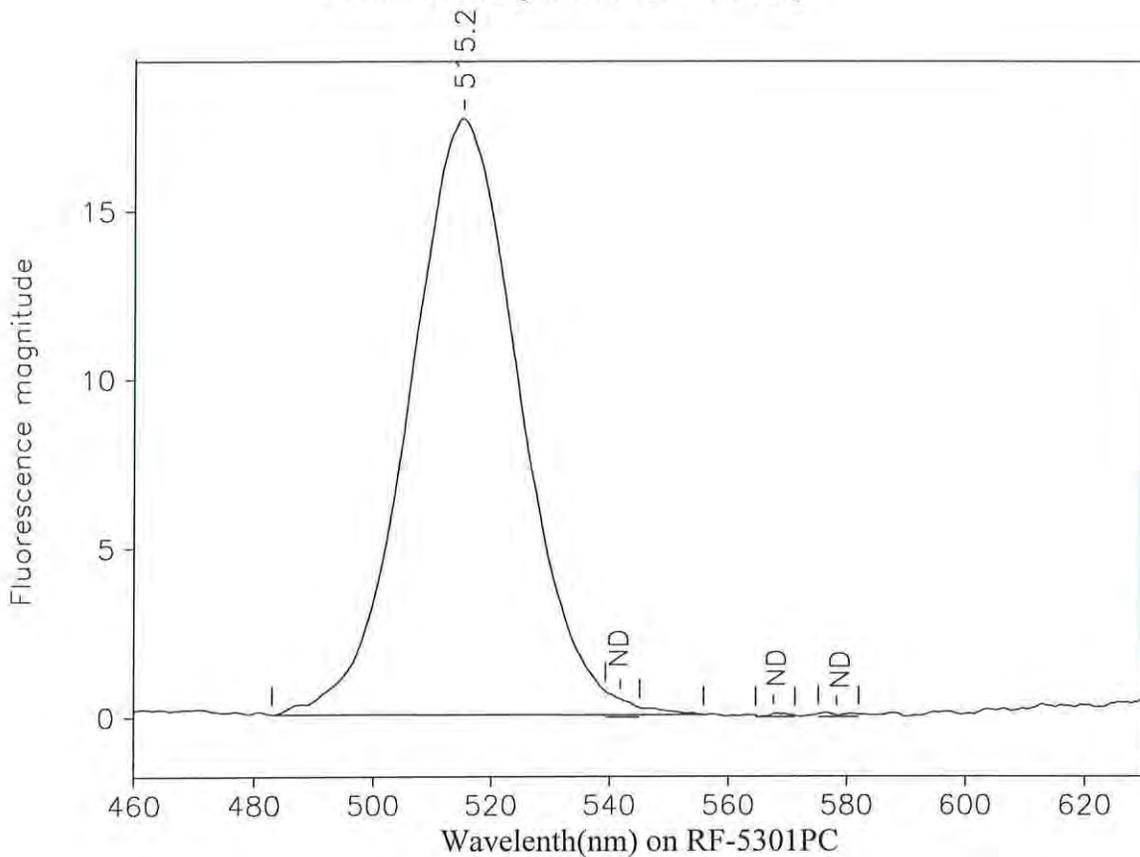
Analyzed: 9/1/17
 Duration: 0.323 days
 Date collected: 8/24/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.4	483.4	555.2	10.46	232.80	27.0	8.74 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824
 OUL Number: C4846D
 Matrix: Elutant
 Date Placed: 8/24/17 1045

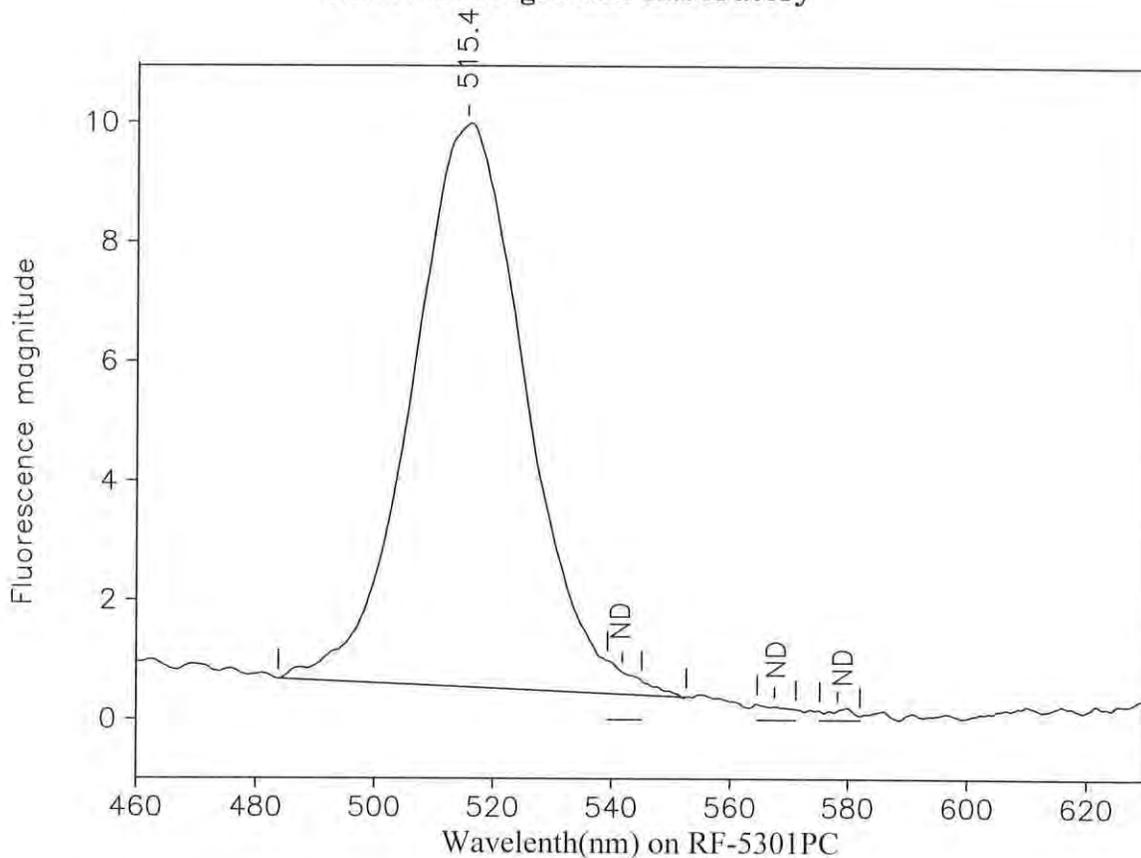
Analyzed: 9/1/17
 Duration: 0.323 days
 Date collected: 8/24/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.2	483.0	555.8	17.64	383.20	44.5	14.4 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170825

OUL Number: C4851

Matrix: Elutant

Date Placed: 8/24/17 1045

Analyzed: 9/1/17

Duration: 1.01 days

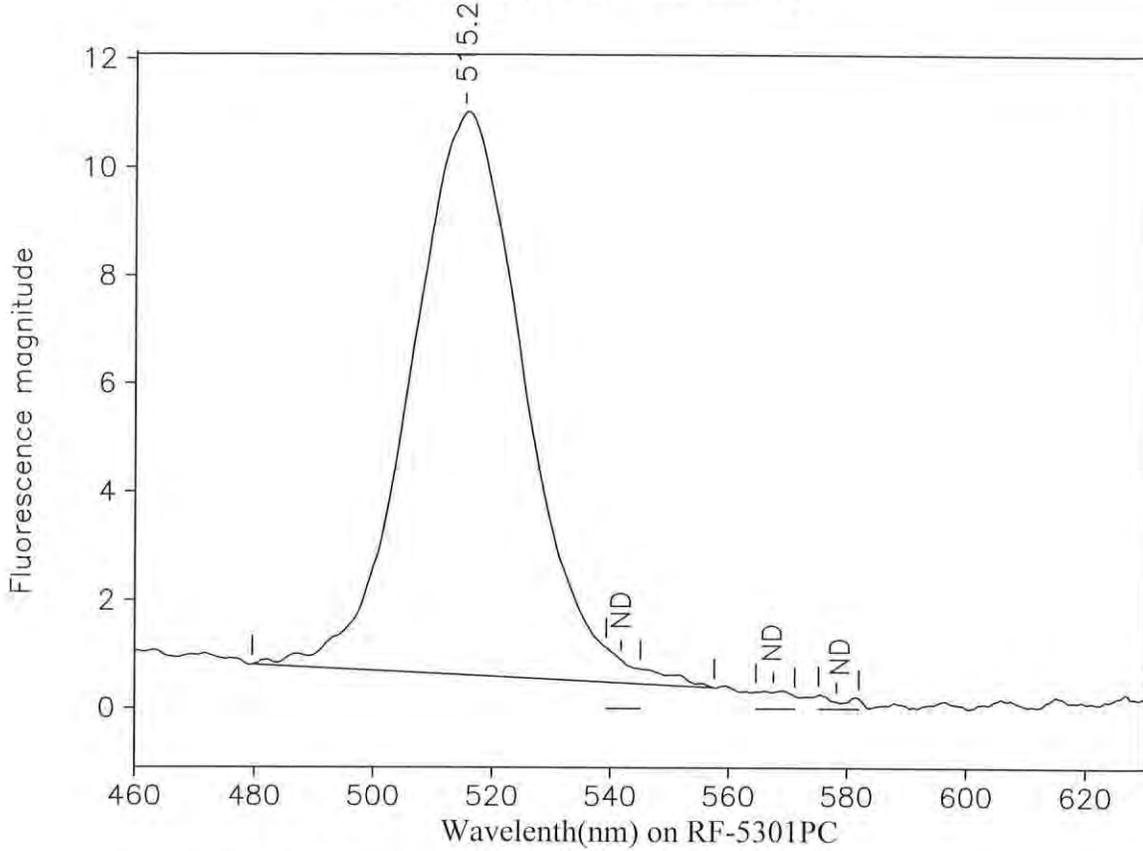
Date collected: 8/25/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.4	483.8	552.6	9.42	210.64	7.83	7.90 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170825
 OUL Number: C4851D
 Matrix: Elutant
 Date Placed: 8/24/17 1045

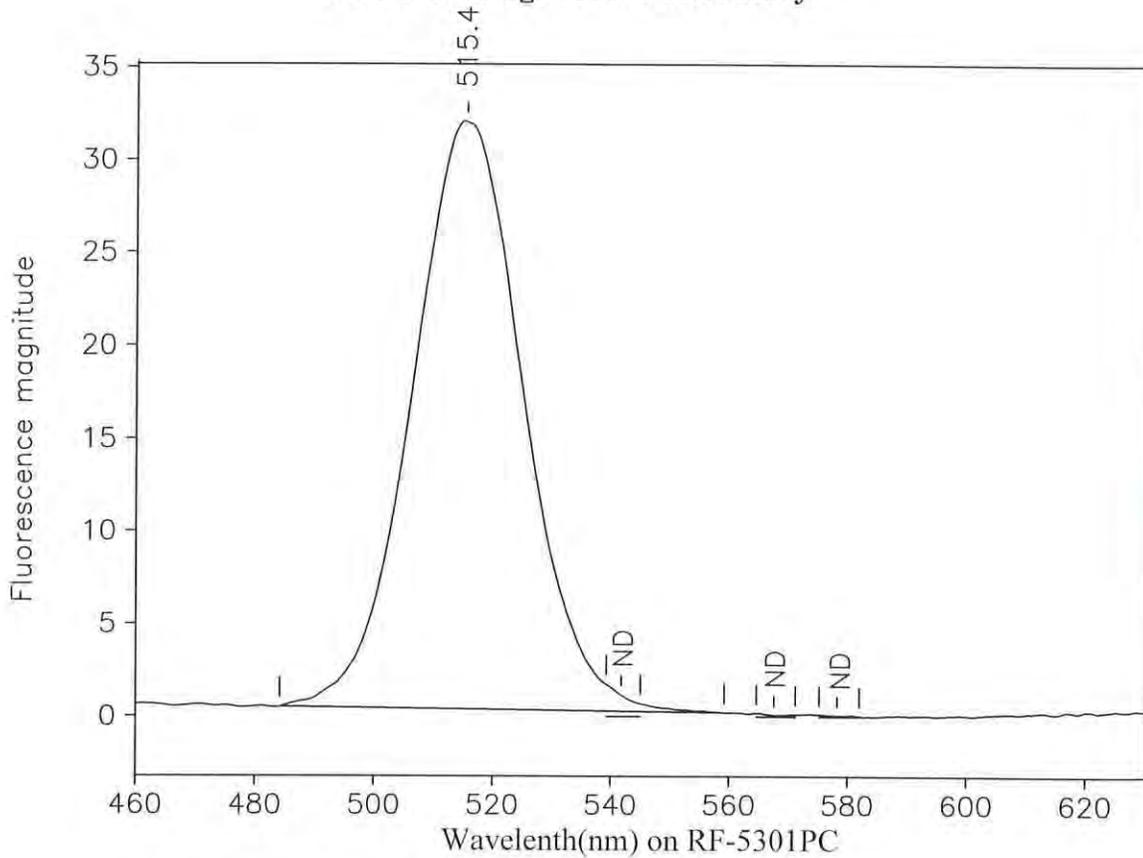
Analyzed: 9/1/17
 Duration: 1.01 days
 Date collected: 8/25/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.2	479.6	557.6	10.38	232.08	8.62	8.71 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170825
 OUL Number: C4852
 Matrix: Elutant
 Date Placed: 8/24/17 1100

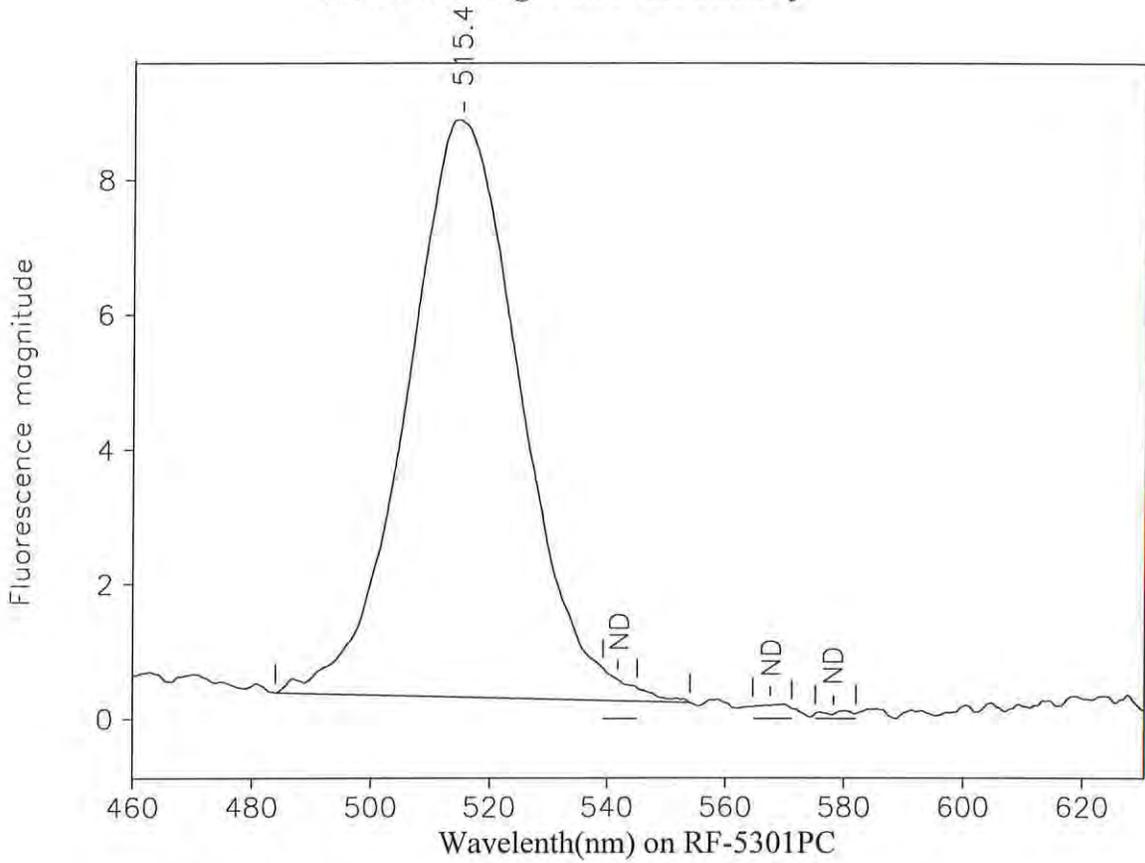
Analyzed: 9/1/17
 Duration: 1.31 days
 Date collected: 8/25/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.4	484.2	559.2	31.65	690.22	19.8	25.9 FI
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170825
 OUL Number: C4852D
 Matrix: Elutant
 Date Placed: 8/24/17 1100

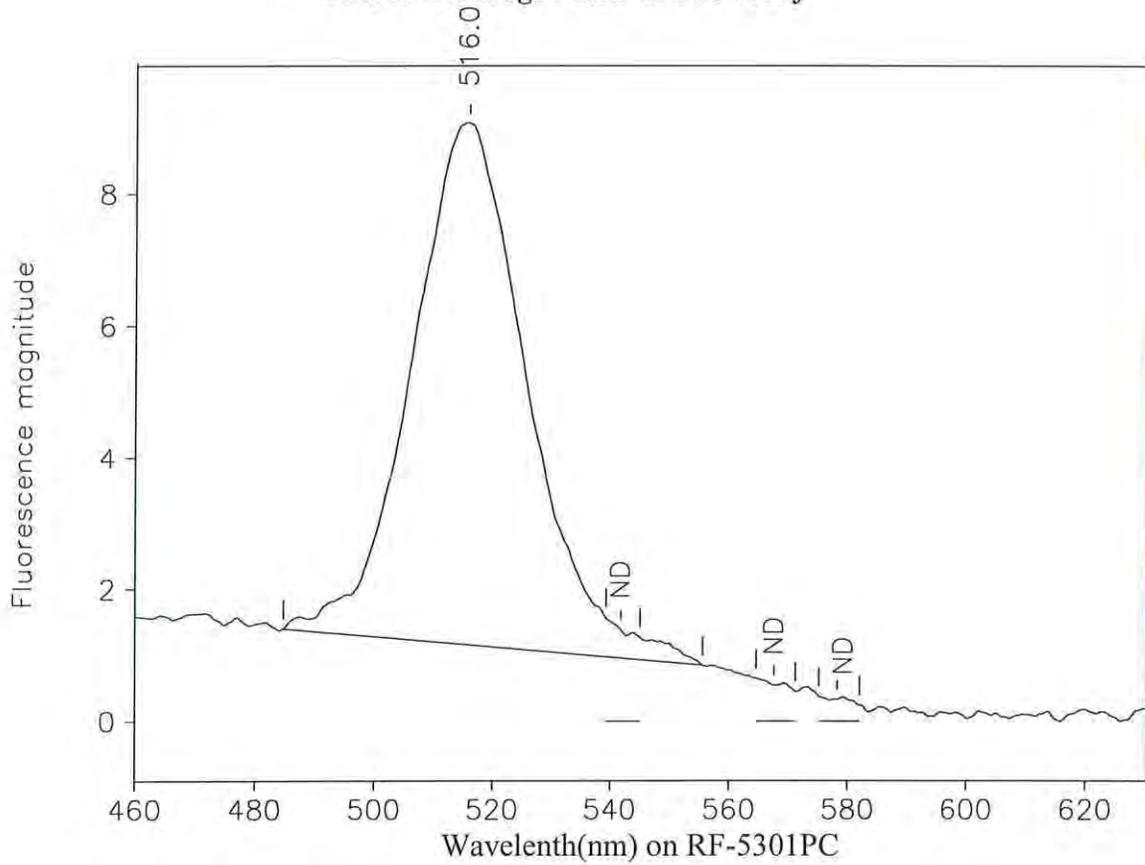
Analyzed: 9/1/17
 Duration: 1.31 days
 Date collected: 8/25/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
515.4	484.0	554.0	8.55	189.95	5.44	7.13 F1
541.8	539.3	545.1	0.00	0.00		ND
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170828
 OUL Number: C4853
 Matrix: Elutant
 Date Placed: / /

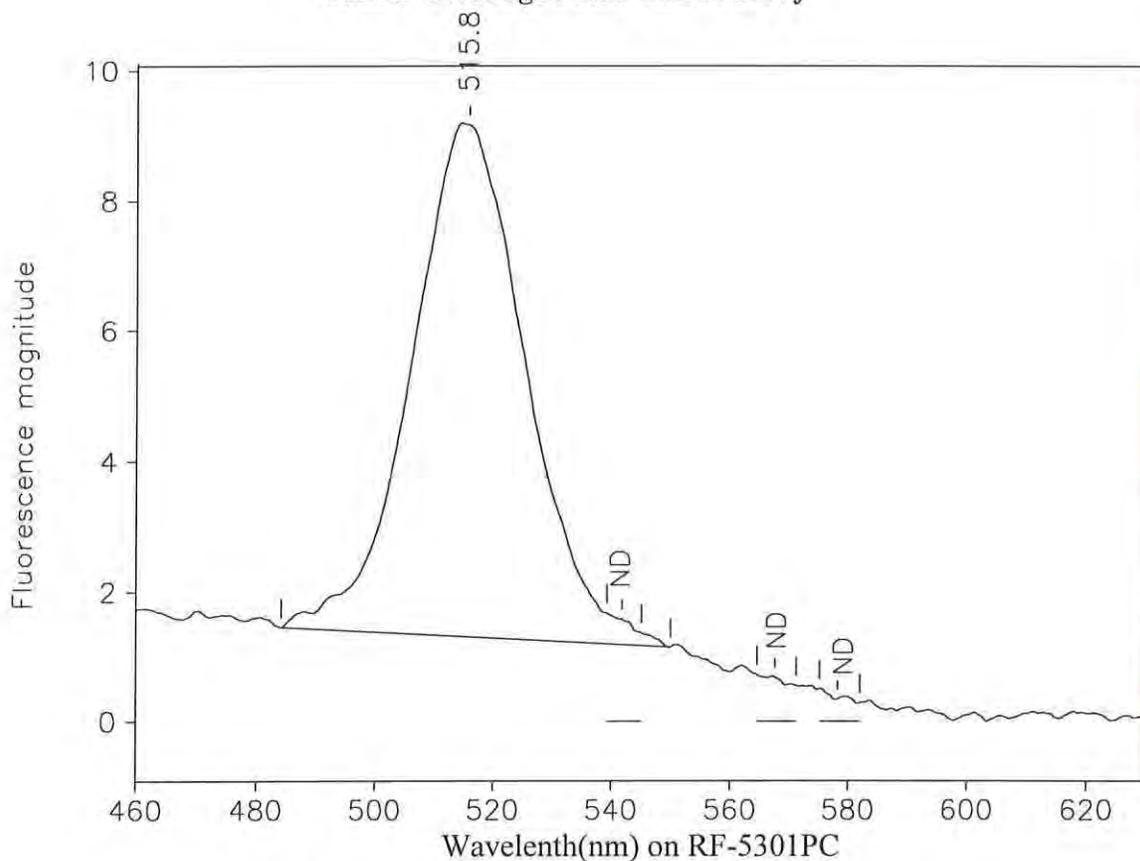
Analyzed: 9/1/17
 Duration: N/A
 Date collected: 8/28/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
516.0	484.8	555.6	7.91	179.82	6.75 FI
541.8	539.3	545.1	0.00	0.00	ND
567.5	564.6	571.2	0.00	0.00	ND
578.2	575.2	582.0	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170828

OUL Number: C4853D

Matrix: Elutant

Date Placed: / /

Analyzed: 9/1/17

Duration: N/A

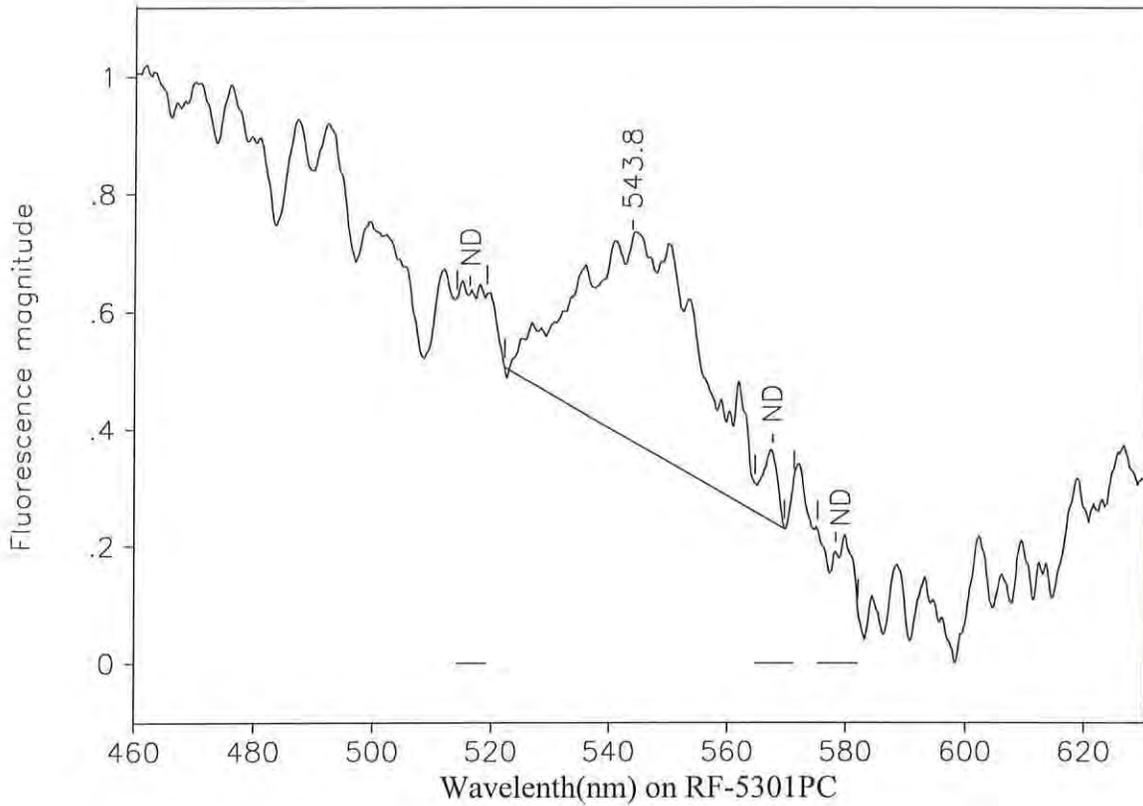
Date collected: 8/28/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
515.8	484.2	550.0	7.87	176.88	6.64 F1
541.8	539.3	545.1	0.00	0.00	ND
567.5	564.6	571.2	0.00	0.00	ND
578.2	575.2	582.0	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170822
 OUL Number: C4837
 Matrix: Elutant
 Date Placed: 8/21/17 1345

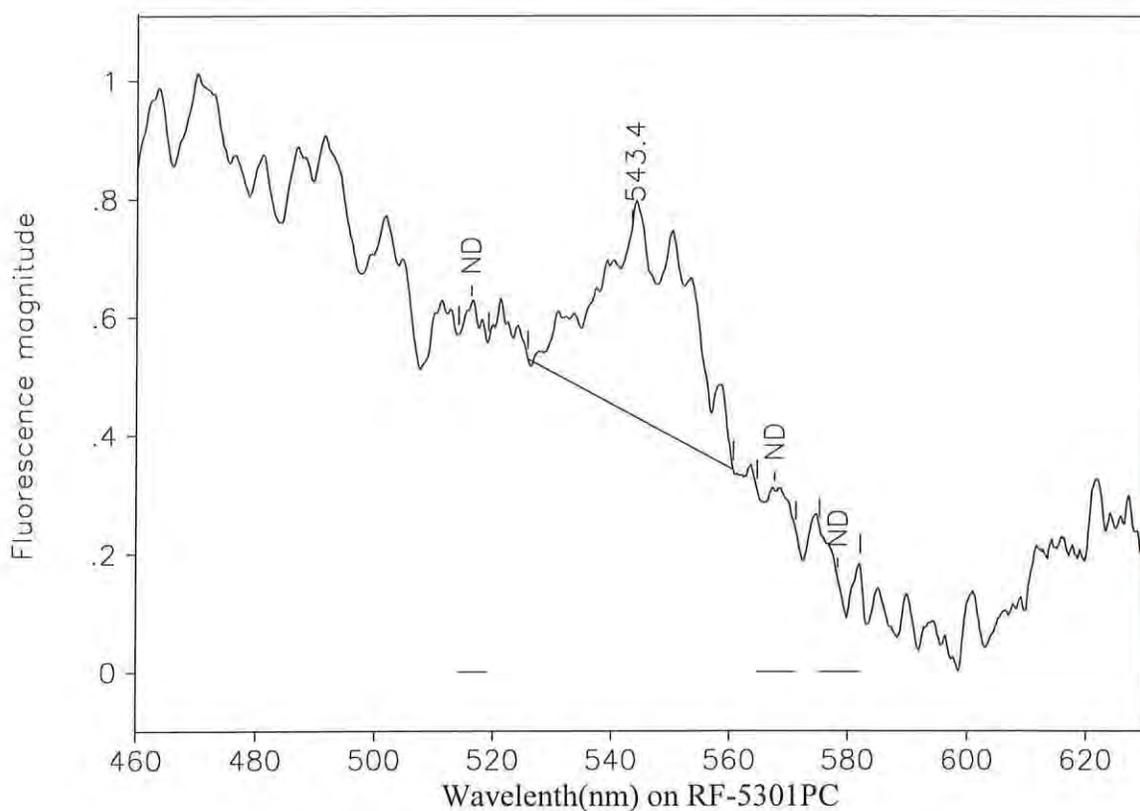
Analyzed: 9/1/17
 Duration: 0.948 days
 Date collected: 8/22/17 1230

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.8	522.2	569.6	0.34	9.05	0.451	0.427 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170822
 OUL Number: C4837D
 Matrix: Elutant
 Date Placed: 8/21/17 1345

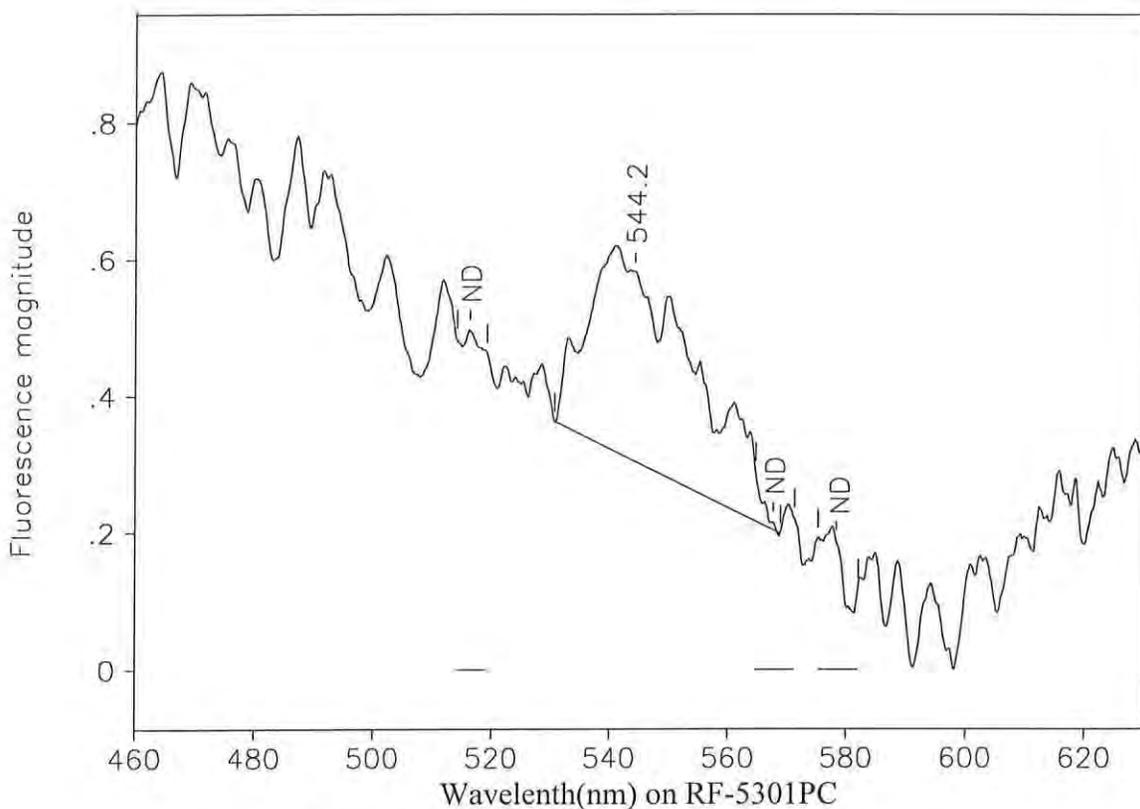
Analyzed: 9/1/17
 Duration: 0.948 days
 Date collected: 8/22/17 1230

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	
516.3	514.1	519.2	0.00	0.00		ND	
543.4	525.8	560.6	0.31	6.24	0.311	0.295	Eo
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170823
 OUL Number: C4843
 Matrix: Elutant
 Date Placed: 8/22/17 1230

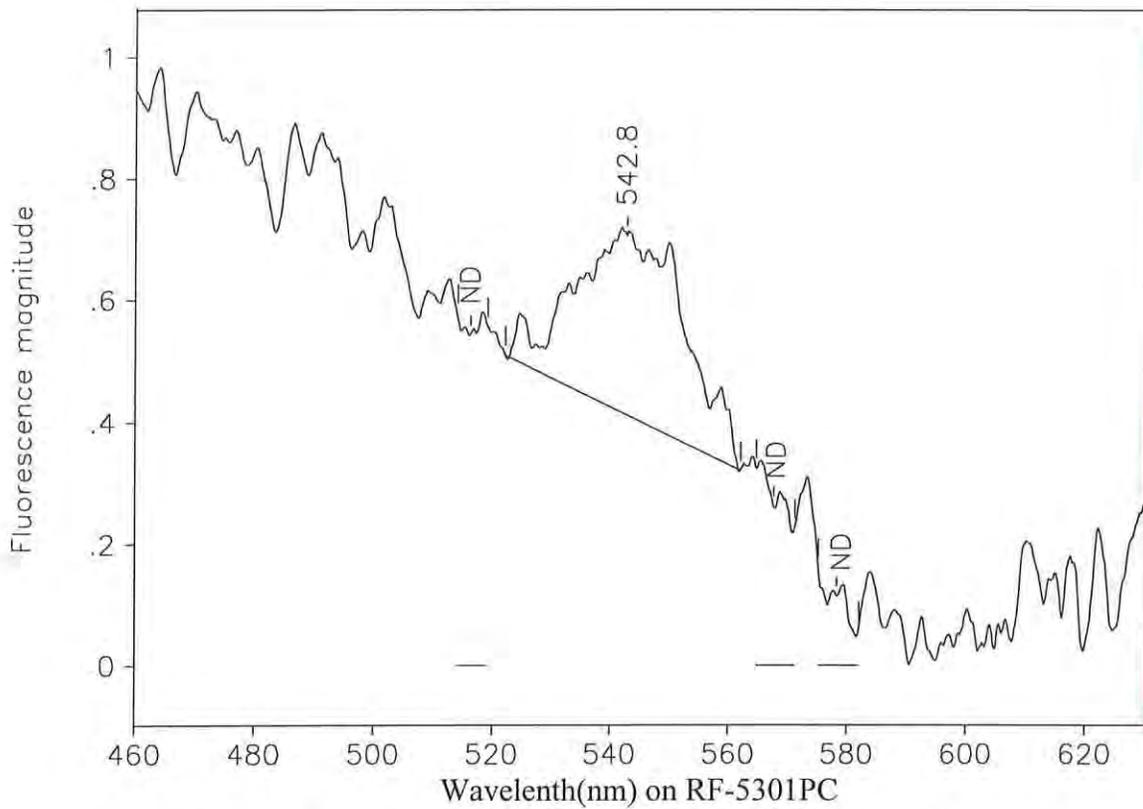
Analyzed: 9/1/17
 Duration: 0.889 days
 Date collected: 8/23/17 0950

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
544.2	530.6	568.8	0.28	6.39	0.340	0.302 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170823
 OUL Number: C4843D
 Matrix: Elutant
 Date Placed: 8/22/17 1230

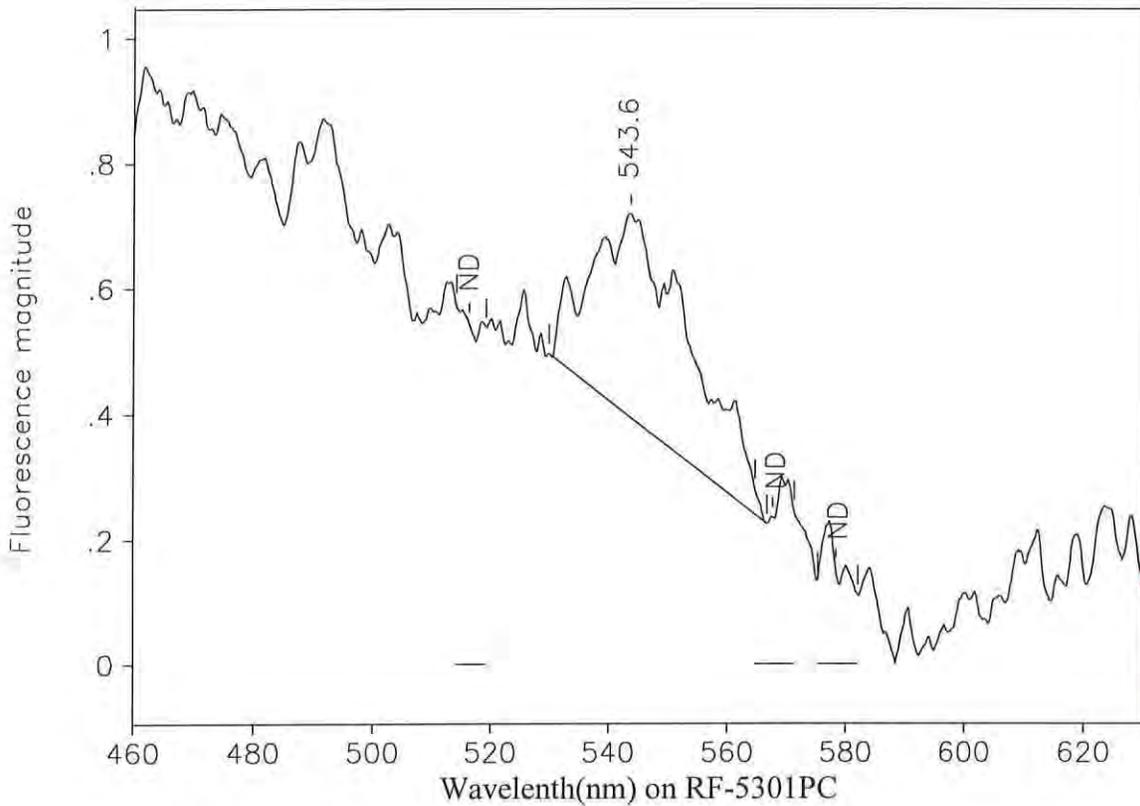
Analyzed: 9/1/17
 Duration: 0.889 days
 Date collected: 8/23/17 0950

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
542.8	522.2	562.0	0.29	6.53	0.347	0.309 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170824
 OUL Number: C4847
 Matrix: Elutant
 Date Placed: 8/23/17 0950

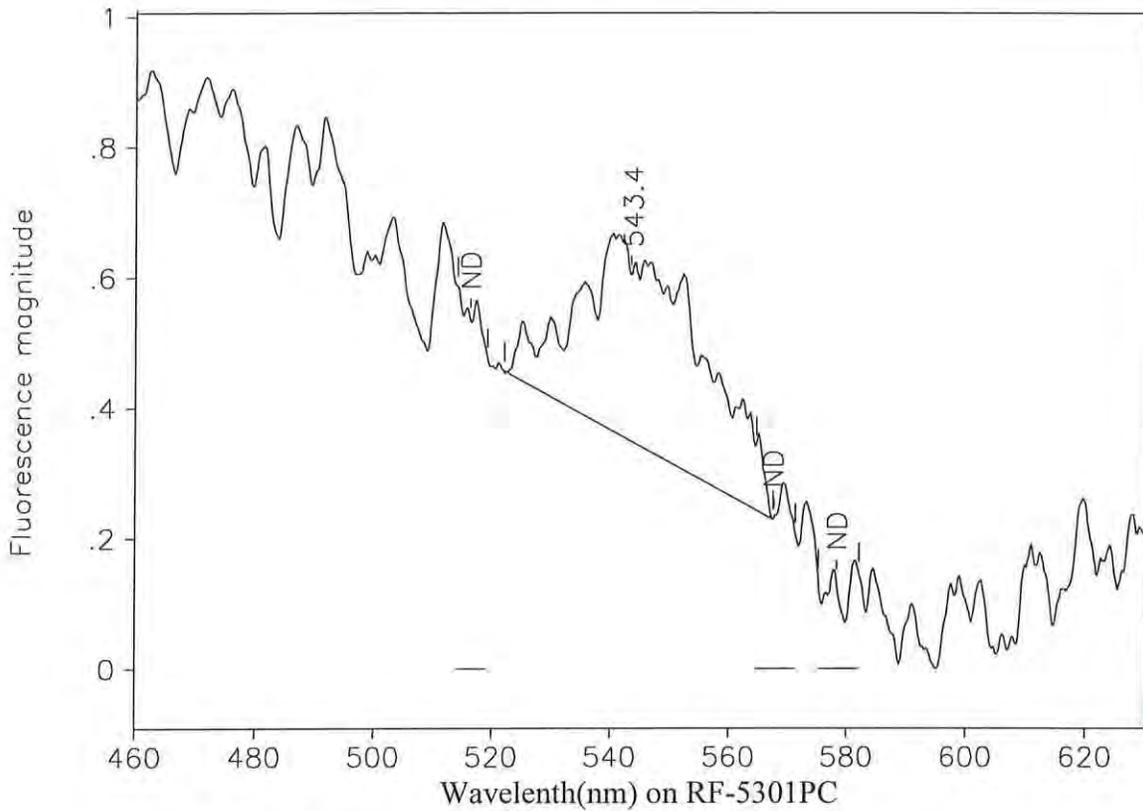
Analyzed: 9/1/17
 Duration: 1.05 days
 Date collected: 8/24/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.	
516.3	514.1	519.2	0.00	0.00		ND	
543.6	529.8	566.6	0.32	6.40	0.288	0.303	Eo
567.5	564.6	571.2	0.00	0.00		ND	
578.2	575.2	582.0	0.00	0.00		ND	

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170824
 OUL Number: C4847D
 Matrix: Elutant
 Date Placed: 8/23/17 0950

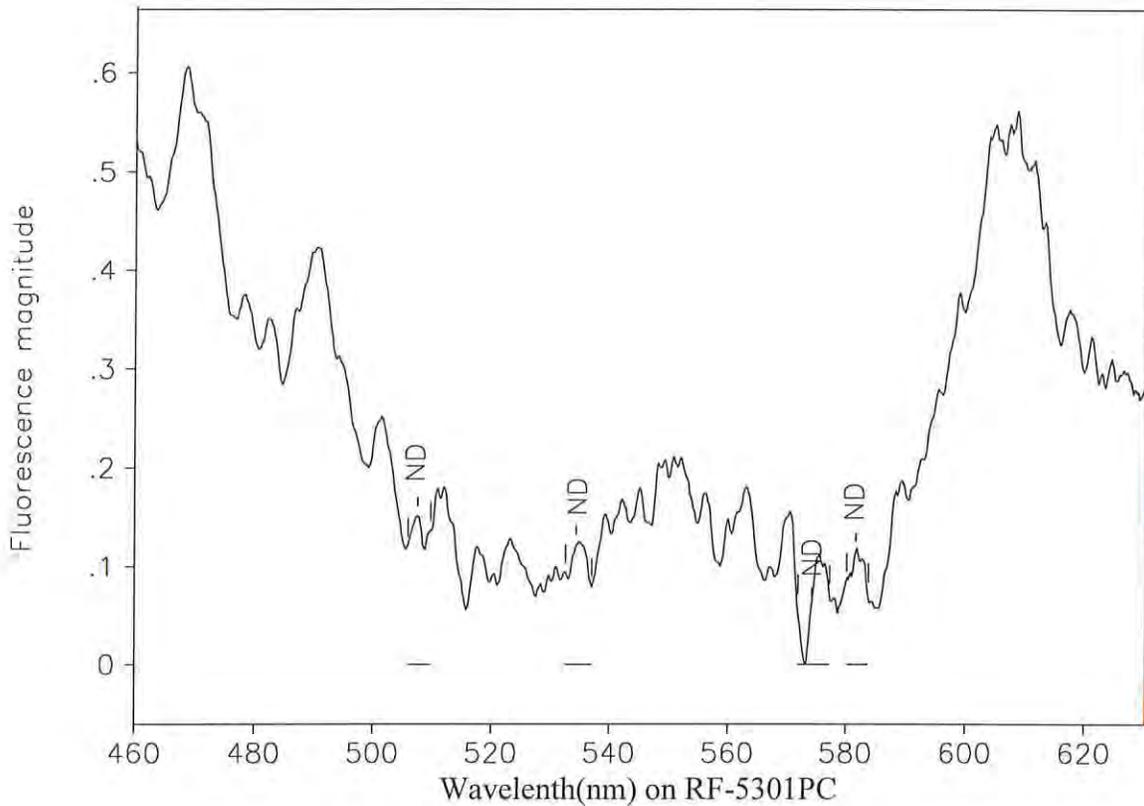
Analyzed: 9/1/17
 Duration: 1.05 days
 Date collected: 8/24/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc/Day	Conc.
516.3	514.1	519.2	0.00	0.00		ND
543.4	522.0	567.4	0.25	7.75	0.348	0.366 Eo
567.5	564.6	571.2	0.00	0.00		ND
578.2	575.2	582.0	0.00	0.00		ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170821OZ

OUL Number: C4871

Analyzed: 9/5/17

Matrix: Water

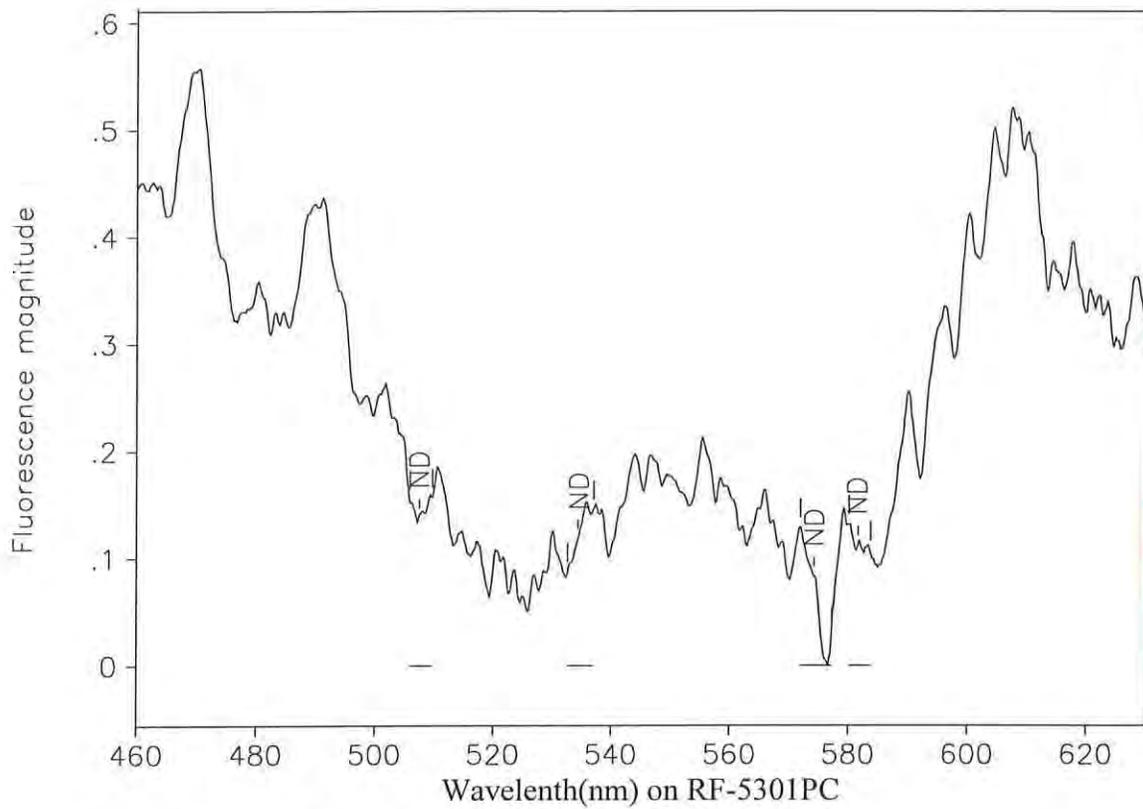
Date collected: 8/21/17 1215

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170822OZ

OUL Number: C4870

Analyzed: 9/5/17

Matrix: Water

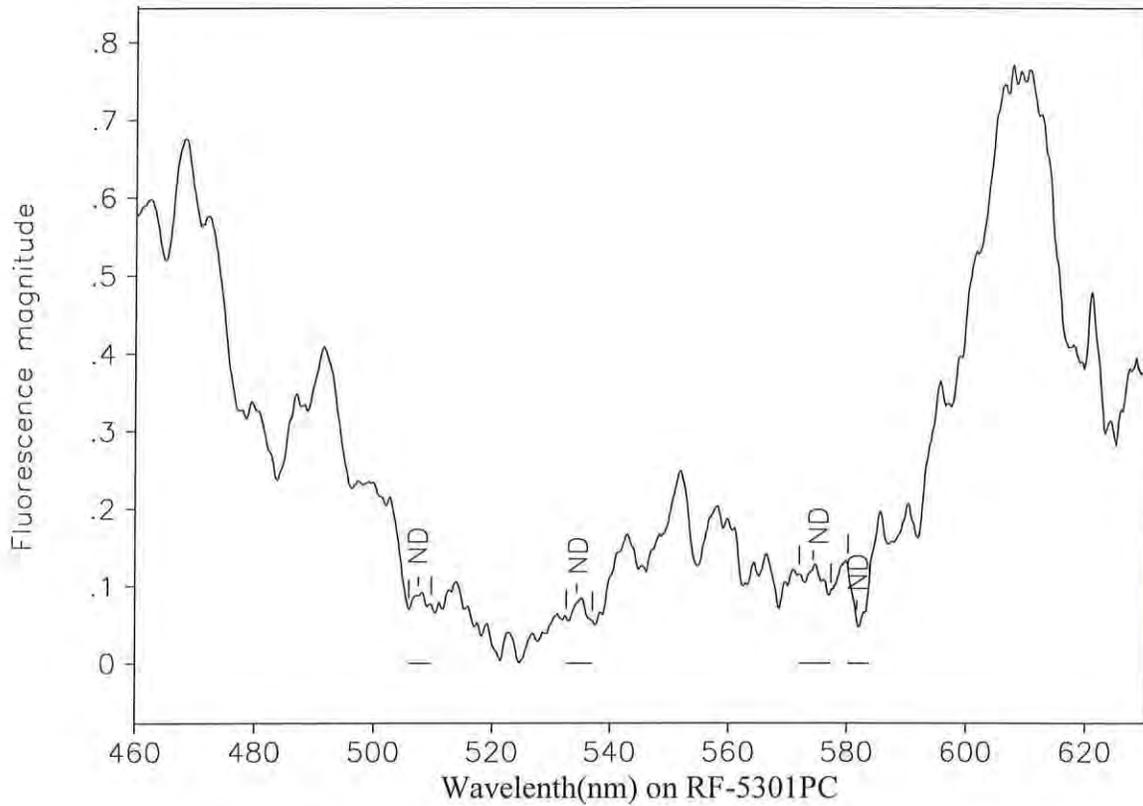
Date collected: 8/22/17 1130

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170823OZ

OUL Number: C4875

Analyzed: 9/5/17

Matrix: Water

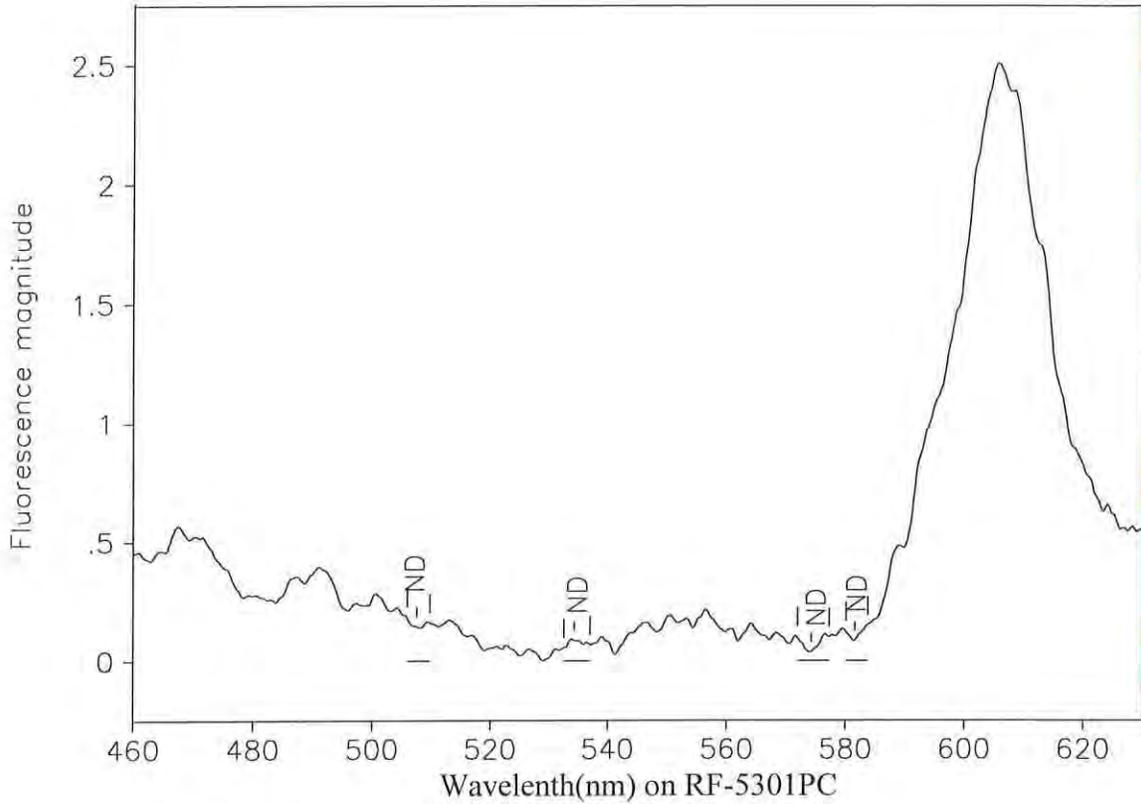
Date collected: 8/23/17 1150

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170824OZ

OUL Number: C4881

Analyzed: 9/5/17

Matrix: Water

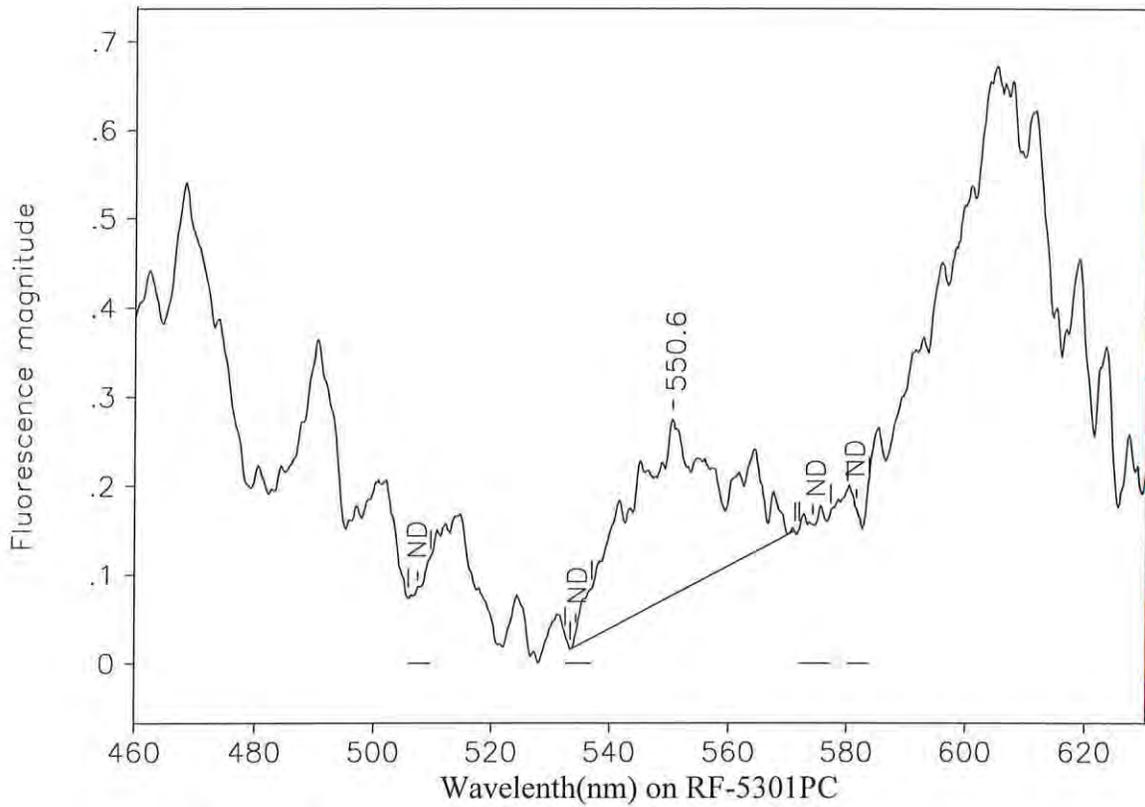
Date collected: 8/24/17 1145

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP1: MP120170825OZ

OUL Number: C4879

Analyzed: 9/5/17

Matrix: Water

Date collected: 8/25/17 1230

Peaks within the normal range of tracer dyes:

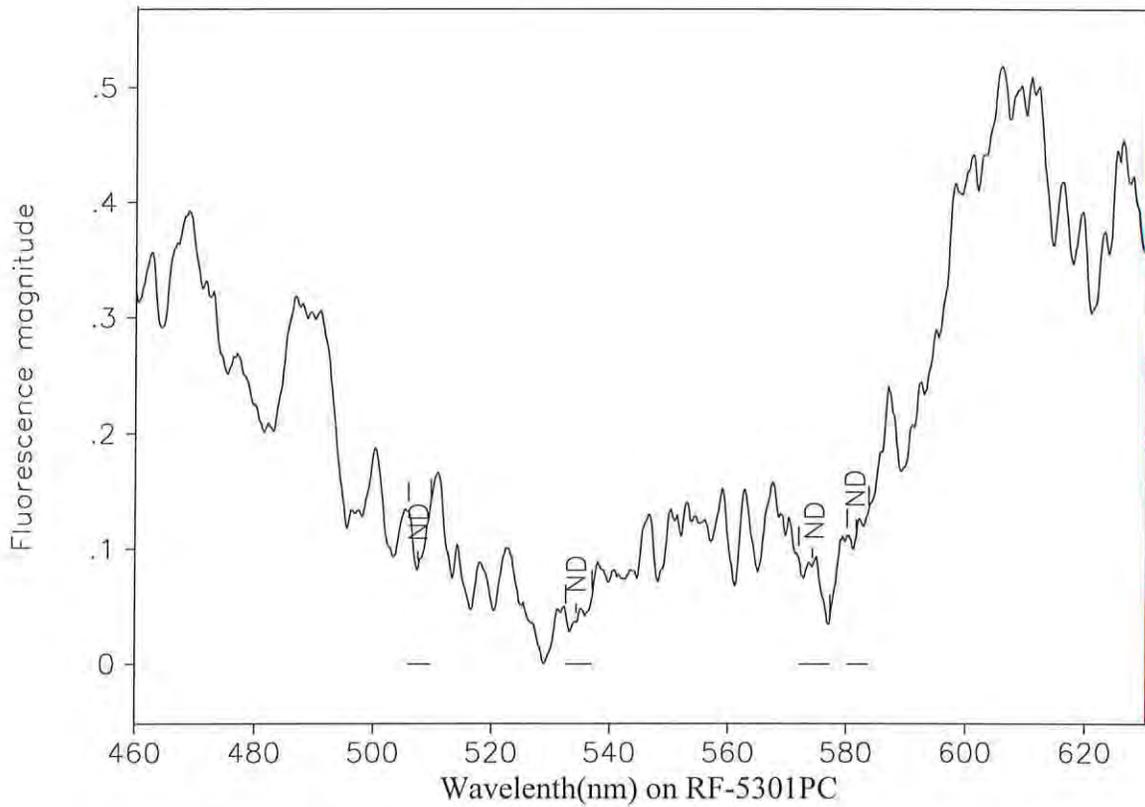
Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

550.6	533.4	571.2	0.20	3.76	
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~~0.035~~ Eo
ca/ow

Ozark Underground Laboratory



Station MP3: MP320170822OZ

OUL Number: C4869

Analyzed: 9/5/17

Matrix: Water

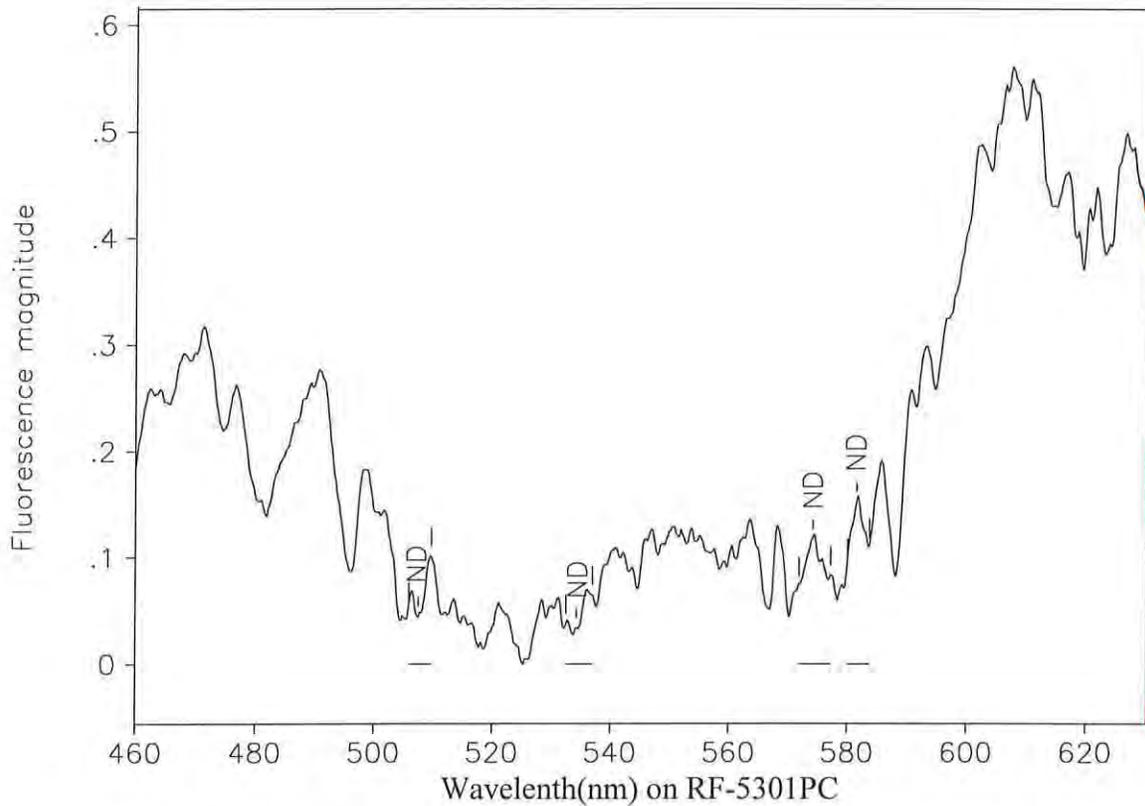
Date collected: 8/22/17 1015

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170823OZ

OUL Number: C4877

Analyzed: 9/5/17

Matrix: Water

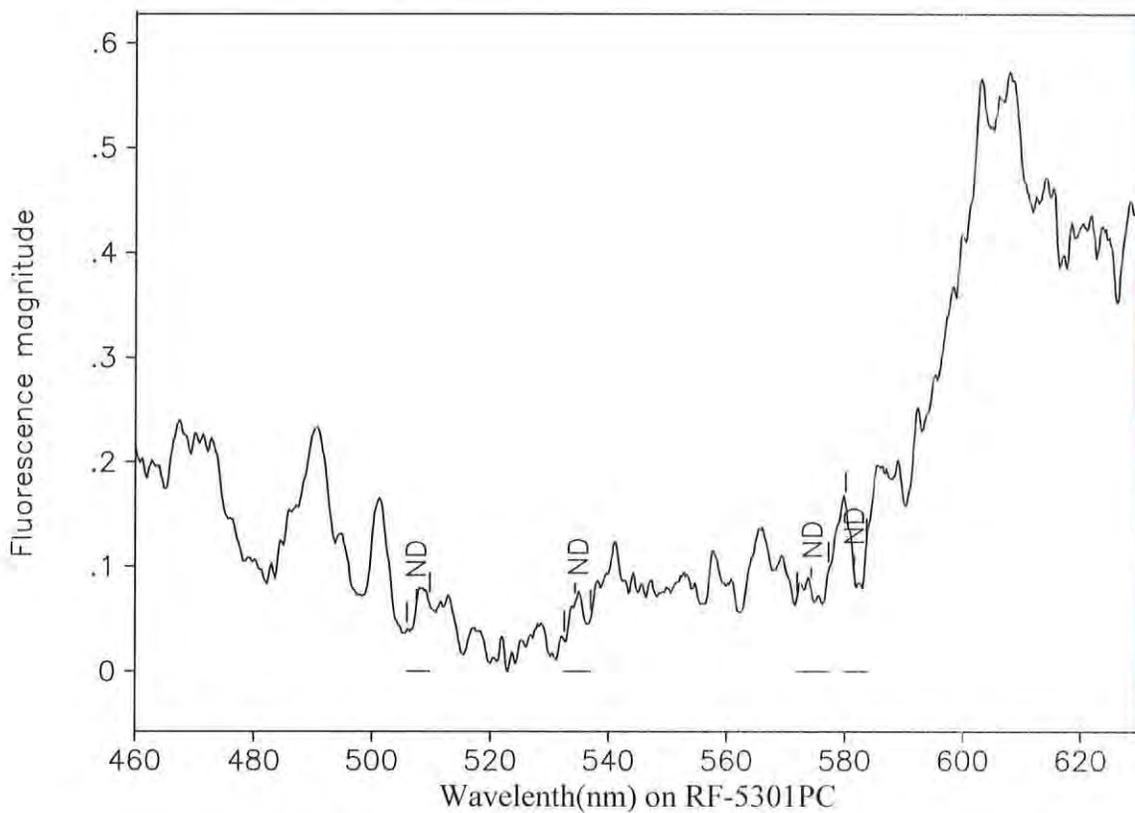
Date collected: 8/23/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170824OZ

OUL Number: C4878

Analyzed: 9/5/17

Matrix: Water

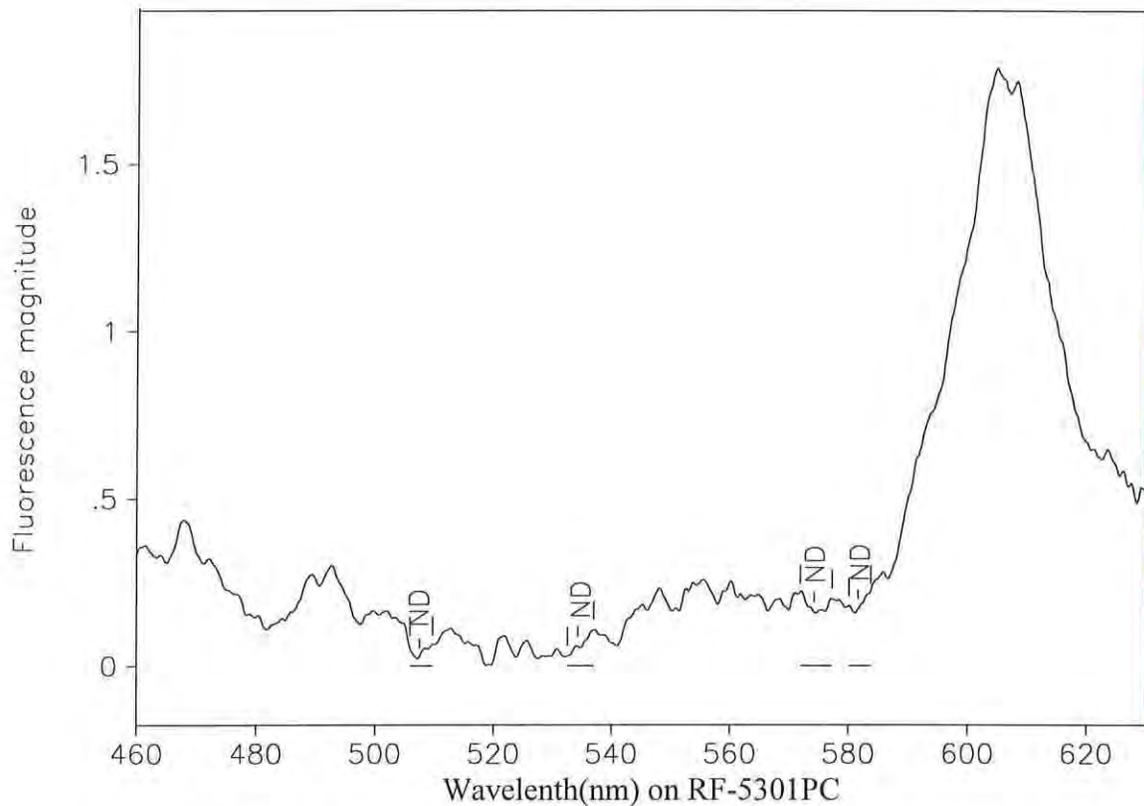
Date collected: 8/24/17 1015

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP3: MP320170825OZ

OUL Number: C4882

Analyzed: 9/5/17

Matrix: Water

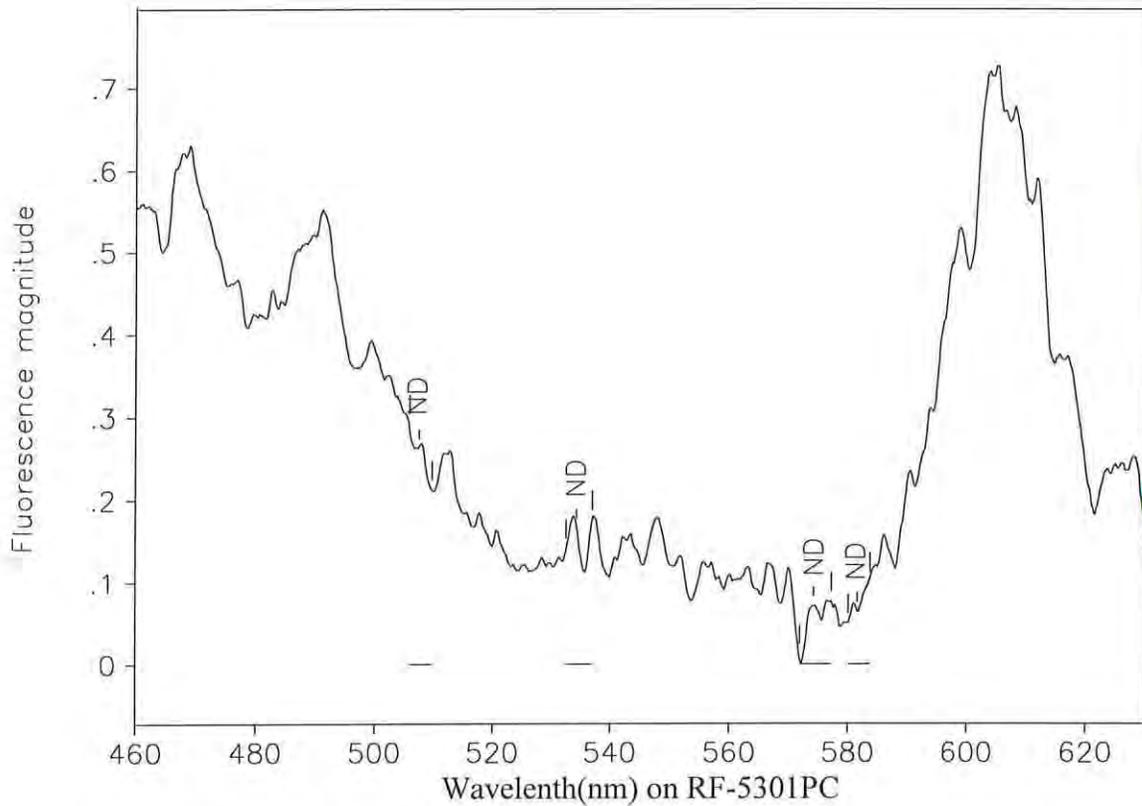
Date collected: 8/25/17 1030

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170821OZ

OUL Number: C4865

Analyzed: 9/5/17

Matrix: Water

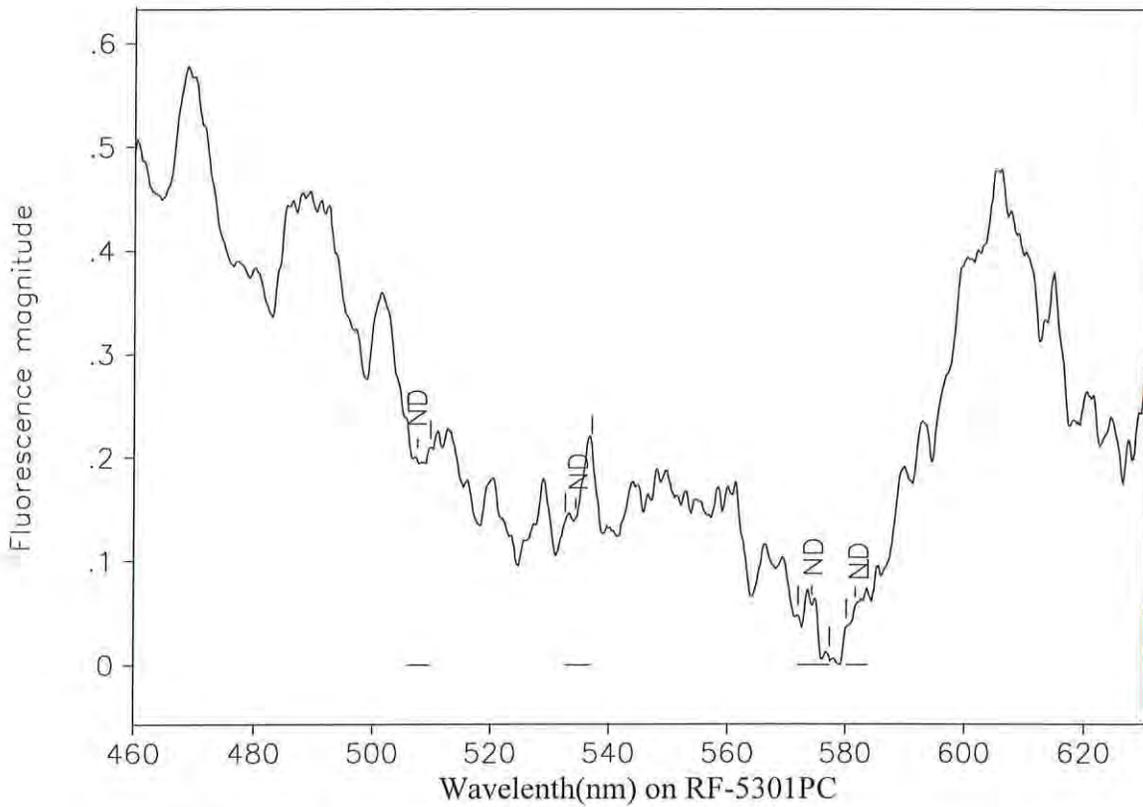
Date collected: 8/21/17 0956

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170821OZ

OUL Number: C4866

Analyzed: 9/5/17

Matrix: Water

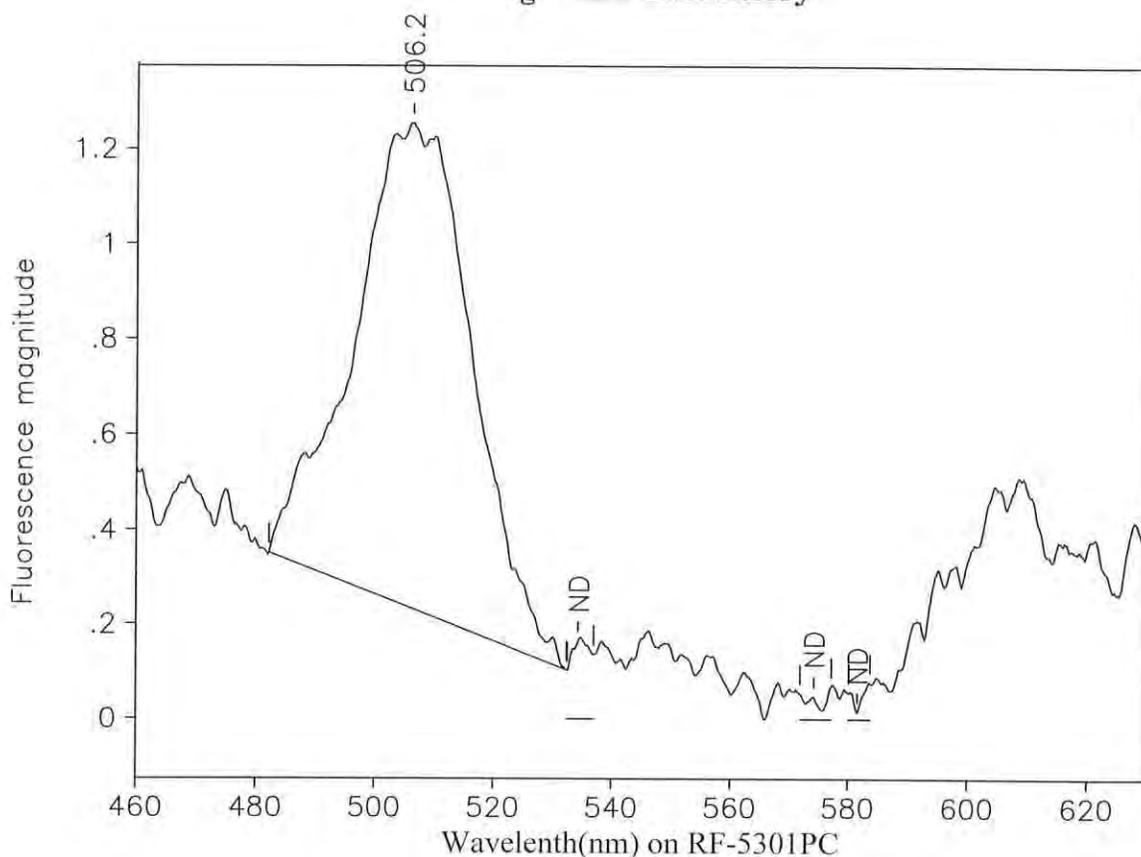
Date collected: 8/21/17 1556

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170822OZ

OUL Number: C4867

Analyzed: 9/5/17

Matrix: Water

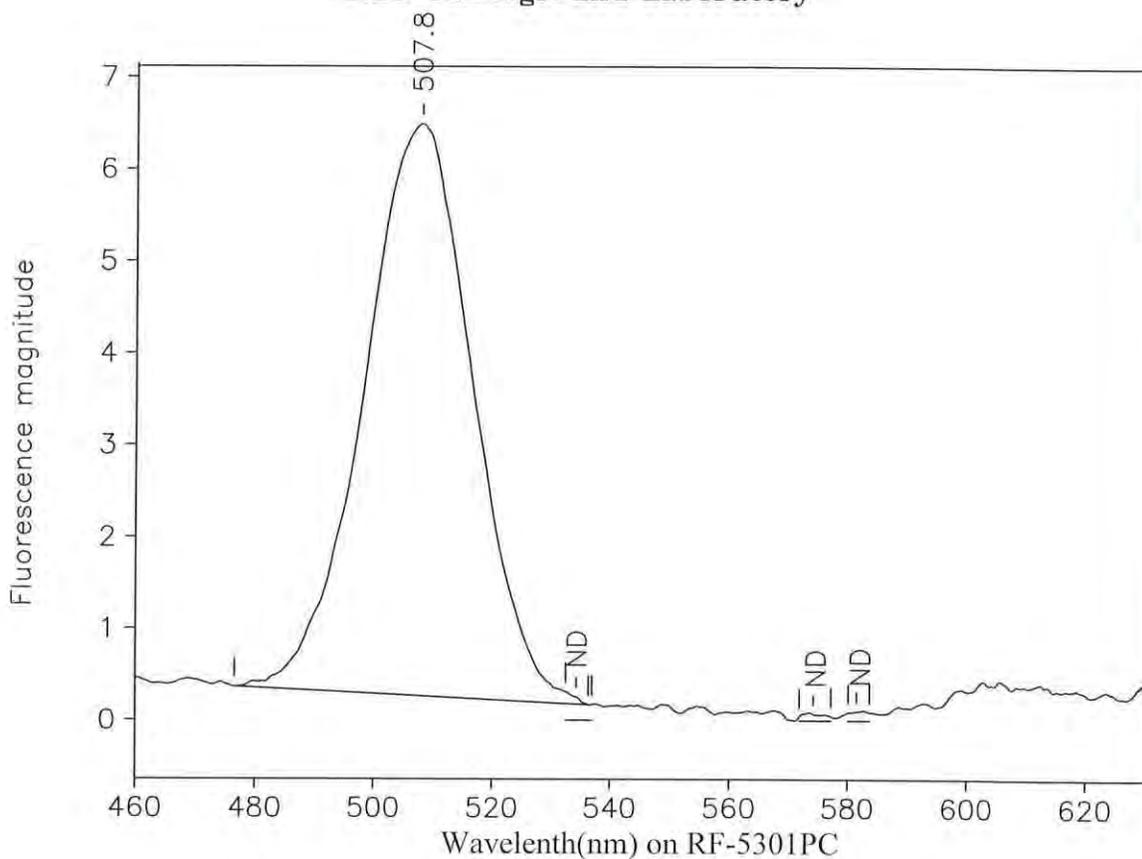
Date collected: 8/22/17 0745

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
506.2	482.2	532.4	1.02	23.77	0.060 FI
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170822OZ

OUL Number: C4868

Analyzed: 9/5/17

Matrix: Water

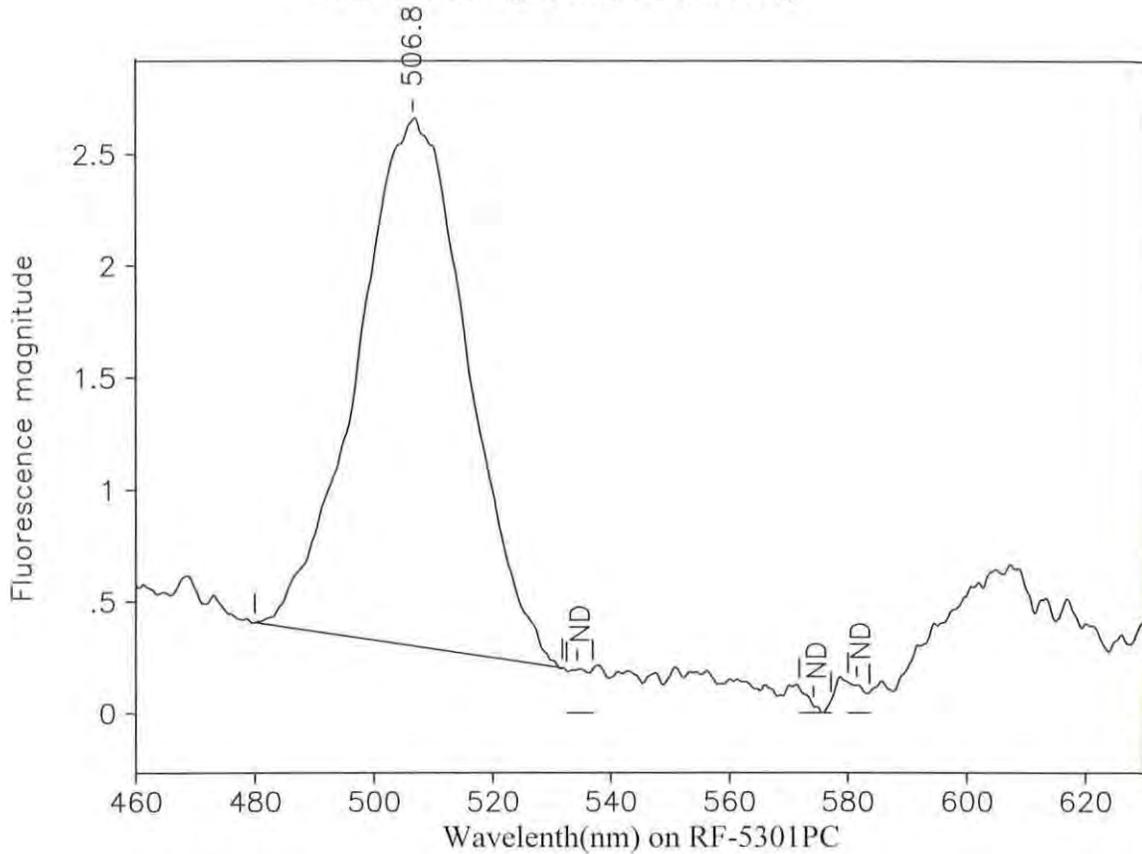
Date collected: 8/22/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.8	476.6	536.4	6.23	132.15	0.333 FI
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170823OZ

OUL Number: C4873

Analyzed: 9/5/17

Matrix: Water

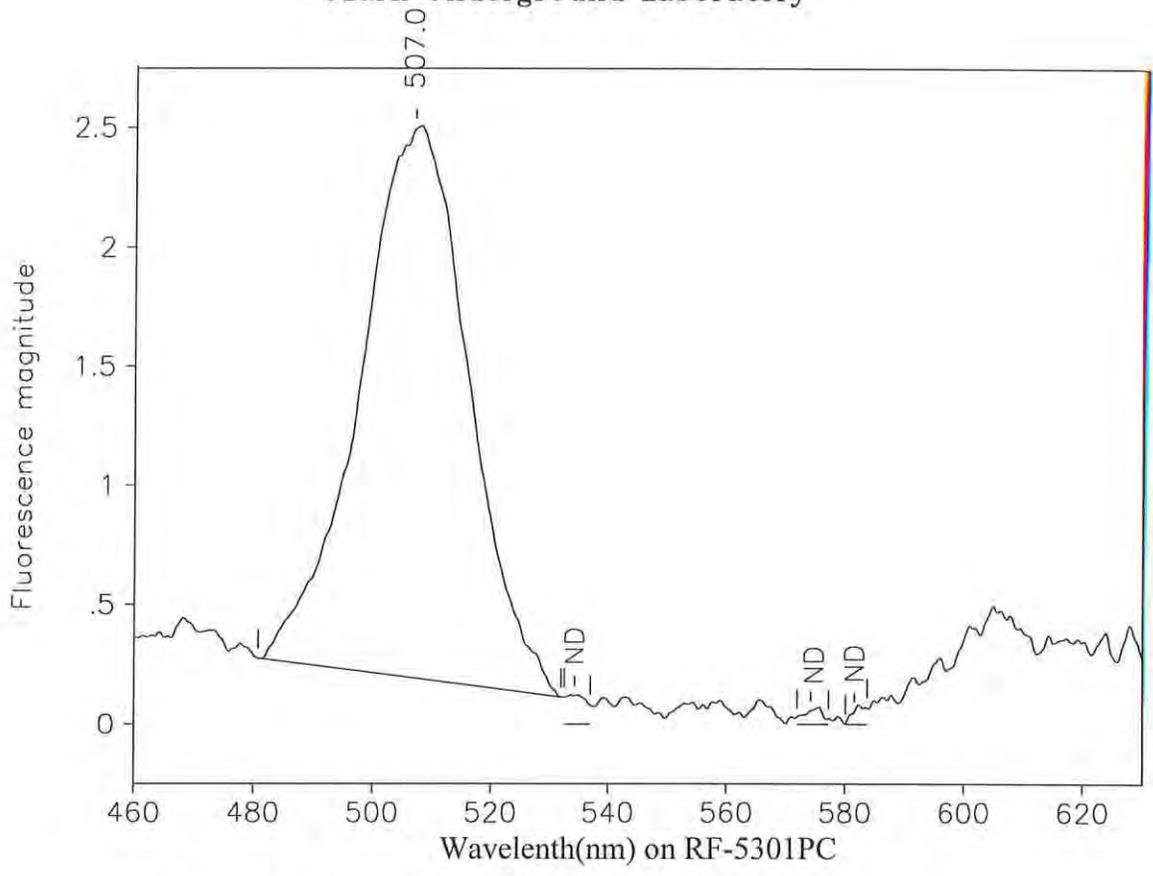
Date collected: 8/23/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
506.8	480.0	531.8	2.35	50.69	0.128 FI
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170823OZ

OUL Number: C4874

Analyzed: 9/5/17

Matrix: Water

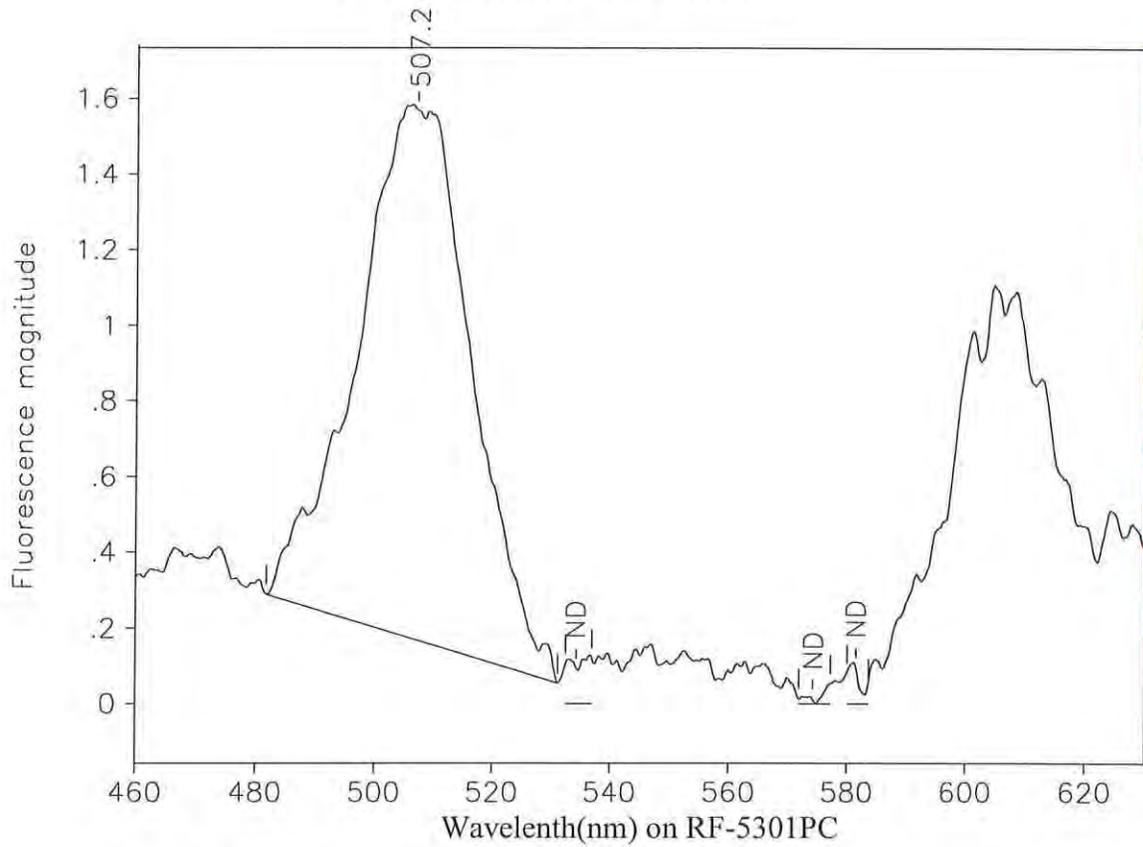
Date collected: 8/23/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.0	480.8	532.0	2.30	49.40	0.124 FI
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824OZ

OUL Number: C4883

Analyzed: 9/5/17

Matrix: Water

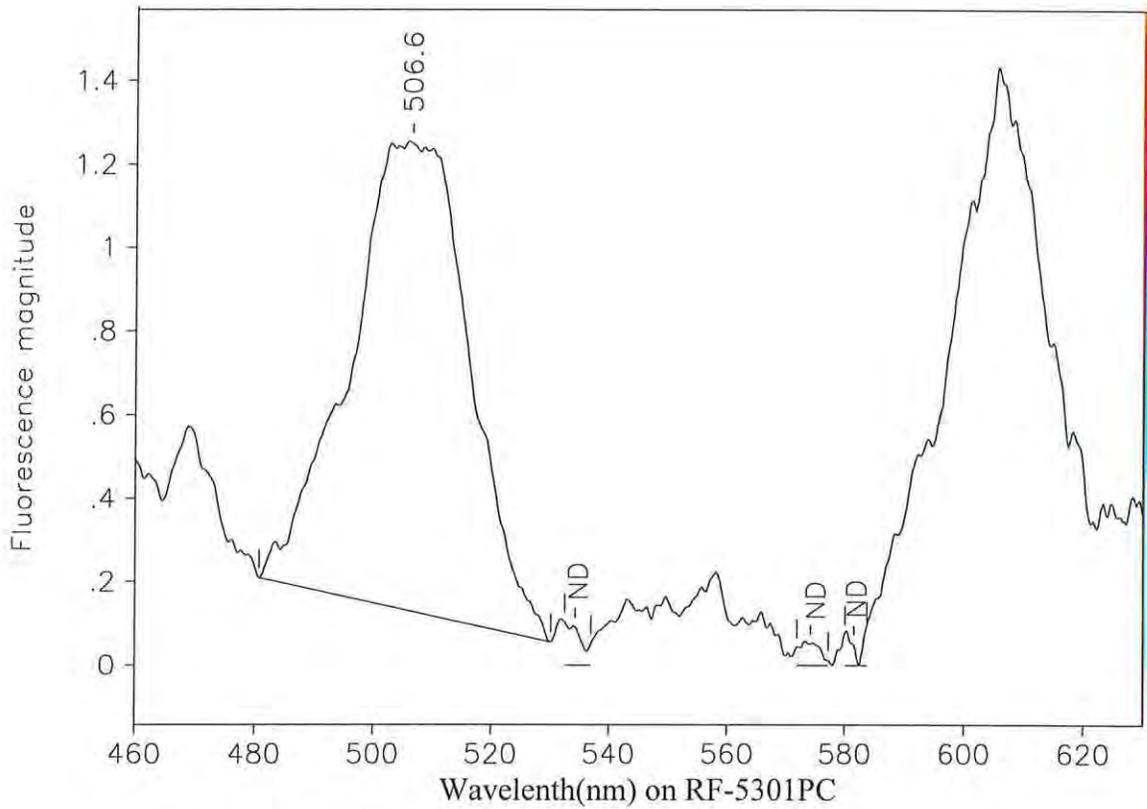
Date collected: 8/24/17 1045

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.2	481.8	531.2	1.40	31.99	0.081 Fl
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170824OZ

OUL Number: C4884

Analyzed: 9/5/17

Matrix: Water

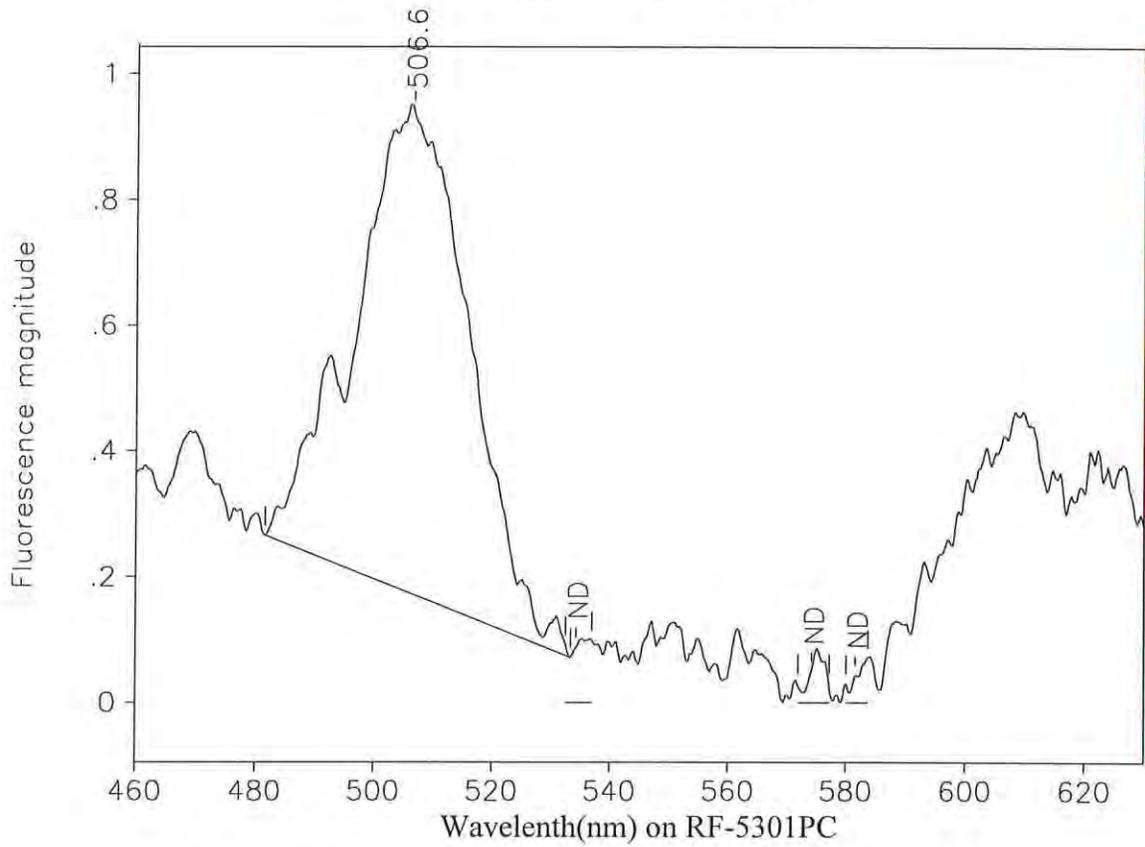
Date collected: 8/24/17 1830

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
506.6	480.8	530.2	1.12	26.57	0.067 Fl
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP4: MP420170825OZ

OUL Number: C4887

Analyzed: 9/5/17

Matrix: Water

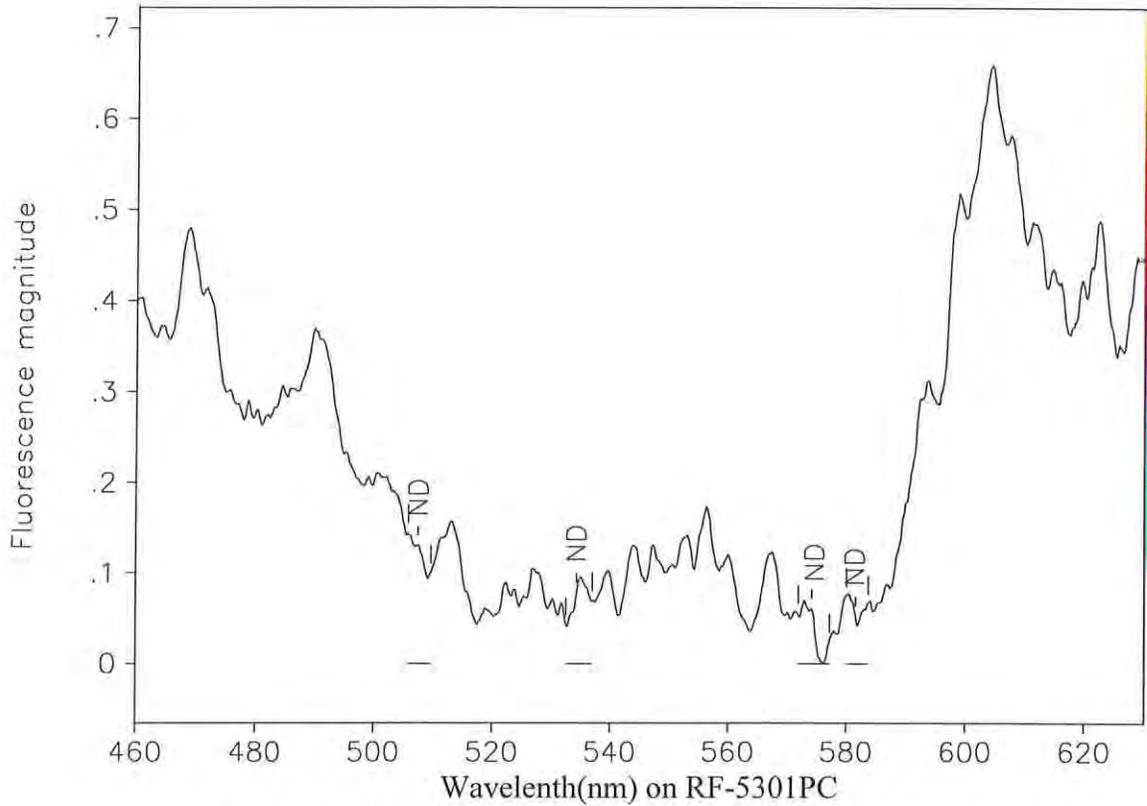
Date collected: 8/25/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
506.6	481.6	533.4	0.77	17.60	0.044 FI
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170821OZ

OUL Number: C4872

Analyzed: 9/5/17

Matrix: Water

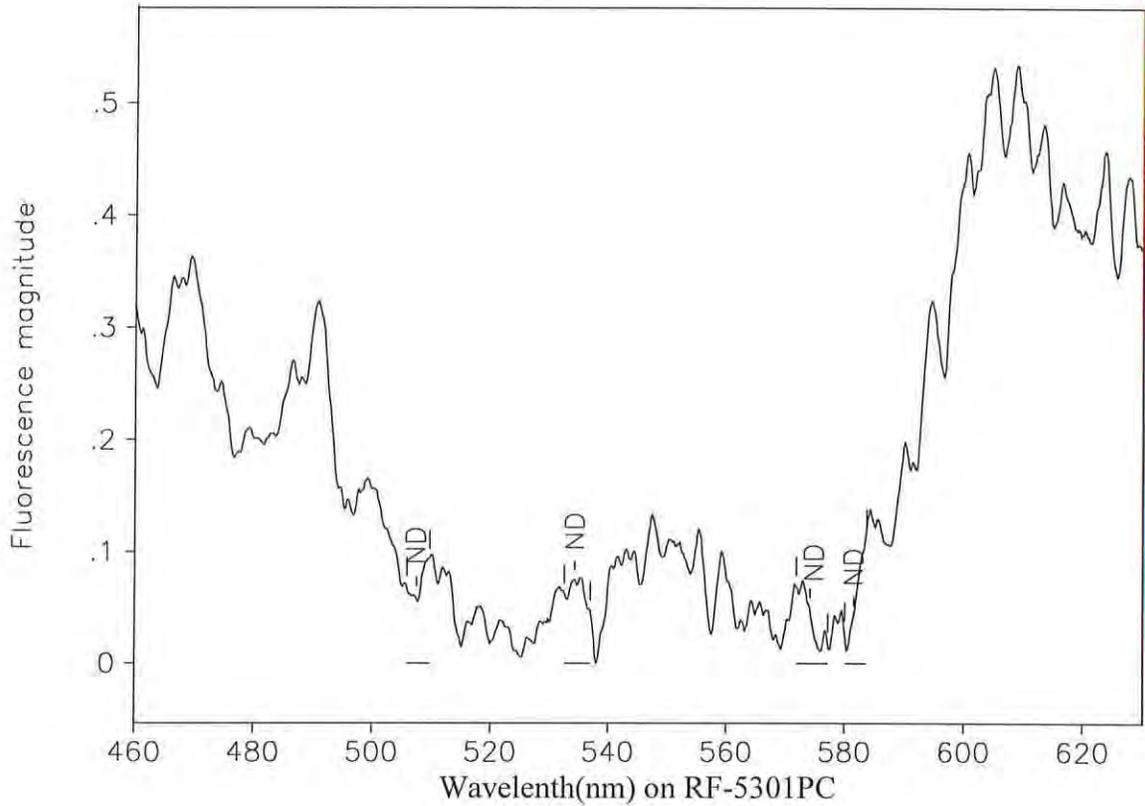
Date collected: 8/21/17 1338

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170822OZ

OUL Number: C4888

Analyzed: 9/5/17

Matrix: Water

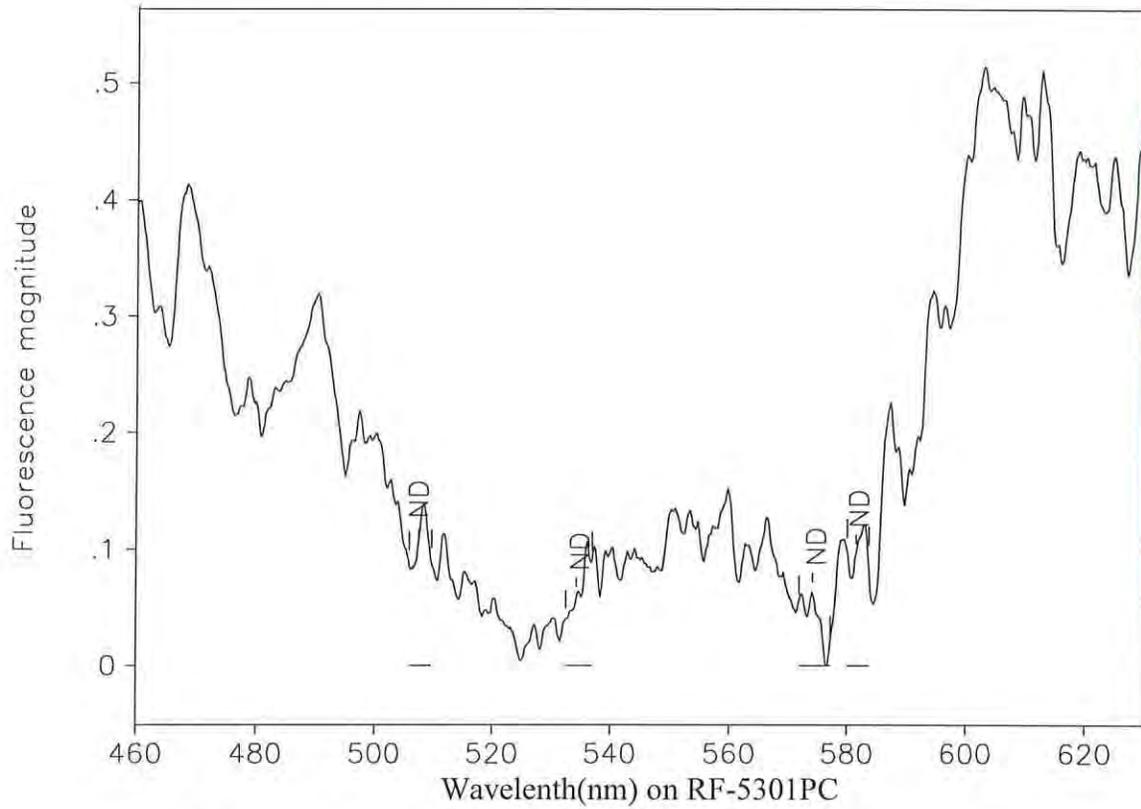
Date collected: 8/22/17 1230

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170823OZ

OUL Number: C4876

Analyzed: 9/5/17

Matrix: Water

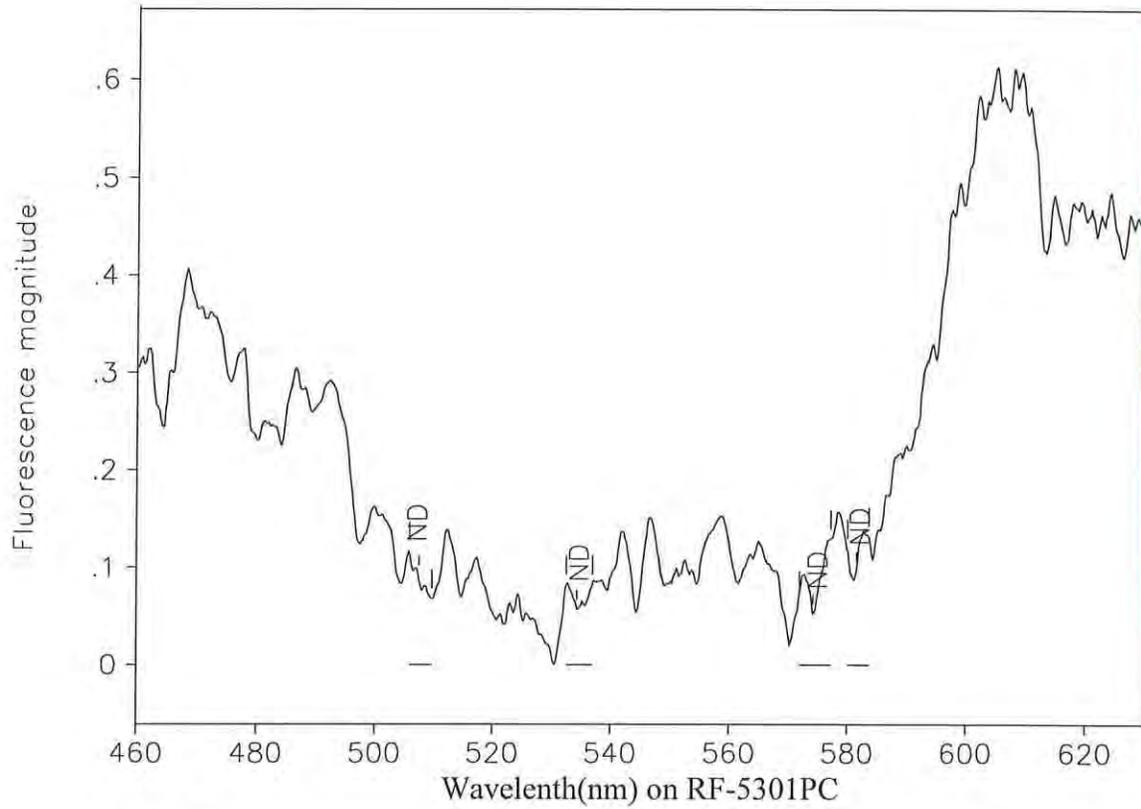
Date collected: 8/23/17 0950

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170824OZ

OUL Number: C4885

Analyzed: 9/5/17

Matrix: Water

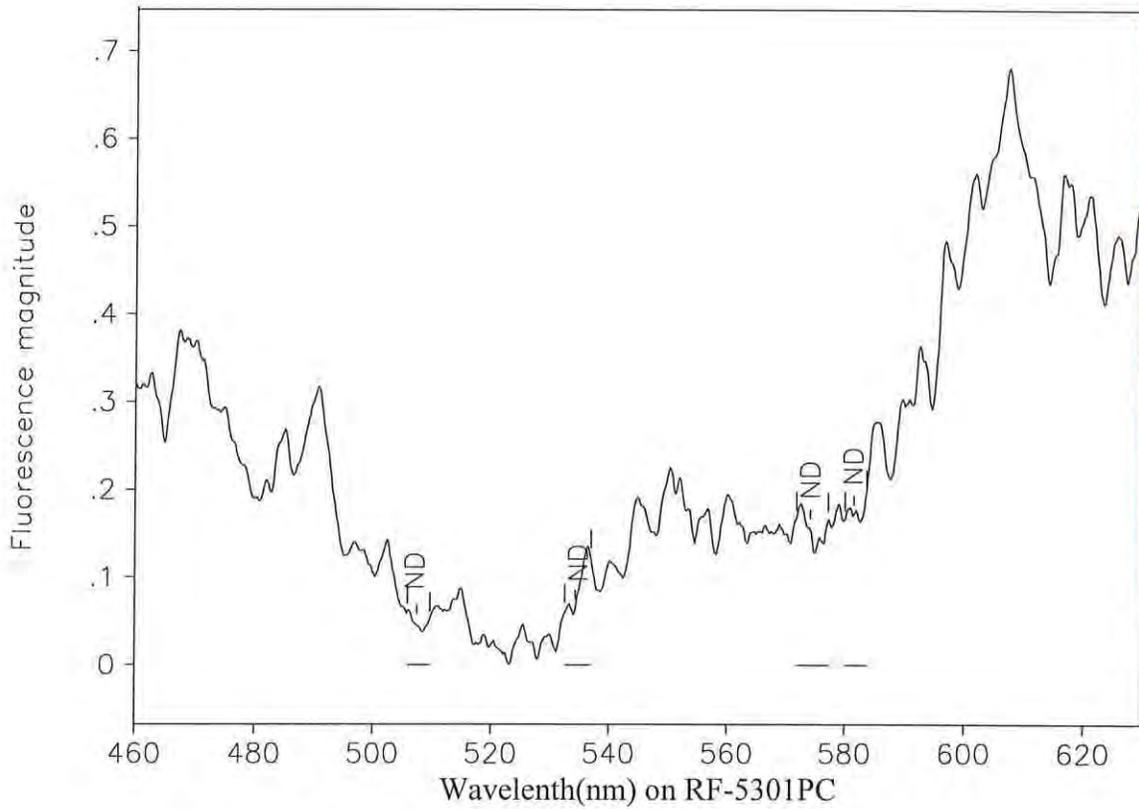
Date collected: 8/24/17 1100

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

Ozark Underground Laboratory



Station MP5: MP520170825OZ

OUL Number: C4886

Analyzed: 9/5/17

Matrix: Water

Date collected: 8/25/17 1130

Peaks within the normal range of tracer dyes:

Peak nm	Left X	Right X	Height	Area	Conc.
507.5	505.9	509.7	0.00	0.00	ND
534.3	532.5	537.0	0.00	0.00	ND
574.2	571.9	577.2	0.00	0.00	ND
581.5	580.1	583.7	0.00	0.00	ND

Peaks close to the normal range of tracer dyes:

**PROCEDURES AND CRITERIA
ANALYSIS OF FLUORESCENT DYES
IN WATER AND CHARCOAL SAMPLERS:

FLUORESCEIN, EOSINE, RHODAMINE WT,
AND SULFORHODAMINE B DYES**

Revision Date:
March 3, 2015

Thomas Aley, PHG, PG
President
and
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INTRODUCTION

This document describes standard procedures and criteria currently in use at the Ozark Underground Laboratory (OUL) as of the date shown on the title page. Some samples may be subjected to different procedures and criteria because of unique conditions; such non-standard procedures and criteria are identified in reports for those samples. Standard procedures and criteria change as knowledge and experience increases and as equipment is improved or upgraded. The OUL maintains a summary of changes in standard procedures and criteria.

TRACER DYES AND SAMPLE TYPES

Dye Nomenclature

Dye manufacturers and retailers use a myriad of names for the dyes. This causes confusion among dye users and report readers. The primary dyes used at the OUL and described in this document are included in Table 1 below.

Table 1. Primary OUL Dye Nomenclature.

OUL Common Name	Color Index Number	Color Index Name	Other Names
Fluorescein	45350	Acid Yellow 73	uranine, uranine C, sodium fluorescein, fluorescein LT and fluorescent yellow/green
Eosine	45380	Acid Red 87	eosin, eosine OJ, and D&C Red 22
Rhodamine WT	None assigned	Acid Red 388	fluorescent red (but not the same as rhodamine B)
Sulforhodamine B	45100	Acid Red 52	pontacyl brilliant pink B, lissamine red 4B, and fluoro brilliant pink

The OUL routinely provides dye for tracing projects. Dyes purchased for groundwater tracing are always mixtures that contain both dye and an associated diluent. Diluents enable the manufacturer to standardize the dye mixture so that there are minimal differences among batches. Additionally, diluents are often designed to make it easier to dissolve the dye mixture in water, or to produce a product which meets a particular market need (groundwater tracing is only a tiny fraction of the dye market). The percent of dye in “as-sold” dye mixtures often varies dramatically among manufacturers and retailers, and retailers are sometimes incorrect about the percent of dye in their products. The OUL subjects all of its dyes to strict quality control (QC) testing. Table 2 summarizes the as-sold dye mixtures used by the OUL.

Table 2. As-Sold Dye Mixtures at the OUL.

OUL Common Name	Form	Dye Equivalent
Fluorescein	Powder	75% dye equivalent, 25% diluent
Eosine	Powder	75% dye equivalent, 25% diluent
Rhodamine WT	Liquid	20% dye equivalent, 80% diluent
Sulforhodamine B	Powder	75% dye equivalent, 25% diluent

Analytical results are based on the as-sold weights of the dyes provided by the OUL. The use of dyes from other sources is discouraged due to the wide variability of dye equivalents within the market. However, if alternate source dyes are used, a sample should be provided to the OUL for quality control and to determine if a correction factor is necessary for the analytical results.

Types of Samples

Typical samples that are collected for fluorescent tracer dye analysis include charcoal samplers (also called activated carbon or charcoal packets) and water samples.

The charcoal samplers are packets of fiberglass screening partially filled with 4.25 grams of activated coconut charcoal. The charcoal used by the OUL is Calgon 207C coconut shell carbon, 6 to 12 mesh, or equivalent. The most commonly used charcoal samplers are about 4 inches long by 2 inches wide. A cigar-shaped sampler is made for use in very small diameter wells (such as 1-inch diameter piezometers); this is a special order item and should be specifically requested in advance when needed. All of the samplers are closed by heat sealing.

In specialized projects, soil samples have been collected from soil cores and analyzed for fluorescent tracer dyes. Project-specific procedures have been developed for projects such as these. For additional information, please contact the OUL.

FIELD PROCEDURES

Field procedures included in this section are intended as guidance, and not firm requirements. Placement of samplers and other field procedures require adjustment to field conditions. Personnel at the OUL are available to provide additional assistance for implementation of field procedures specific to specialized field conditions.

Placement of Samplers

Charcoal samplers are placed so as to be exposed to as much water as possible. Water should flow through the packet. In springs and streams they are typically attached to a rock or other anchor in a riffle area. Attachment of the packets often uses plastic tie wires. In swifter water galvanized wire (such as electric fence wire) is often used. Other types of anchoring wire can be used. Electrical wire with plastic insulation is also good. Packets are attached so that they extend outward from the anchor rather than laying flat against it. Two or more separately anchored packets are typically used for sampling springs and streams. The placement of multiple packets is recommended in order to minimize the chance of loss during the sampling period. The use of fewer packets is discouraged except when the spring or stream is so small that there is not appropriate space for placing multiple packets.

When pumping wells are being sampled, the samplers are typically placed in sample holders made of plastic pipe fittings. Brass hose fittings can be at the end of the sample holders so that the sample holders can be installed on outside hose bibs and water which has run through the samplers can be directed to waste through a connected garden hose. The samplers can be unscrewed in the middle so that charcoal packets can be changed. The middle portions of the samplers consist of 1.5 inch diameter pipe and pipe fitting.

Charcoal packets can be lowered into monitoring wells for sampling purposes. In general, if the well is screened, samplers should be placed approximately in the middle of the screened interval. Due to the typically lower volume of water that flows through a well, only one charcoal sampler should be used per well. However, multiple packets can be placed in a single well at depths to test different depth horizons when desirable. A weight should be added near the charcoal packet to ensure that it will not float. The weight should be of such a nature that it will not affect water quality. One common approach is to anchor the packets with a white or uncolored plastic cable tie to the top of a dedicated weighted disposable bailer. We typically run nylon cord from the top of the well to the charcoal packet and its weight. ***Do not use colored cord*** since some of them are colored with fluorescent dyes. Nylon fishing line should not be used since it can be readily cut by a sharp projection in the well.

In some cases, especially with small diameter wells and appreciable well depths, the weighted disposable bailers sink very slowly or may even fail to sink because of friction and floating of the anchoring cord. In such cases a weight may be added to the top of the disposable bailer. Stainless steel weights are ideal, but are not needed in all cases. All weights should be cleaned prior to use; the cleaning approach should comply with decontamination procedures in use at the project site.

Optional Preparation of Charcoal Samplers

Charcoal packets routinely contain some fine powder that washes off rapidly when they are placed in water. While not usually necessary, the following optional preparation step is suggested if the fine charcoal powder is problematic.

Charcoal packets can be triple rinsed with distilled, demineralized, or reagent water known to be free of tracer dyes. This rinsing is typically done by soaking. With this approach,

approximately 25 packets are placed in one gallon of water and soaked for at least 10 minutes. The packets are then removed from the water and excess water is shaken off the packets. The packets are then placed in a second gallon of water and again soaked for at least 10 minutes. After this soaking they are removed from the water and excess water is shaken off the packets. The packets are then placed in a third gallon of water and the procedure is again repeated. Rinsed packets are placed in plastic bags and are placed at sampling stations within three days. Packets can also be rinsed in jets of water for about one minute; this requires more water and is typically difficult to do in the field with water known to be free of tracer dyes.

Collection and Replacement of Samplers

Samplers are routinely collected and replaced at each of the sampling stations. The frequency of sampler collection and replacement is determined by the nature of the study. Collections at one week intervals are common, but shorter or longer collection frequencies are acceptable and sometimes more appropriate. Shorter sampling frequencies are often used in the early phases of a study to better characterize time of travel. As an illustration, we often collect and change charcoal packets 1, 2, 4, and 7 days after dye injection. Subsequent sampling is then weekly.

The sampling interval in wells at hazardous wastes sites should generally be no longer than about a week. Contaminants in the water can sometimes use up sorption sites on the charcoal that would otherwise adsorb the dye. This is especially important if the dye might pass in a relatively short duration pulse.

Where convenient, the collected samplers should be briefly rinsed in the water being sampled to remove dirt and accumulated organic material. This is not necessary with well samples. The packets are shaken to remove excess water. Next, the packet (or packets) are placed in a plastic bag (Whirl-Pak® bags are ideal). The bag is labeled on the outside with a black permanent type felt marker pen, such as a Sharpie®. *Use only pens that have black ink;* colored inks may contain fluorescent dyes. The notations include station name or number and the date and time of collection. Labels must not be inserted inside the sample bags.

Collected samplers are kept in the dark to minimize algal growth on the charcoal prior to analysis work. New charcoal samplers are routinely placed when used charcoal packets are collected. The last set of samplers placed at a stream or spring is commonly not collected.

Water Samples

Water samples are often collected. They should be collected in either glass or plastic; the OUL routinely uses 50 milliliter (mL) research-grade polypropylene copolymer Perfector Scientific vials (Catalog Number 2650) for such water samples. No more than 30 mL of water is required for analysis. The sides of the vials should be labeled with the project name, sample ID, sample date and time with a black permanent felt tip pen. *Do not label the lid only.* The vials should be placed in the dark and refrigerated immediately after collection, and maintained under refrigeration until shipment. The OUL supplies vials for the collection of water samples.

Sample Shipment

When water or charcoal samplers are collected for shipment to the OUL they should be shipped promptly. We prefer (and in some studies require) that samples be refrigerated with frozen re-usable ice packs upon collection and that they be shipped refrigerated with frozen ice packs by overnight express. ***Do not ship samplers packed in wet ice*** since this can create a potential for cross contamination when the ice melts. Our experience indicates that it is not essential for samplers to be maintained under refrigeration; yet maintaining them under refrigeration clearly minimizes some potential problems. A product known as "green ice" should not be used for maintaining the samples in a refrigerated condition since this product contains a dye which could contaminate samples if the "green ice" container were to break or leak.

We receive good overnight and second day air service from both UPS and FedEx. The U.S. Postal Service does not typically provide next day service to us. DHL does not provide overnight service to us. FedEx is recommended for international shipments. The OUL does not receive Saturday delivery.

Each shipment of charcoal samplers or water samples ***must be accompanied by a sample custody document***. The OUL provides a sheet (which bears the title "Samples for Fluorescence Analysis") that can be used if desired. These sheets can be augmented by a client's chain-of-custody forms or any other relevant documentation. OUL's custody document works well for charcoal samplers because it allows for both the placement date and time as well as the collection date and time. Many other standard chain-of-custody documents do not allow for these types of samples. Attachment 1 includes a copy of OUL's Sample Collection Data Sheet.

Please write legibly on the custody documents and ***use black ink***. Check the accuracy of the sample sheet against the samples prior to shipment to identify and correct errors that may delay the analysis of your samples following receipt at the laboratory.

Supplies Provided by the OUL

The OUL provides supplies for the collection of fluorescent tracer dyes. Supplies provided upon request are charcoal packets, Whirl-Pak® bags (to contain the charcoal packets after collection for shipment to the laboratory), and water vials. These supplies are subjected to strict QA/QC procedures to ensure the materials are free of any potential tracer dye contaminants. The charge for these materials is included in the cost of sample analysis. Upon request, coolers and re-freezable ice packs are also provided for return shipment of samples.

The OUL also has tracer dyes available for purchase. These dyes are subject to strict QA/QC testing. All analytical work is based upon the OUL as-sold weight of the dyes.

LABORATORY PROCEDURES

The following procedures are followed upon receipt of samples at the laboratory.

Receipt of Samples

Samplers shipped to the OUL are logged in and refrigerated upon receipt. Prior to cleaning and analysis, samplers are assigned a laboratory identification number.

It sometimes occurs that there are discrepancies between the sample collection data sheet and the actual samples received. When this occurs, a "Discrepancy Sheet" form is completed and sent to the shipper of the sample for resolution. The purpose of the form is to help resolve discrepancies, even when they may be minor. Many discrepancies arise from illegible custody documents. *Please write legibly* on the custody documents and *use black ink*. Check the accuracy of the sample sheet against the samples prior to shipment to identify and correct errors that may delay the analysis of your samples following receipt at the laboratory.

Cleaning of Charcoal Samplers

Samplers are cleaned by spraying them with jets of clean water from a laboratory well in a carbonate aquifer. OUL uses non-chlorinated water for the cleansing to minimize dye deterioration. We do not wash samplers in public water supplies. Effective cleansing cannot generally be accomplished simply by washing in a conventional laboratory sink even if the sink is equipped with a spray unit.

The duration of packet washing depends upon the condition of the sampler. Very clean samplers may require less than a minute of washing; dirtier samplers may require several minutes of washing.

Elution of the Charcoal

There are various eluting solutions that can be used for the recovery of tracer dyes. The solutions typically include an alcohol, water, and a strong basic solution such as aqueous ammonia and /or potassium hydroxide.

The standard elution solution used at the OUL is a mixture of 5% aqua ammonia and 95% isopropyl alcohol solution and sufficient potassium hydroxide pellets to saturate the solution. The isopropyl alcohol solution is 70% alcohol and 30% water. The aqua ammonia solution is 29% ammonia. The potassium hydroxide is added until a super-saturated layer is visible in the bottom of the container. This super-saturated layer is not used for elution. Preparation of eluting solutions uses dedicated glassware which is never used in contact with dyes or dye solutions.

The eluting solution will elute fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes. It is also suitable for separating fluorescein peaks from peaks of some naturally present materials found in may be found in samplers.

Fifteen mL of the eluting solution is poured over the washed charcoal in a disposable sample beaker. The sample beaker is capped. The sample is allowed to stand for 60 minutes. After this time, the liquid is carefully poured off the charcoal into a new disposable beaker which has been appropriately labeled with the laboratory identification number. A few grains of charcoal may inadvertently pass into the second beaker; no attempt is made to remove these from the second sample beaker. After the pouring, a small amount of the elutant will remain in the initial sample beaker. After the transfer of the elutant to the second sample beaker, the contents of the first sample beaker (the eluted charcoal) are discarded. Samples are kept refrigerated until analyzed.

pH Adjustment of Water Samples

The fluorescence intensity of several of the commonly used fluorescent tracer dyes is pH dependent. The pH of samples analyzed for fluorescein, eosine, and pyranine dyes are adjust to a target pH of greater than 9.5 in order to obtain maximum fluorescence intensities.

Adjustment of pH is achieved by placing samples in a high ammonia atmosphere for at least two hours in order to increase the pH of the sample. Reagent water standards are placed in the same atmosphere as the samples. If dye concentrations in a sample are off-scale and require dilution for quantification of the dye concentration, the diluting water used is OUL reagent water that has been pH adjusted in a high ammonia atmosphere. Samples that are only analyzed for rhodamine WT or sulforhodamine B are not required to be pH adjusted.

Analysis on the Shimadzu RF-5301

The OUL uses a Shimadzu spectrofluorophotometer model RF-5301. This instrument is capable of synchronous scanning. The OUL also owns a Shimadzu RF-540 spectrofluorometers that is occasionally used for special purposes.

A sample of the elutant or water is withdrawn from the sample container using a disposable polyethylene pipette. Approximately 3 mL of the sample is then placed in disposable rectangular polystyrene cuvette. The cuvette has a maximum capacity of 3.5 mL. The cuvette is designed for fluorometric analysis; all four sides and the bottom are clear. The acceptable spectral range of these cuvettes is 340 to 800 nm. The pipettes and cuvettes are discarded after one use.

The cuvette is then placed in the RF-5301. This instrument is controlled by a programmable computer and operated by proprietary software developed for dye tracing applications.

Our instruments are operated and maintained in accordance with the manufacturer's recommendations. On-site installation of our first instrument and a training session on its use was provided by the instrument supplier. Repairs are made by a Shimadzu-authorized repairman.

Our typical analysis of an elutant sample where fluorescein, eosine, rhodamine WT, or sulforhodamine B dyes may be present includes synchronous scanning of excitation and emission spectra with a 17 nm separation between excitation and emission wavelengths. For these dyes,

the excitation scan is from 443 to 613 nm; the emission scan is from 460 to 630 nm. The emission fluorescence from the scan is plotted on a graph. The typical scan speed setting is "fast" on the RF-5301. The typical sensitivity setting used is "high."

Table 3. Excitation and emission slit width settings routinely used for dye analysis.

Parameter	Excitation Slit (nm)	Emission Slit (nm)
ES, FL, RWT, and SRB in elutant	3	1.5
ES, FL, RWT, and SRB in water	5	3

Note: ES = Eosine. FL = Fluorescein. RWT = Rhodamine WT. SRB = Sulforhodamine B.

The instrument produces a plot of the synchronous scan for each sample; the plot shows emission fluorescence only. The synchronous scans are subjected to computer peak picks using proprietary software; peaks are picked to the nearest 0.1 nm. Instrument operators have the ability to manually adjust peaks as necessary based upon computer-picked peaks and experience. All samples run on the RF-5301 are stored electronically with sample information. All samples analyzed are recorded in a bound journal.

Quantification

We calculate the magnitude of fluorescence peaks for fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes in both elutant and water samples. Dye quantities are expressed in microgram per liter (parts per billion; ppb). The dye concentrations are calculated by separating fluorescence peaks due to dyes from background fluorescence on the charts, and then calculating the area within the fluorescence peak. This area is proportional to areas obtained from standard solutions.

We run dye concentration standards each day the RF-5301 is used. Six standards are used; the standard or standards appropriate for the analysis work being conducted are selected. All standards are based upon the as-sold weights of the dyes. The standards are as follows:

- 1) 10 ppb fluorescein and 100 ppb rhodamine WT in well water from the Jefferson City-Cotter Formation
- 2) 10 ppb eosine in well water from the Jefferson City-Cotter Formation
- 3) 100 ppb sulforhodamine B in well water from the Jefferson City-Cotter Formation.
- 4) 10 ppb fluorescein and 100 ppb rhodamine WT in elutant.
- 5) 10 ppb eosine in elutant.
- 6) 100 ppb sulforhodamine B in elutant.

Preparation of Standards

Dye standards are prepared as follows:

Step 1. A small sample of the as-sold dye is placed in a pre-weighed sample vial and the vial is again weighed to determine the weight of the dye. We attempt to use a sample weighing between 1 and 5 grams. This sample is then diluted with well water to make a 1% dye solution by weight (based upon the as-sold weight of the dye). The resulting dye solution is allowed to sit for at least four hours to ensure that all dye is fully dissolved.

Step 2. One part of each dye solution from Step 1 is placed in a mixing container with 99 parts of well water. Separate mixtures are made for fluorescein, rhodamine WT, eosine, and sulforhodamine B. The resulting solutions contain 100 mg/L dye (100 parts per million dye mixture). The typical prepared volume of this mixture is appropriate for the sample bottles being used; we commonly prepare about 50 mL of the Step 2 solutions. The dye solution from Step 1 that is used in making the Step 2 solution is withdrawn with a digital Finnpiquette which is capable of measuring volumes between 0.200 and 1.000 mL at intervals of 0.005 mL. The calibration certificate with this instrument indicates that the accuracy (in percent) is as follows:

At 0.200 mL, 0.90%

At 0.300 mL, 0.28%

At 1.000 mL, 0.30%

The Step 2 solution is called the long term standard. OUL experience indicates that Step 2 solutions, if kept refrigerated, will not deteriorate appreciably over periods of less than a year. Furthermore, these Step 2 solutions may last substantially longer than one year.

Step 3. A series of intermediate-term dye solutions are made. Approximately 45 mL of each intermediate-term dye solution is made. All volume measurements of less than 5 mL are made with a digital Finnpiquette. (see description in Step 2). All other volume measurements are made with Rheinland Kohn Geprüfte Sicherheit 50 mL capacity pump dispenser which will pump within plus or minus 1% of the set value. The following solutions are made; all concentrations are based on the as-sold weight of the dyes:

- 1) 1 ppm fluorescein dye and 10 ppm rhodamine WT dye.
- 2) 1 ppm eosine.
- 3) 10 ppm sulforhodamine B dye.

Step 4. A series of six short-term dye standards are made from solutions in Step 3. These standards were identified earlier in this section. In the experience of the OUL these standards have a useful shelf life in excess of one week. However, in practice, Step 4 elutant standards are made weekly, and Step 4 water standards are made daily.

Dilution of Samples

Samples with peaks that have arbitrary fluorescence unit values of 500 or more are diluted a hundred fold to ensure accurate quantification.

Some water samples have high turbidity or color which interferes with accurate detection and measurement of dye concentrations. It is often possible to dilute these samples and then measure the dye concentration in the diluted sample.

The typical dilutions are either 10 fold (1:10) or 100 fold (1:100). A 1:10 dilution involves combining one part of the test sample with 9 parts of water (if the sample is water) or elutant (if the sample is elutant). A 1:100 dilution involves combining one part of the test sample is combined with 99 parts of water or elutant, based upon the sample media. Typically, 0.300 mL of the test solution is combined with 29.700 mL of water (or elutant as appropriate) to yield a new test solution.

All volume measurements of less than 5 mL are made with a digital Finnpiquette. All other volume measurements are made with Rheinland Kohn Geprüfte Sicherheit 50 mL capacity pump dispenser which will pump within plus or minus 1% of the set value.

The water used for dilution is from a carbonate aquifer. All dilution water is pH adjusted to greater than pH 9.5 by holding it in open containers in a high ammonia concentration chamber. This adjustment takes a minimum of two hours.

Quality Control

Laboratory blanks are run for every sample where the last two digits of the laboratory numbers are 00, 20, 40, 60, or 80. A charcoal packet is placed in a pumping well sampler and at least 25 gallons of unchlorinated water is passed through the sampler at a rate of about 2.5 gallons per minute. The sampler is then subjected to the same analytical protocol as all other samplers.

System functioning tests of the analytical instruments are conducted in accordance with the manufacturer's recommendations. Spiked samples are also analyzed when appropriate for quality control purposes.

All materials used in sampling and analysis work are routinely analyzed for the presence of any compounds that might create fluorescence peaks in or near the acceptable wavelength ranges for any of the tracer dyes. This testing includes approximately 1% of materials used.

Project specific QA/QC samples may include sample replicates and sample duplicates. A replicate sample is when a single sample is analyzed twice. A sample duplicate is where two samples are collected in a single location and both are analyzed. Sample replicates and duplicates are run for QA/QC purposes upon request of the client. These results are reported in the Certificate of Analysis.

Reports

Sample analysis results are typically reported in a Certificate of Analysis. However, specialized reports are provided in accordance with the needs of the client. Certificates of Analysis typically provide a listing of station number, sample ID, and dye concentrations if detected. Standard data format includes deliverables in MS Excel and Adobe Acrobat (.pdf)

format. Hard copy of the data package, and copies of the analytical charts are available upon request.

Work at the OUL is directed by Mr. Thomas Aley. Mr. Aley has 45 years of professional experience in hydrology and hydrogeology. He is certified as a Professional Hydrogeologist (Certificate #179) by the American Institute of Hydrology and licensed as a Professional Geologist in Missouri, Arkansas, Kentucky, and Alabama. Additional details regarding laboratory qualifications are available upon request.

Waste Disposal

All laboratory wastes are disposed of according to applicable state and federal regulations. Waste elutant and water samples are collected in 15 gallon poly drums and disposed with a certified waste disposal facility as non-hazardous waste.

In special cases, wastes for a particular project may be segregated and returned to the client upon completion of the project. These projects may have samples that contain contaminants that the client must account for all materials generated and disposed. These situations are managed on a case-by-case basis.

CRITERIA FOR DETERMINATION OF POSITIVE DYE RECOVERIES

Normal Emission Ranges and Detection Limits

The OUL has established normal emission fluorescence wavelength ranges for each of the four dyes described in this document. The normal acceptable range equals mean values plus and minus two standard deviations. These values are derived from actual groundwater tracing studies conducted by the OUL.

The detection limits are based upon concentrations of dye necessary to produce emission fluorescence peaks where the signal to noise ratio is 3. The detection limits are realistic for most field studies since they are based upon results from actual field samples rather than being based upon values from spiked samples in a matrix of reagent water or the elutants from unused activated carbon samplers. In some cases detection limits may be smaller than reported if the water being sampled has very little fluorescent material in it. In some cases detection limits may be greater than reported; this most commonly occurs if the sample is turbid due to suspended material or a coloring agent such as tannic compounds. Turbid samples are typically allowed to settle, centrifuged, or, if these steps are not effective, diluted prior to analysis.

Table 4 provides normal emission wavelength ranges and detection limits for the four dyes when analyzed on the OUL's RF-5301 for samples analyzed as of March 3, 2015.

Table 4. RF-5301 Spectrofluorophotometer. Normal emission wavelength ranges and detection limits for fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes in water and elutant samples.

Fluorescent Dye	Normal Acceptable Emission Wavelength Range (nm)		Detection Limit (ppb)	
	Elutant	Water	Elutant	Water
Eosine	539.3 to 545.1	532.5 to 537.0	0.050	0.015
Fluorescein	514.1 to 519.2	505.9 to 509.7	0.025	0.002
Rhodamine WT	564.6 to 571.2	571.9 to 577.2	0.170	0.015
Sulforhodamine B	575.2 to 582.0	580.1 to 583.7	0.080	0.008

Note: Detection limits are based upon the as-sold weight of the dye mixtures normally used by the OUL.

Fluorescein and eosine detection limits in water are based on samples pH adjusted to greater than 9.5.

It is important to note that the normal acceptable emission wavelength ranges are subject to change based on instrument maintenance, a change in instrumentation, or slight changes in dye formulation. Significant changes in normal acceptable emission wavelength ranges will be updated in this document as they occur.

Fluorescence Background

Due to the nature of fluorescence analysis, it is important to identify and characterize any potential background fluorescence at dye introduction and monitoring locations prior to the introduction of any tracer dyes.

There is generally little or no detectable fluorescence background in or near the general range of eosine, rhodamine WT, and sulforhodamine B dyes encountered in most groundwater tracing studies. There is often some fluorescence background in or near the range of fluorescein dye present at some of the stations used in groundwater tracing studies.

Criteria for Determining Dye Recoveries

The following sections identify normal criteria used by the OUL for determining dye recoveries. The primary instrument in use is a Shimadzu RF-5301.

EOSINE

Normal Criteria Used by the OUL for Determining Eosine Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the range of 540.0 to 545.8 nm in the sample.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. The eosine detection limit in elutant samples is 0.050 ppb, thus this dye concentration limit equals 0.150 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of eosine. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of eosine. In addition, there must be no other factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work.

Normal Criteria Used by the OUL for Determining Eosine Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain eosine dye in accordance with the criteria listed above. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work. The fluorescence peak should generally be in the range of 532.8 to 537.3 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our eosine detection limit in water samples is 0.015 ppb, thus this dye concentration limit equals 0.045 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

FLUORESCEIN

Normal Criteria Used by the OUL for Determining Fluorescein Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the range of 514.5 to 519.6 nm in the sample.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. The fluorescein detection limit in elutant samples is 0.025 ppb, thus this dye concentration limit equals 0.075 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of fluorescein. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of fluorescein. In addition, there must be no other factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work.

Normal Criteria Used by the OUL for Determining Fluorescein Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain fluorescein dye in accordance with the criteria listed above. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work. The fluorescence peak should generally be in the range of 506.8 to 510.6 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our fluorescein detection limit in water samples is 0.002 ppb, thus this dye concentration limit equals 0.006 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

RHODAMINE WT

Normal Criteria Used by the OUL for Determining Rhodamine WT Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the sample in the range of 565.2 to 571.8 nm.

Criterion 2. The dye concentration associated with the rhodamine WT peak must be at least 3 times the detection limit. The detection limit in elutant samples is 0.170 ppb, thus this dye concentration limit equals 0.510 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of rhodamine WT. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the OUL for Determining Rhodamine WT Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain rhodamine WT dye in accordance with the criteria listed above. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be rhodamine WT dye from the tracing work under investigation. The fluorescence peak should generally be in the range of 572.4 to 577.7 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our rhodamine WT detection limit in water samples is 0.015 ppb, thus this dye concentration limit is 0.045 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

SULFORHODAMINE B

Normal Criteria Used by the OUL for Determining Sulforhodamine B Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the sample in the range of 576.4 to 583.2 nm.

Criterion 2. The dye concentration associated with the sulforhodamine B peak must be at least 3 times the detection limit. The detection limit in elutant samples is 0.080 ppb, thus this dye concentration limit equals 0.240 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of sulforhodamine B. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the OUL for Determining Sulforhodamine B dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain sulforhodamine B dye in accordance with the criteria listed earlier. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be sulforhodamine B dye from the tracing work under investigation. The fluorescence peak should generally be in the range of 580.8 to 584.4 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. The detection limit in water is 0.008 ppb, thus this dye concentration limit equals 0.024 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Standard Footnotes

Sometimes not all the criteria are met for a straight forward determination of tracer dye in a sample. For these reasons, the emission graph is scrutinized carefully by the analytical technician and again during the QA/QC process. Sometimes the emission graphs require interpretation as to whether or not a fluorescence peak represents the tracer dye or not. Background samples from each of the sampling stations aid in the interpretation of the emission fluorescence graphs. When the results do not meet all the criteria for a positive dye detection, often the fluorescence peak is quantified and flagged with a footnote to the result as not meeting all the criteria for a positive dye detection. Standard footnotes are as follows:

Single asterisk (*): A fluorescence peak is present that does not meet all the criteria for a positive dye recovery. However, it has been calculated as though it were the tracer dye.

Double asterisk (**): A fluorescence peak is present that does not meet all the criteria for this dye. However, it has been calculated as a positive dye recovery.

Other footnotes specific to the fluorescence signature are sometimes also used. These footnotes are often developed for a specific project.

The quantification of fluorescence peaks that do not meet all the criteria for a positive dye detection can be important for interpretation of the dataset as a whole.

ATTACHMENT 1
Sample Collection Data Sheet

